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Application of Photothermal Deflection Spectroscopy to Electrochemical Interfaces

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APPLICATION OF PHOTOTHERMAL DEFLECTION SPECTROSCOPY TO ELECTROCHEMICAL INTERFACES

by

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James D. Rudnicki

ABSTRACT

This dissertation discusses the theory and practice of Photothermal Deflection Spectroscopy (PDS, which is also known as probe beam deflection spectroscopy, PBDS, probe deflection technique, and mirage effect spectroscopy) with respect to electrochemical systems. Much of the discussion is also relevant to non-electrochemical systems. PDS can measure the optical absorption spectrum of interfaces and concentration gradients in the electrolyte adjacent to the electrode. These measurements can be made on a wide variety of electrode surfaces and can be performed under dynamic conditions. The first three chapters discuss the theory of the phenomena that can be detected by PDS, and the equipment used in a PDS system. A "secondary gradient technique" is proposed, which places the probe beam on the back of an electrode. The secondary gradient technique allows the study of systems unamenable to conventional PDS and provides a method of separating phenomena. The alignment of the probe beam with the electrode surface is discussed in detail. The results of a numerical model yield a method for determining the offset of the probe beam from the electrode surface based on the frequency response of the PDS signal. The origin and control of noise in the PDS signal are discussed. A majority of the signal

noise appears to be acoustic in origin. The electrochemical oxidation of platinum is used to demonstrate that PDS has sub-monolayer sensitivity necessary to study interfacial chemistry. The results allow us to propose a two-reaction oxidation mechanism: the platinum is electrochemically oxidized to form platinum dihydroxide and dehydrated by a non-electrochemical second-order reaction. The final chapter discusses the relation of PDS to similar and competing techniques, and considers possibilities for the future of the technique.

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List of Symbols

c_i	concentration of species i (mol l^{-1})
c	heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
D_+	diffusivity of ionic species ($\text{m}^2 \text{s}^{-1}$)
f	modulation frequency (Hz)
F	Faraday constant ($96,487 \text{ C equiv}^{-1}$)
i	electrochemical current (A, positive values are anodic currents)
I	intensity of excitation (W m^{-2})
k	thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
k	reaction rate constant
L	length of sample (m)
m	reaction order
M_i	molecular weight of species i (g mol^{-1})
n	refractive index
n_0	refractive index of the bulk solution
n	number of electrons in reaction
$P(\lambda)$	power of excitation light (W)
q	heat input (W m^{-3})
s	stoichiometric coefficient of reactant or product

$S(\lambda)$	PDS signal from spectral scan
T	temperature (K)
T_{xx}	second spatial derivative of temperature ($K\ m^{-2}$)
T_t	time derivative of temperature ($K\ s^{-1}$)
t	time dimension (s)
t_c	time constant of the lockin (s)
t_+	transference number of the cation
x	spatial dimension perpendicular to sample surface (m)
x_1	probe beam offset when sample is parallel (x_0 when $\beta=0$) (m)
x_e	probe beam offset at trailing edge of sample (m)
x_0	probe beam offset at leading edge of sample (m)
x_r	distance of rotation center from sample surface (m)
y	spatial dimension along the width of the sample surface (m)
z_+	the charge on the cation of a binary electrolyte (always positive)
z_-	the charge on the anion of a binary electrolyte (always negative)
α	thermal diffusivity ($m^2\ s^{-1}$)
$\alpha(\lambda)$	absorption spectrum of sample
β	cell rotation (degrees)
β	Beer-Lambert Law absorption coefficient (m^{-1})
$\delta\lambda$	bandpass of excitation light (nm)
ϵ	concentrative absorptivity
Γ	surface concentration ($mol\ m^{-2}$)

ϕ	phase (degrees)
η	signal collection efficiency
λ	excitation light wavelength (nm)
μ	thermal diffusion length (m)
ν	modulation frequency (Hz)
ν_+	the number of moles of cation per mole of electrolyte
ν_-	the number of moles of anion per mole of electrolyte
θ	phase offset (degrees)
θ_{OH}	fractional surface coverage of hydroxide
ρ	density (kg m^{-3})
ω	modulation frequency (rad s^{-1})
ψ	concentrative refractivity, $\partial n / \partial c$ (M^{-1})

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This thesis represents the solstice of a lifelong adventure. After this it's all downhill. I'll never be one of those bright young students again, but I don't have to take anymore tests either, so maybe it's okay. Given the chunk of my life invested in this effort, fairness allows me the indulgence to put whatever I want into the record (as long as there are no spelling errors and the margins are correct). I take advantage of this opportunity to record for all time the names of those (animate and inanimate) without whom this thesis would not exist.

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Most electrochemical reactions are poorly understood. Although studied and applied for over 100 years, electrochemical knowledge remains largely empirical. The lack of *in situ* tools is the major cause of the sad state of liquid-solid heterogeneous chemistry compared to that of homogeneous chemistry. Although interfacial chemistry in the gas phase can be studied effectively, only recently has interfacial chemistry in condensed phases begun to be accessible. The potentiostat remains the major tool of the electrochemist. The need for new tools is of primary importance [1, 2].

The importance of new *in situ* techniques cannot be understated. Only the *in situ* techniques can monitor dynamic processes. Removal of an electrode from its environment introduces serious questions. Armstrong and Muller have shown with *in situ* scanning tunneling microscopy (STM)¹ that the microtopography of copper electrodeposits changes within 1 minute after the electrode is removed from potential control [3].

We have turned to a new technique, photothermal deflection spectroscopy (PDS), to study electrochemical interfaces. The technique is performed *in situ* and does not place many restrictions on the electrode surface. The electrode is only required to be planar. Polished, smooth, and rough electrodes can be studied. The PDS signals improve as the electrode surface becomes darker. This is the opposite of reflection-based spectroscopies that only succeed on reflective surfaces. PDS also yields information about mass transport to the surface. We will see in Chapter 6 that reaction mechanisms can be deduced from this information.

This document is largely a manual for the technique. We describe the many considerations that we have uncovered during the development of PDS for electrochemical systems. To the limits of our knowledge, this document contains everything a researcher should be considering when embarking on a PDS project. Much of the discussion is applicable to non-electrochemical systems as well.

The remainder of this chapter describes the theory of PDS. We discuss the processes, minor and major, which can be detected with PDS. Chapter 2

¹ The expansions of acronyms are in the index.

describes a numerical model of PDS that is used to analyze the technique. Chapters 3, 4 and 5 discuss the technique from a practical perspective. Solutions to problems that are ignored in the theoretical treatments available in the literature are discussed. Examples are included throughout which demonstrate the results when PDS is applied to electrochemical systems. Chapter 6 contains a case study of the platinum oxidation reaction. This study demonstrates the interpretation of PDS experiments and the conclusions that can be derived.

A. Introduction

There are many photothermal techniques of which photothermal deflection spectroscopy (PDS) is a subset. Reference 4 contains a comprehensive review of the various photothermal techniques. Photothermal deflection spectroscopy is a family of optical spectroscopies that directly measures the absorption of light. Two characteristics are common to the family members:

- 1) The sample is immersed in a fluid and excitation light is applied to the sample surface. Excitation light that is absorbed by the sample is converted to heat. This heat is conducted away from the area of absorption into the fluid phase. Thermal conduction results in a temperature gradient in the fluid phase, and thereby a refractive index gradient. This is the *photothermal* aspect of the name.
- 2) A probe beam is passed through the refractive index gradient. The Schlieren effect deflects the probe beam. A position detector measures the deflection. This is the *deflection* aspect of the name.

PDS can be applied to interfaces or homogeneous phases. In the homogeneous phase form, the excitation light is applied non-uniformly. Typically a laser beam illuminates a cylindrical region of the sample and heat is radially conducted away from the excitation beam. The probe beam passes parallel to the excitation beam and is deflected by the refractive index gradient. Figure 1-1 shows the

Figure 1-1. PDS measures the refractive index gradient formed near an electrode by passing a probe beam parallel to the electrode.

interfacial form. The excitation light is applied normal to the sample surface and heat is conducted away from the surface. Any type of interface can be studied: solid-gas, solid-liquid, solid-solid, liquid-liquid, *etc.*

In an electrochemical system, there are other processes that can cause a refractive index gradient, in particular reactions at the surface that generate concentration gradients. A PDS system will detect these gradients also (the method of discerning the two is discussed shortly). Some researchers are only interested in concentration gradients and use a technique termed probe beam deflection (PBD). With respect to the equipment required, PBD is a subset of a PDS system. We will refer to PDS throughout this document, but much of the discussion is equally applicable to PBD.

Short Historical Review

Fournier and Boccarra, *et al.* are generally credited with originating PDS in its modern form [5 - 11]. The original application was for homogeneous phases followed by extension to interfacial spectroscopy [12 - 15].

The technique has been extended into the infrared with air as the deflecting medium [16 - 20]. IR PDS at liquid-solid interfaces has been slow to develop. If the solid is transparent, an interesting technique is reverse illumination, as described in Reference 21. Another promising development is Step-scan FTIR PDS described in Reference 22.

It is only recently that PDS has been applied to electrochemical systems. Among the electrochemical literature the following researchers have used either PDS or PBD: Bard, *et al.* [23, 24]; Mandelis, *et al.* [25, 26]; Decker, *et al.* [27, 28]; Haas, *et al.* [29 - 31]; Royce, *et al.* [32]; Pawliszyn, *et al.* [33, 34]; Plichon, *et al.* [35 - 38]; Cairns, *et al.* [39 - 43]; and Tamor [44]. We have reviewed the electrochemical PDS research in Reference 39.

Theory of Beam Deflection

The basis of PDS is measurement of the refractive index gradient. The deflection of a ray is described by (see Figure 1-1)

$$\theta(x,t) = \frac{L}{n_0} \cdot \frac{\partial n(x,t)}{\partial x}, \quad [1-1]$$

where x and t are the spatial and temporal dimensions, L is the length of the sample, n is the refractive index, n_0 is the bulk refractive index, and θ is the deflection of the beam. This equation is greatly simplified from the full

equations describing ray propagation. Reference 45 describes ray propagation and References 12 and 9 describe the simplification of the equations. The assumptions in Equation 1-1 are: 1) deflection of the probe beam is small, 2) the distance of the probe beam from the surface is constant, and 3) the perturbation of the refractive index from the bulk value is small. In Equation 1-1, much is based on the assumption that the probe beam deflection is small. Angular deflections of mrad and μ rad magnitude are typical. The detection limit is currently about 1 nrad [9].

The other major assumption in the above derivation is that the probe beam has an infinitely small diameter. Typically the refractive index profile in the electrolyte is curved, *i.e.* as is shown in Figure 1-1, dn/dx varies with x . Because the probe beam has a finite diameter, different regions of the beam are affected by gradients of different magnitude. As a result, the beam distorts as it deflects. Mandelis and Royce derived an analytical solution for the deflection and distortion of a circular beam in a concentration gradient [26]. Their results show that the beam develops an elliptical shape as it deflects.² The elliptical distortion is not large and should be negligible in most situations. The model described in the next chapter allows for the effect of beam diameter to be explored.

The two quantities that change the refractive index are temperature and concentration. To relate the beam deflection to these quantities, the

² This effect is the basis of Thermal Lensing Spectroscopy, a related technique which measures the curvature of the refractive index.

refractive index of the electrolyte can be approximated by a Taylor series expansion with only the first-order terms included:

$$n \equiv n_o + (T - T_o) \left. \frac{\partial n}{\partial T} \right|_{T_o} + (c - c_o) \left. \frac{\partial n}{\partial c} \right|_{c_o}, \quad [1-2]$$

where T is temperature and c is concentration (a binary electrolyte is assumed). Taking the derivative of this expansion results in

$$\frac{dn}{dx} = \frac{dT}{dx} \cdot \frac{\partial n}{\partial T} + \frac{dc}{dx} \cdot \frac{\partial n}{\partial c}. \quad [1-3]$$

This equation apparently shows that a single measurement of the probe beam deflection, θ , and therefore dn/dx , cannot determine both dT/dx and dc/dx (the physical parameters, $\partial n/\partial c$ and $\partial n/\partial T$ are known).

PDS uses modulation of the excitation light and lockin detection to improve the sensitivity. A side effect is that modulation allows dT/dx to be separated from dc/dx . Any process that is dependent on the modulated excitation light will produce a modulated deflection of the probe beam. A lockin amplifier will measure only these components. Processes not dependent on the excitation light will not produce periodic probe beam deflections. A low-pass filter is used to measure the non-periodic deflections. The thermal signal is essentially an AC signal. The concentration signal will vary slowly and is essentially a DC signal.

In the remaining sections of this chapter we will discuss the processes that cause the two classes of refractive index gradients, AC and DC, and then discuss cross effects. Cyclic voltammetry of copper in alkaline electrolyte will demonstrate these effects.

Differences from Reflection and Transmission Spectroscopies

We note here that under some circumstances a spectroscopy that directly measures absorption will not yield the same results as a reflection or transmission spectroscopy. The RAT law,

$$\text{Reflection} + \text{Absorption} + \text{Transmission} = 1,$$

shows how the difference occurs. In any spectroscopy, only one of the above quantities is measured and usually one of the quantities is zero. For transparent samples, none of the quantities will be zero and the three forms of spectroscopy will yield different results.

An example of this difference occurred when we studied thin polymer films on metal electrodes. It became evident that PDS does not respond to optical interference in the same manner as a typical spectrometer [46]. Despite the name, destructive interference does not result in the conversion of light into heat. Optical interference can affect a PDS experiment, but the mechanism is different from conventional spectroscopies.

B. AC signals

Any process that originates from the modulated excitation light will produce an AC signal. Two main processes are of interest: absorption of light at the interface and absorption of light in the electrolyte. These two processes can be separated.

A lockin amplifier (hereafter referred to as lockin) is used to measure the magnitude of only those deflections that are at the same frequency as the modulation frequency. The lockin measures both the magnitude and phase

of the AC signal. See Reference 47 or 48 for further discussion of lock-in detection.

Surface Signal

The absorption of light at the interface is the primary process studied with PDS. Light is directed through the electrolyte onto the interface. Light absorbed at the interface is converted to heat within a negligible time [49].³ The temperature of the interface increases, and conduction of heat away from the interface (into both the electrolyte and the electrode), causes temperature gradients in both phases. Many electrolytes exhibit a decrease in refractive index as temperature increases. For such an electrolyte, the heating of the interface causes the refractive index of the electrolyte to be lowered adjacent to the electrode. The probe beam will be deflected away from the electrode, as indicated in Figure 1-1.

PDS uses modulation of the excitation light and lock-in detection of the probe beam deflection. While the excitation light illuminates the electrode, the interface heats and the thermal gradient propagates into the electrolyte. The gradient relaxes while the excitation light is off. The probe beam thereby exhibits periodic deflections.

The probe beam passes through the electrolyte at a small but finite distance from the electrode. A delay exists between when the excitation light

³ Some electrode surfaces may exhibit behaviors contradictory to this statement, e.g. fluorescence, phosphorescence, and photocurrents. Such systems must be treated in a more complex manner.

is converted to heat at the interface and when the heat has been conducted to the position of the probe beam. The delay is expressed as a phase (expressed as an angle between 0° and 360°), and is measured by the lockin. To distinguish the probe deflection caused by absorption of light at the interface from other components of the deflection to be discussed in the following sections, and because the phase is variable, it is referred to as the 'AC deflection at x^* '.

The AC deflection has been investigated by many researchers. The references cited in the historical section contain many theoretical treatments. Analytic solutions of temperature profiles have been derived for many geometries. Other solutions can be found in the photoacoustic spectroscopy (PAS) and photothermal spectroscopy (PTS) literature [13, 50].

Two simple equations can describe the basic characteristics of the PDS signal. For a planar system with an thin opaque sample mounted on an insulator, the PDS signal can be described by

$$\ln S \propto \frac{-x_o}{\mu} \text{ and } \phi \propto \frac{-x_o}{\mu} \text{ where } \mu \equiv \sqrt{\frac{\alpha}{\pi f}} \quad [1-4]$$

where S is the AC signal magnitude, ϕ is the signal phase, x_o is the probe offset (the distance between the probe beam and the sample surface), and μ is the thermal diffusion length. The thermal diffusion length is defined in terms of the thermal diffusivity, α , and the modulation frequency, f , in cycles per second. This equation shows several basic characteristics of the PDS signal:

- The signal magnitude decreases exponentially from the sample surface. The probe beam must be very close to the sample surface to measure a

significant signal. At 3 thermal diffusion lengths from the surface the signal has decreased to 5% of the maximum magnitude. The thermal diffusion length in water at 40 Hz is 40 μm (see Table V-2 for examples of the thermal diffusion length for other materials and frequencies).

- The signal magnitude decreases exponentially with the square root of modulation frequency. This dependence limits the usable frequency range to below 100 Hz., and is the motivation to use very low frequencies. We typically use 10 - 40 Hz.
- The signal phase varies through 2π over a distance of $2\pi \mu$.

The accuracy of Equation 1-4 has been experimentally confirmed in Reference 10. For any discussion these characteristics are a good starting point.

To acquire an absorption spectrum, the excitation wavelength is scanned over the range of interest while the AC signal magnitude is measured (the phase is constant). We typically repeat the scan several times and average the results. The low modulation frequencies require that the lockin average for about 1 s to measure the signal. Thereby, about 1 minute is required for each spectral scan, and a complete experiment can take several minutes.

One criticism is that PDS is not sufficiently fast to acquire spectra under dynamic conditions. Acquisition times for an absorption spectrum are typically several minutes. But even Raman spectroscopy using a photodiode array detector requires on the order of 100 s to acquire a spectrum. This is not sufficient for potentiodynamic experiments with medium sweep rates

(10-100 mV s⁻¹). Chapter 3 describes a cross plotting technique that allows spectra to be acquired effectively in a few seconds.

Electrolyte Signal

Absorption of light in the electrolyte can generate a signal by two mechanisms. The first is the basis of homogeneous-phase PDS. A temperature gradient is formed by non-uniform excitation:

$$\frac{dT}{dx} = \frac{\epsilon c}{C_p \rho} \cdot \frac{dI}{dx} \quad [1-5]$$

In this equation, I is the intensity of the excitation, ϵ is the absorptivity, C_p is the heat capacity, ρ is the density, and c is the concentration. In our system, the excitation light is focused onto the sample surface, and thereby dI/dx is not zero. But, because the distance between the focusing lens and sample surface is large, we assume that dI/dx is negligible.

The second mechanism is a concentration gradient with uniform excitation intensity forming a thermal gradient:

$$\frac{dT}{dx} = \frac{\epsilon I}{C_p \rho} \cdot \frac{dc}{dx} \quad [1-6]$$

The AC signal which results is distinct from the AC signal at x^* . There is no time delay between when the excitation light is applied and when the temperature gradient forms. Because the probe beam is passing through the temperature gradient there is no time delay. This signal we call the AC signal at 0^* . This signal is not dependent on the thermal diffusion length, and therefore is not dependent on modulation frequency.

The phase difference between the two AC signals is used to separate the two. By adjusting the probe offset and the modulation frequency, the surface signal can be made to occur at 90 or 270°. With the two AC signals orthogonal, a two-phase lockin will be able to separately measure each signal.

This description is limited to weakly absorbing systems. Either the concentration, c , or the absorptivity, ϵ , must be small. If these parameters are not small, the absorption process will cause the intensity of the excitation light to decrease as it passes through the electrolyte. The model described in Chapter 2 does allow for strongly absorbing systems. In Chapter 3 we will discuss the effect of highly absorbing electrolytes on the PDS signal.

This signal can be used to determine the absorption spectrum of electrolyte species. An important feature, is that only species that are optically absorbing and present in a concentration gradient are detected. As we will describe in the next section, when multiple species are participating in the electrode reaction, the effect of all species are added together and cannot be separated. If one species absorbs at a unique wavelength, the mechanism of Equation 1-6 can be used to "illuminate" a specific concentration gradient. This is called selective measurement of concentration gradients. Pawliszyn, *et al.* have demonstrated that the AC signal at 0° can be used to measure the concentration gradient of a single electrolyte species and can measure the absorption spectrum of the species [25].

Photoelectrochemical Effects

Photoelectrochemical systems are easily studied with a PDS system. Addition of a lockin amplifier to the current output from the potentiostat is all that is required. Photoelectrochemistry at the electrode surface will cause modulated current (assuming a controlled-potential experiment) and modulated concentration gradients. Because the response time of mass transfer is slow, large concentration gradients are not likely in the frequency range of 10 to 50 Hz (when modulated concentration gradients are studied the frequency is less than 1 Hz). Nonetheless, the possibility should be kept in mind that photochemistry can cause an AC signal that is not thermal in origin. This effect can be considered either a feature or an interference.

C. DC signals

In this section, we discuss all the effects that would produce a DC probe deflection. These effects can be studied independently from the AC signals by removing the excitation source. When studied alone, the technique has been referred to as Probe Beam Deflection (PBD) or mirage effect. The main effect which causes a DC probe deflection in which we have interest is the concentration gradients. These gradients are directly related to the reactions at the electrode surface, and may be used to deduce the reaction mechanism. The other processes discussed below would be considered interference by us, but may be of interest to others.

The effects we discuss in this section are not true DC, but rather are slowly varying. Any signal can be represented as a summation of sines by a Fourier transform. The slowly varying signals we investigate will have

components all across the frequency domain. Some of these components will be at the modulation frequency. A blank experiment with the excitation light removed and the lockin operating can be performed to determine if the DC signal contains frequency components at the modulation frequency.

Concentration Gradients

Electrochemical reactions will cause concentration gradients and corresponding refractive index gradients in the electrolyte. For a single-solute electrolyte, measurement of the DC deflection provides direct information about the concentration gradient. For a two-solute electrolyte, Equation 1-2 is extended to

$$\frac{dn}{dx} = \frac{dT}{dx} \cdot \frac{\partial n}{\partial T} + \frac{dc_1}{dx} \cdot \frac{\partial n}{\partial c_1} + \frac{dc_2}{dx} \cdot \frac{\partial n}{\partial c_2} \quad [1-7]$$

From a single measurement of dn/dx , the concentration gradients of species 1 and 2 are indeterminate. Because of the inability to discern individual concentration gradients for electrolytes with two or more solutes, the DC deflection measurement is referred to as the non-selective measurement of concentration gradients.

Assumptions can be made to overcome the non-selectivity of the DC deflection. A background or blank experiment can be performed with only one component present in the electrolyte. In some situations, one term of Equation 1-7 may dominate the sum; either one concentration gradient can be much larger than the other, $dc_1/dx \gg dc_2/dx$, or one species can have a larger effect on the refractive index than the other, $\partial n/\partial c_1 \gg \partial n/\partial c_2$. Also, the concentrations of the two species may be related to one another through

chemical reactions. When no appropriate assumptions exist, we must revert to a model of the concentration gradients.

Ferri/Ferrocyanide

The ferri/ferrocyanide redox couple is a classic electrochemical experiment and has been studied with PDS. The reaction is:

The reaction is reversible, and the two species are present in the solution at low concentrations. The goal was to determine the diffusion coefficients, but the results were mixed. The problem is that the models used to interpret the results were inadequate.

In Reference 39 we review the evolution of the mass transfer models used for this redox couple. The first models considered only the reactant. We expanded the model to account for both reactant and product and fast reversible kinetics. The response of the reaction $A \rightarrow B + ne^-$ to a potential step was determined assuming a dilute solution. The gradient was [39]:⁴

$$\frac{\partial n}{\partial x} = \frac{-(\theta C_B^o - C_A^o)}{(1 + \theta \xi) \sqrt{\pi D_A t}} \psi_A \exp\left[\frac{-x^2}{4 D_A t}\right] + \frac{\xi(\theta C_B^o - C_A^o)}{(1 + \theta \xi) \sqrt{\pi D_B t}} \psi_B \exp\left[\frac{-x^2}{4 D_B t}\right] \quad [1-8]$$

where $\theta \equiv \exp\left[\frac{nF}{RT}(E - E^o)\right]$, $\psi_i \equiv \frac{\partial n}{\partial C_i}$, and $\xi \equiv \sqrt{\frac{D_A}{D_B}}$

⁴ For a similar theoretical development see Reference 51. Our treatment differs only in that the bulk concentration of reactant and product are allowed to independently change.

In this equation, A is the reactant, and B is the product. D_i is the diffusion coefficient, E and E^0 are the electrode potential and the reversible potential, C_i^0 are the bulk concentrations, and ψ_i are the concentrative refractivities. If the mass-transfer-limited potential step is considered, the above equation simplifies to

$$\frac{\partial n}{\partial x} = \frac{C_A^0}{\sqrt{\pi D_A t}} \psi_A \exp\left[\frac{-x^2}{4D_A t}\right] - \frac{\xi C_A^0}{\sqrt{\pi D_B t}} \psi_B \exp\left[\frac{-x^2}{4D_B t}\right] \quad [1-9]$$

This equation can produce very different responses depending on the ratio of the diffusion coefficients and the ratio of the concentrative refractivities. The determining parameters are D_i and ψ_i . The parameter for species A can be greater than, less than, or equal to that for species B. Variation of the two parameters yield the nine distinct characteristic behaviors shown in Figure 1-2.

Figure 1-2 is very complicated and that is part of the message—the DC probe beam response is more complicated than previously treated in the literature. The underlying basis of the complex behavior is the counteracting concentration gradients of species A and B; one is negative and the other positive. If the diffusion coefficient and concentrative refractivity are equal for both species, there will be no probe beam response. If one species has a larger concentrative refractivity, it will dominate the response.

Curves 3 and 7 correspond to the anodic and cathodic potential steps for the ferri/ferrocyanide redox couple. The species with the larger concentrative refractivity has the smaller diffusion coefficient. The weak species (with respect to ψ_i) diffuses to the probe beam first and begins to deflect the beam. Soon after, the strong species reaches the probe beam and

reverses the deflection. This explains small reverse deflections initially seen for curves 3 and 7 in the right pane of Figure 1-2. Others and ourselves have seen this effect experimentally.

We hoped that the experimental data could be fitted to Equation 1-9 to allow the diffusion coefficients to be determined. But least squares methods were unable to produce a fit to the data. (For an entertaining diatribe on this curve-fitting problem, see "What Not to Compute," page 252, in Reference 51).

Recently the theoretical response for the potential-step experiment was further revised to include the effect of the supporting electrolyte. Because we have assumed dilute solutions for the product and reactant, the transference number for the supporting electrolyte species will be high. Therefore a significant gradient in the supporting electrolyte concentration will develop. Gasteiger has developed an analytic solution to confirm the effect of the supporting electrolyte [52]. The supporting electrolyte contributes to the DC deflection, but does not modify the qualitative results.

Figure 1-2. The nine possible types of probe beam response to a potential step experiment. The left pane shows the behavior during the first ten seconds. The right pane is a magnification of the response during the first second.

What the study of the ferri/ferrocyanide redox couple appears to show is that PDS can tell us nothing about this electrochemical system. Even when the mechanism is known, we cannot determine the diffusion coefficients. The study of this system has taught us the detail that must be included in the transport model used to interpret the experimental results. The mass-transfer-limited potential step with dilute species is a very simple experiment, but the theory with respect to PDS went through several evolutions before being complete. Combined with an adequate model, PDS is useful in determining reaction mechanisms. The model results are compared with the experimental data. Models which do not agree with the experimental evidence can be rejected. In Chapter 6 we demonstrate how the mass transfer model of cyclic voltammetry of platinum is compared with the experimental data to determine the reaction mechanism.

Heats of Reaction

Concentration gradients are not the only effect that can cause DC signals. Electrochemical reactions will produce heat due to the irreversible and reversible heats of reaction [53].

$$Q = i\eta - \frac{i}{nF} T\Delta S \quad [1-10]$$

The irreversible heat of reaction is $i\eta$, where i is the current and η is the overpotential. This heat is always exothermic. The reversible heat is $T\Delta S$, which is usually exothermic. The combination of these two heats is called the Peltier heat. This heat has been experimentally measured for some systems [54, 55]. These heats produce thermal gradients, which vary slowly, similar to the concentration gradients. There is no way to deconvolute these effects from the concentration gradient. If these effects are expected to be

significant, a specially-designed cell can be used. The method of separating the heats of reaction from the concentration gradients is discussed in Chapter 3 in the cell section.

The quantification of the irreversible heat is possible. But, quantification of the reversible heat is difficult because the calculation of ΔS for a half-cell requires partial molar entropies of ionic species. Determination of the partial molar entropy of ionic species may be impossible [53]. Recently the partial molar entropy of the hydrogen ion in aqueous electrolytes has been reported [56]. Given that data for this very common species has only recently been reported, it is no surprise that data for other systems are not available.

Platinum Oxidation

One system we have studied is cyclic voltammetry of platinum, which will be used as an example of the heats of reaction. To make an estimate of the reversible heat of reaction for platinum oxidation,

we assumed that the $T\Delta S$ for the whole reaction could be assigned to the half cell. Using literature values [57], the entropy change for platinum oxidation is $18.0 \text{ cal mol}^{-1} \text{ K}^{-1}$. The oxidation current for smooth platinum is about 0.2 mA cm^{-2} . At 290 K, the reversible heat of reaction is approximately 0.02 mW cm^{-2} . A reasonable overpotential is 300 mV. The irreversible heat of reaction is 0.05 mW cm^{-2} . The value of both of these heats is 3 orders of magnitude smaller than the intensity of the excitation light. For the

platinum system, we can safely assume that these heats are negligible for the conditions of our experiment.

Steady State from Excitation Light

The excitation light is not purely an AC signal. The power of the excitation can be represented as (ignoring for the moment that the shape is not a pure sine wave)

$$P(t) = \frac{P_{\text{peak}}}{2} (1 + \sin[\omega t]) , \quad [1-11]$$

where P_{peak} is the peak power of the excitation and ω is the modulation frequency (the excitation light has by definition a 0° phase). This equation shows that the excitation consists of a constant input plus a periodic input. Therefore, there will be a DC deflection of the probe beam caused by the constant portion of the excitation light. The presence of this effect can be tested by running a blank experiment with the excitation light removed. In our experience this signal is detectable, but has never interfered with the larger concentration signal.

Soret Effect

The Soret effect is a concentration gradient that is produced as a result of a temperature gradient.⁵ Because the activity of electrolyte components is a function of temperature, the components will redistribute themselves if a

⁵ Credit to the anonymous reviewer who pointed out this esoteric effect.

steady temperature gradient is imposed. This effect has been known for a long time [58, 59]. Concentration gradients caused by the Soret effect are very slow to develop. The temperature gradient induced by PDS is so small that it is unlikely that any significant concentration gradient could be induced.

D. Interference of Signals

The DC signal can cause the AC signal to change. The AC signals are a strong function of probe offset. The DC signals cause the probe offset to change. The magnitude and phase of the AC signal will change according to

$$\frac{S(x_o + \Delta x)}{S(x_o)} = \exp\left[\frac{-\Delta x}{\mu}\right] \text{ and } \Delta\phi = \Delta x/\mu. \quad [1-12]$$

For a 1 mrad DC deflection, the change in probe offset, Δx , over the length of a 10 mm electrode is 10 μm . With a thermal diffusion length of 40 μm , the signal phase will change 7° and the signal magnitude will decrease 12%. (For the 1 mrad deflection, the average change in probe offset over the length is half the change at the exit). The next section demonstrates this interference. The secondary gradient technique discussed in Chapter 3 allows this interference to be eliminated.

E. Example: Copper Cyclic Voltammetry

Figure 1-3 shows cyclic voltammetry of a copper electrode in alkaline electrolyte. The potentials refer to a DHE in the same electrolyte [60]. The current trace contains two anodic peaks, AI and AII. These represent the

oxidation of the copper to Cu(I) and Cu(II) oxides/hydroxides. On the cathodic sweep the oxidized species are reduced to Cu(0). The proposed reactions are:

The DC deflection detects the concentration gradients. The vertical axis indicates the displacement of the probe beam along the face of the detector. Because the detector is about 0.5 m from the cell, the linear displacements are equivalent to angular deflections ranging from -0.4 to 0.4 mrad. The upward direction in the figure represent probe deflections away from the electrode, which indicate that the electrolyte concentration near the electrode is decreasing. The anodic peaks represent the consumption of the hydroxide ion and the production of water. The electrolyte is diluted near the electrode and the probe deflects away from the electrode (toward the region of higher refractive index). The cathodic peaks produce the opposite effect.

The deflection marked X is an interesting feature. This strong deflection toward the electrode must be caused by the refractive index increasing near the electrode. Dissolution of a soluble species would cause this. Dissolution of copper species has been observed with a rotating ring disk experiment [61].

To resolve the two AC signals, the phase of the AC signal at x^* must be adjusted to 90° . This is done before the experiment is begun by varying the modulation frequency and probe offset. The AC at x^* been discussed in detail in Reference 40. Basically, as the surface is oxidized its absorption increases

(Cu_2O is dark red and CuO is black). The oxide remains on the surface during the cathodic sweep until it is completely reduced at CII. We will discuss the anodic sweep from 700 to 1500 mV in Chapter 3 when we cross plot a series of the experiments at different wavelengths.

We had originally attributed the AC at 0° signal to concentration gradients. But, because the absorption coefficient of potassium hydroxide is small, it seems unlikely that absorption of light in the electrolyte is measurable. Further consideration leads us to conclude that this is interference of the type discussed in the previous section. The DC deflection of the probe beam moves the probe beam closer to the electrode. A 0.4 mrad deflection moves the probe beam 4 μm closer to the electrode at the exit of the cell. For a thermal diffusion length of 40 μm , the phase will shift about 6° . The lockin is separating the total AC signal into two components at 0° and 90° . As the surface signal changes from its initial phase of 90° it begins to appear on the 0° channel proportional to $\sin \phi^{\text{shift}}$. The phase shift of 6° should cause about 0.9 mV to appear on the 0° channel (using the average value of 9 mV present on the other channel). This is close to what is seen in Figure 1-3. Because the signal on the 90° channel changes with $\cos \phi^{\text{shift}}$, the 6° phase shift will only decrease the signal by about 0.5%.

Figure 1-3. Cyclic voltammetry of a Cu electrode in 0.1 M KOH from -100 to 1600 mV vs. DHE in the same electrolyte. The sweep rate was 20 mV s^{-1} . The excitation wavelength was 550 nm and the modulation frequency was 20 Hz. The curves are single traces recorded directly on a x-y recorder.

Conclusion

The detailed theory presented here is the minimum necessary to perform experiments. To measure the surface spectrum, all we require is that the AC signal is proportional to the absorption coefficient. This requirement is always true on opaque samples. To measure concentration gradients only knowledge of Equation 1-1 is necessary. With this minimal theory many qualitative, useful experiments can be performed.

The model we develop in Chapter 2 is useful for making the transition to a quantitative technique. The model is helpful in three ways: First, it allows experiments to be simulated that would be difficult or extremely time consuming to perform. With the model we have explored changing the shape of the modulation waveform (discussed in Chapter 3). To do this experimentally would require an expensive series of graded neutral density filters. With the model, we can explore infinite possibilities and determine the best waveform. Second, the model allows us to gain information that cannot be obtained experimentally. In Chapter 4, we develop a method of using the frequency response of the AC PDS signal to determine the offset of the probe beam from the electrode surface. Before this development, we had no method of determining the offset of the probe beam, and therefore we could not correlate the frequency response with the probe offset. In the model, the probe offset is a fixed parameter, which allows us to correlate the frequency response with the probe offset. Lastly, because the model is free from noise, the information derived from the model is far more precise than experimental data.

The transition from the theory to a physical system is always more difficult than apparent. In the following chapters, we discuss engineering aspects of PDS for electrochemical interfaces. Notably, Chapter 5 discusses noise, which is a topic almost ignored in the literature. One might assume by the absence of the discussion of noise that it is unimportant, but PDS is currently a very low signal-to-noise ratio (SNR) technique. There are few available routes to increase the signal. The largest benefits appear to be through reduction of noise.

The theory of PDS does not directly indicate its usefulness. To date, most of the experimental work has concentrated on electrochemical systems which are thought to be well understood. It was necessary to study known systems so that we could understand PDS. The copper example just discussed did demonstrate that non-electrochemical processes can be detected. But, for the most part the peaks in the concentration gradient response appear very similar to the peaks in the cyclic voltammogram. Since we now understand the technique, we can begin to explore systems which are not so well understood. In Chapter 6 we demonstrate how the concentration gradients measured during cyclic voltammetry of platinum can be used to deduce the reaction mechanism for the oxidation of platinum.

Chapter 2:

Thermal Model

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A numerical model of the PDS system was developed. The model consists of three major components: a temperature module which calculates the thermal transport and the refractive index profile, a probe beam module which calculates the deflection of the probe beam as it travels through the refractive index gradient, and a lockin module which calculates the magnitude and phase of the signal. In this chapter the governing equations and general features are discussed. Only a few examples are presented here, as most of the results obtained from the model are discussed in later chapters.

The numerical details of the model are discussed in the appendices. Appendix I discusses the numerical implementation of the thermal and probe beam modules. The thermal equation is solved using implicit finite difference techniques [62, 63]. Appendix II is devoted to the numerical

implementation of the lockin and contains a functional description of the lockin. The code for all of the modules is contained in Appendix III.

A. Thermal Module

Figure 2-1. The region solved by the model contains 4 layers. The film is optional. The probe beam is allowed to pass through the primary or secondary phase.

Several models of PDS were developed, however the most useful geometry is shown in Figure 2-1. This geometry contains 4 layers: the primary and secondary phases, which are the regions through which the probe beam can pass, and the sample, which is thermally thick and has an optional thermally thin film

on the surface. This model is very flexible. We can explore thermally thin or thick samples. By setting the thermal conductivity of the secondary phase to a small value, we can model samples mounted on insulator. We also model conditions for which the secondary phase is water or a transparent solid. The boundaries at $x=0$ and $x=L$ are assumed to be isothermal. Because the boundaries are placed relatively far from the sample, they often have little effect.

The one-dimensional thermal conduction equation is:

$$q + k \frac{\partial^2 T}{\partial x^2} = \rho c \frac{\partial T}{\partial t} \quad [2-1]$$

$$T(0, t) = T(L, t) = T_0 \quad \text{and} \quad T(x, 0) = T_0 \quad \text{BC's and IC}$$

where q is the heat input, k is the thermal conductivity, ρ is the density and c is the heat capacity. We solve this equation over the entire domain, with the interfaces treated as discontinuities in the thermal properties.

The differential equation is solved for the excess temperature, which is defined by:

$$T(x,t) \equiv T^E(x,t) + T_0. \quad [2-2]$$

When Equation 2-2 is substituted into Equation 2-1, the constant term, T_0 , is eliminated. The remaining differential equation is identical to Equation 2-1, except that T is replaced by T^E . This replacement allows more precise calculations of the small temperature changes that occur. The heat input term in Equation 2-1 is caused by absorption of the modulated excitation light. The model allows the waveform of the modulation to have any shape, *e.g.*, square wave, sine wave, or triangular shapes. The effects of various modulation waveforms are discussed in the next chapter.

The excitation light is absorbed at the sample/primary interface and inside the primary phase. The absorption at the surface is simply characterized by a fraction between 0 and 1. The excitation light is absorbed throughout the primary phase according to the Beer-Lambert Law:

$$\frac{dI}{I} = -\beta dx \quad [2-3]$$

where I is the intensity of the excitation and β is the absorption coefficient of the medium. The excitation light that reaches the sample surface can be diffusely scattered or specularly reflected; both circumstances have been modeled. The difference between the two types of reflection affects the excitation light absorbed in the primary phase. If the sample scatters, it is

assumed that no excitation is absorbed as the excitation light leaves the cell. If the sample reflects, the excitation light is absorbed as it leaves the cell, according to Equation 2-3.

Figure 2-2. The side view of an electrochemical cell used in the PDS system. The assembly is contained in a 10x10x40 mm cuvette. The counter electrode (CE) and working electrode (WE) are mounted on vertical wires.

We do not account for focusing of the excitation light as it propagates towards the sample (see Figure 2-2). The excitation area is reduced from 50x50 mm to 2x10 mm over a distance of 70 or 100 mm (depending on the optics). This area reduction causes the excitation light intensity to increase by about 40% as the light traverses the last millimeter before reaching the sample surface. Because we are currently interested only in the qualitative behavior of absorbing electrolytes, we have neglected this increase in the model. To make the results more precise a term should be added to Equation 2-3 to account for the increasing intensity of the excitation light caused by focusing.

Example

Figure 2-3 shows temperature profiles calculated by the model for the second cycle of an experiment. The geometry corresponds to the cell shown in Figure 2-2. Because electrolyte is in contact with the back of the electrode, the model evaluates 1 mm of water, 125 μm of platinum, and 1 mm of water. As the temperature profiles show, 1 mm of water encompasses the thermal boundary layer. The parameters used in the model are typical values. Platinum is about 20% absorbing in visible

wavelengths [57]. The excitation light intensity used in the model corresponds to a typical excitation power of 2.5 mW focused to a 9x2 mm rectangle on the sample surface. The thermophysical data and refractive index data are tabulated in Appendix IV.

The temperature profiles are not surprising. The first temperature profile in the heating cycle shows that the system does not return to its original state after the first cycle. During the heating cycle, there is a small thermal gradient through the platinum sample, and the temperature profiles on the front and back of the sample are similar. This similarity is the foundation for the secondary gradient technique, which is discussed further in the next chapter. The cooling curves show that the sample does not cool to its original value. The temperature profiles begin to approach steady state after 10 cycles (as will be shown in Figure 2-6 in the next section).

Figure 2-3. The calculated temperature profile of the system is shown at a series of instances during cycle 2. The left pane shows the heating half of the cycle and the right pane shows the relaxation half. The arrows show the progression of the temperature profiles. The excitation light is applied from the right. The primary/sample interface is at node 450, and the secondary/sample interface is at node 400. The system is a 1 mm layer of water, 125 μm of platinum, and 1 mm of water. Only 200 μm of water on each side of the sample are shown. The nodes in the liquids are spaced 1 μm apart; those in the sample are 2.5 μm apart. The excitation is a 20 Hz square wave with an intensity of 139 W m^{-2} . The surface is 20% absorbing.

B. Probe Beam Modules

The refractive index profile is calculated from the temperature profile by a linearization.

$$n \cong n_0 + \left. \frac{\partial n}{\partial T} \right|_{T_0} (T - T_0) \quad [2-4]$$

The temperature changes are on the order of milliKelvins, so negligible error is introduced by this approximation. The model only calculates the excess temperature, $T - T_0$, and similarly we calculate the excess refractive index:

$$n^{\text{excess}} = \frac{\partial n}{\partial T} T^{\text{excess}} \quad [2-5]$$

Only the gradient of the refractive index is needed. Therefore the use of the excess refractive index is suitable and increases the precision of the calculations.

Figure 2-4. Exaggerated probe deflection.

Figure 2-4 shows a greatly exaggerated view of the probe deflection. Given the refractive index gradient, the probe module calculates the angular deflection of the probe beam, θ . The deflections are assumed to be small in all cases, allowing simplified equations to be used. A 10 μrad deflection over the 10 mm path length of

the sample will move the probe beam only 0.1 μm farther from or closer to the sample.

A correction for refraction at the exit of the cell must be made by using Snell's law. Because the angles are assumed to be small, the correction reduces to the ratio of the refractive indices.

$$n_{\text{ext}} \sin \theta_{\text{ext}} = n_{\text{int}} \sin \theta_{\text{int}} \Rightarrow \theta_{\text{ext}} \cong \frac{n_{\text{int}}}{n_{\text{ext}}} \theta_{\text{int}} \quad [2-6]$$

The external refractive index is assumed to be 1 (that of air).

Two algorithms were used to calculate the deflection of the probe beam as it passes through the refractive index gradient:

- 1) The beam is assumed to be an infinitely thin ray, and may pass by the electrode at an angle to the sample surface.
- 2) The beam has finite size and a Gaussian intensity profile, and passes parallel to the sample surface.

Single Ray

An infinitely thin ray, parallel to the surface, obeys the simple equation discussed in Chapter 1:

$$\theta = \frac{L}{n_o} \cdot \frac{dn}{dx} \quad [2-7]$$

When the beam is not parallel to the sample surface, the probe deflection is the integral of the gradient along the beam path (see Figure 2-4 for axes).

$$\theta = \frac{1}{n_o} \int_{z=0}^L \frac{dn(x)}{dx} dz \quad [2-8]$$

Here it is assumed that the path of the beam is unchanged from its path when no gradient is present. The offset of the beam is a linear function of z

$$x = x_o + z \tan \beta. \quad [2-9]$$

where x_o is the offset at the entrance to the cell, and β is the angle of the beam to the sample surface. This relation is combined with Equation 2-8, resulting in an integrand which only depends on z . The integral is numerically evaluated with trapezoidal integration.

The node pattern of the probe beam is different than the node pattern of the temperature gradient. The refractive index gradient was calculated using a second-order Lagrange interpolating polynomial [64].

$$\left. \frac{df}{dx} \right|_{x_i} \equiv f(x_a) \frac{2x_i - x_b - x_c}{(x_a - x_b)(x_a - x_c)} + f(x_b) \frac{2x_i - x_a - x_c}{(x_b - x_a)(x_b - x_c)} + f(x_c) \frac{2x_i - x_a - x_b}{(x_c - x_a)(x_c - x_b)} \quad [2-10]$$

This formula calculates the gradient of a function at the point x_i using the values of the function at three known points. For each node on the probe beam, x_i , we find three adjacent nodes in the temperature solution, x_a , x_b , and x_c . Two points nearer to the sample surface and one point farther from the sample surface are used.

Finite Diameter Probe Beam

Figure 2-5. The probe beam is sliced into planar ribbons. Each differential ribbon contains a different amount of energy and experiences a different deflection.

The finite diameter probe beam is required to be parallel to the sample surface to reduce computation time.

The deflection equation for finite beams depends on the type of position detector used.

We have developed a model for the most common detector,

which is the linear position detector.

The linear position detector (LPD) measures the power-weighted centroid of the probe beam spot on the detector face. The probe beam has a Gaussian intensity profile

$$I(x, y) = I_0 \exp \left[\frac{-(x - x_0)^2 - (y - y_0)^2}{r^2} \right]. \quad [2-11]$$

where I is the intensity of the beam, and I_0 is the intensity at the center of the beam, located at coordinates (x_0, y_0) . The size of the beam is characterized by r , the $1/e$ radius. This is the distance from the beam center at which the intensity has dropped to $1/e$ of the centerline value. A more common size indicator is the $1/e^2$ diameter, $d(1/e^2)$. The relation between the two characteristic sizes is

$$d_{1/e^2} = 2\sqrt{2} r_{1/e}. \quad [2-12]$$

Because we are using a 1-D model, the probe beam will be sliced into planar sections (see Figure 2-5). The deflection that the LPD measures is the sum of the deflections of all the differential ribbons (weighted by power).

$$\theta = \frac{\frac{L}{n_o} \int_{-\infty}^{\infty} P'(x) \frac{\partial n(x)}{\partial x} dx}{\int_{-\infty}^{\infty} P'(x) dx}, \quad [2-13]$$

$$\text{where } P'(x) = I_o r \sqrt{\pi} \exp \left[\frac{-(x-x_o)^2}{r^2} \right]. \quad [2-14]$$

The linear power density of each planar slice, $P'(x)$, is obtained by integration of Equation 2-11 in the y direction. The gradient, $\partial n / \partial x$, is then calculated using Equation 2-10.

The infinite limits of integration in Equation 2-13 must be truncated. We typically integrate over $\pm 2.5r_{1/e}$. When the probe beam offset is small, part of the beam will be blocked by the sample. When required, the limits of integration in Equation 2-13 are reduced further to account for only the part of the probe beam which passes the sample. The blocked portion of the probe beam is assumed to be reflected or scattered and not to reach the position detector.

Examples

Figure 2-6 shows the calculated probe beam deflection starting at $t=0$ for 25 cycles. The AC deflections are superimposed on a baseline value. The baseline deflection is the steady-state deflection discussed in Chapter 1. The baseline quickly approaches a steady-state value. The AC deflections have a constant amplitude after the first few cycles.

Figure 2-6. The probe beam deflection is shown for 25 cycles.

Figure 2-7 shows the calculated probe deflections for three probe offsets. At an offset of $80\text{ }\mu\text{m}$, the beam deflection shows a saw tooth shape. There is negligible delay between when the excitation is applied and the beginning of the probe deflection. For the larger probe offsets, the probe deflection becomes smoother and a delay is

seen. The shape of the probe deflection response is an effect of the frequency response of the AC signal to the different modulation frequencies present in the excitation light.

The square wave excitation can be considered in the frequency domain as the sum of the primary modulation frequency and odd harmonics. Each component frequency of excitation waveform produces an independent probe deflection. Because the system is linear, the individual responses are additive. The higher frequencies of the excitation waveform have a shorter thermal diffusion length. Therefore, at the larger probe offsets, the higher frequencies of the probe deflection are attenuated. The probe deflection becomes successively smoother as the probe offset increases. At a sufficiently large offset a sinusoidal probe deflection would result.

Figure 2-7. The calculated probe beam deflection is shown for probe offsets of 80, 120, and 160 μm . As the beam is moved further from the sample surface, the high frequency components disappear.

Figure 2-8 demonstrates the effect of changing the diameter of the probe beam. These results were calculated for the same conditions as the previous figures. The effect of the probe diameter is not large. There are two effects to note: The signal produced by the large beam is smaller, and has sharper peaks.

Figure 2-9 shows the side view of the sample for two probe diameters. The center of each beam is located the same distance from the sample surface. Part of the larger beam is blocked by the sample. The intensity centroid of the remaining beam is farther from the sample surface. Because the offset of the intensity centroid increases, the deflection signal decreases. The larger beam probes the region close to the sample surface. The sharp

peaks in the deflection signal for the larger beam are the high frequency components of the probe deflection that the smaller beam cannot detect.

Figure 2-8. The calculated probe beam deflection is shown for three beam sizes. The labels are the $1/e$ radii in micrometers.

Figure 2-9. Side view of sample showing the center (+) and intensity centroid (X) of the probe beam.

C. Lockin Modules

The probe deflection as calculated by the above two modules is not usable in that form. We need to determine the magnitude and phase of the probe deflections. Our first attempt was to search the deflection data for peaks. The peak-to-peak height was used as a magnitude. The time from the beginning of the excitation light until the first peak was used as the delay. This method is tenuous, because the sharp peaks in the probe deflection are due to higher modulation frequencies in the excitation light, not the base modulation frequency. We decided it was necessary to numerically model the lockin.

Two types of models of the lockin were developed. One operates in the time domain, and the other in the frequency domain. Each has advantages discussed in Appendix II, which also contains a good introduction to the workings and characteristics of a lockin. References 65 and 47 discuss synchronous detection with lockin amplifiers.

The version we use for the results in this thesis operates in the frequency domain. The Fourier transform of the beam deflection signal is calculated. The magnitude and phase are thereby directly determined. As can be seen in Figure 2-6, the beam deflection changes quickly during the first few cycles. The beam deflection signal from the initial cycles is not processed. We typically use 5 cycles starting at cycle 7 to calculate the signal phase and magnitude. Appendix II discusses a filter which can remove the effect of the sloping baseline.

The magnitude that we report is the equivalent of the amplitude, A , of a sine wave.

$$S(t) = A \sin(\omega t + \phi) \quad [2-15]$$

A lockin would typically measure the root-mean-square amplitude.¹ Peak-to-peak amplitude is another common measure. The different measures are directly proportional to each other:

$$A_{p-p} = 2A \quad \text{and} \quad A_{rms} = \frac{\sqrt{2}}{2} A. \quad [2-16]$$

The phase of the AC signal, ϕ , and the delay as we conceive it are not equal. The difference between the two concepts is caused by the different nature of the signal and excitation. The AC signal is a bipolar sine wave, whereas the excitation is a monopolar heat input. The two measures are related by

$$\text{delay} = 270^\circ - \text{phase}. \quad [2-17]$$

The derivation of this relation is given in Appendix II.

With all the pieces in place, we can simulate the PDS signal. Figure 2-10 (see page 45) shows the calculated signal magnitude and phase versus the probe offset. The geometry is the same as the previous figures, but the excitation power has been increased by a factor of ten. The magnitude plot

¹ Intrinsically the lockin measures the average of the absolute value of the sine wave. This value is directly proportional to the rms, peak-to-peak, and amplitude.

Appendix II discusses these relations.

shows the logarithmic relation discussed in Chapter 1. The delay is linearly related to the probe offset. When the slopes of the lines in Figure 2-10 are calculated, we find they are different from those predicted by the simple theory of Chapter 1. In Chapter 4, the model is used to explore the relation between signal magnitude and phase more fully.

The dotted lines from 500 to 800 μm in Figure 2-10 demonstrate that even the numerical lockin eventually loses the signal in the background. The sloping baseline that the AC signal is superimposed upon (see Figure 2-6), has some frequency components at the modulation frequencies. At large probe offsets, the signal becomes lost in the background caused by the sloping baseline.

Running the model for longer times would reduce the slope of the baseline. This would allow the signal to be detected at large probe offsets. However, solving the problem of the sloping baseline is academic. The real PDS system would never be able to measure the signal at such large probe offsets.

Figure 2-10. The calculated signal magnitude and phase are shown versus probe offset. The geometry is the same as in Figure 2-3. The excitation is a 10 Hz square wave and the intensity has been increased to 1390 W m^{-2} . The surface is 20% absorbing. The probe beam has a $1/e$ radius of $20 \mu\text{m}$. The numerical lockin evaluated the probe deflection for cycles 7-11. The dotted portion of each line shows where the signal becomes lost in the baseline.

Conclusion

We chose to calculate the temperature numerically. Analytic solutions exist in the literature for the temperature profile of many geometries (see References 9, 10, 12, 14, 23, 66, and others cited therein). The thermal problem for PDS is the same as for PAS or PTS. Analytic solutions for these close relatives can be found References 50 and 13. The analytic solutions are typically for sinusoidal excitation. The determination of PDS signals for square wave and other modulations requires summing the analytic solution at several modulation frequencies. The determination the effect of the finite probe diameter requires summing the analytic solution at several offsets (typically 50). Each of the analytic solutions is a series solution requiring evaluation of hundreds of terms to converge. The terms of the series contain transcendental functions, bearing a computational penalty. With respect to computer time, it was the author's judgement that it was just as fast to directly solve the temperature profile numerically once at every time step, as to numerically solve the analytic series solution 50 or more times at each time step. The numerical solution also allowed us to incorporate absorbing electrolytes into the model. Solutions for absorbing electrolytes have not been previously reported in the literature.

The model is only one dimensional. Our recently-designed cells are well represented by this geometry. However, many cell designs would be better modelled by a two-dimensional temperature profile. A two-dimensional solution is well within the limits of numerical techniques, but it was just beyond the scope of this research.

The probe beam deflection modules are only accurate for the linear position detector. Another common detector is a bicell position detector, which does not measure the position of the intensity centroid. Future model development could develop modules for this detector. Neither module calculates large deflections. For temperature gradients, the small angle approximations are adequate. In Chapter 6 we discuss a model of the concentration gradients which form near the electrode surface. The equations are extremely similar. Some electrochemical systems cause large probe deflections, which would require another probe module. The method of calculation of large beam deflections for thin rays can be found in Reference 67 and for finite-diameter beams in Reference 26.

To date, most of what we have learned from the model is qualitative. The model development has led to an understanding of the effect of various parameters on the signal. In Chapter 3, we use the model to explore the effect of the modulation waveform, and the feasibility of the secondary gradient technique. We have begun to make quantitative studies using the model in its final developed form. In Chapter 4 the relation between the signal and the probe beam parameters is discussed.

Chapter 3:

PDS Techniques

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This chapter and the next two chapters discuss practical aspects of PDS, subjects often ignored in the literature. This chapter discusses the equipment and methods we use. We have developed the secondary gradient technique to expand the number of electrochemical systems that can be studied. Also, the secondary gradient technique solves some problems of discriminating between various effects. As with other spectroscopic

techniques, PDS requires that the data be corrected for the source spectrum. Several correction methods we have investigated are discussed. The copper system discussed in Chapter 1 is used as an example of the cross-plotting technique.

A. Equipment

Figure 3-1. Schematic of the system. M represents a pair of mirrors. A small mirror directs a part of the modulated excitation light onto a photodiode (PD) that provides a reference signal for the lockin. LPD is the position detector.

The basic PDS system is shown in Figure 3-1. We can consider the system in terms of three subsystems: excitation, detection, and electronics. The source, monochromator, chopper and associated optics comprise the excitation system. This subsystem delivers narrow-band excitation light to the sample surface. The detection subsystem consists of a probe beam, focusing lens and a position detector. The electronics consist of filters, a lockin amplifier, and a computer to record data and control the experiment.

The system is mounted on a vibration-isolated optical table and enclosed in boxes. The boxes prevent air currents from affecting the experiment, and block stray light. As we will discuss further in Chapter 5, the boxes do not prevent acoustic noise. Their purpose is to reduce air currents, therefore they are constructed of a light material and carefully fitted to eliminate openings as much as practical.

Excitation

The light sources we use are commonly available devices. A xenon arc lamp provides excitation light from 200-1000 nm. Quartz lamps were used in the near IR. In the mid IR we use a rare-earth glow bar. An $f/3.5$ Ebert-type monochromator is used to provide narrow-band excitation light. The light which exits the monochromator is then delivered to the sample surface.

Optics

The arrangement of the excitation subsystem was the result of many iterations. Only one lens is required, however we use two lenses and two mirrors arranged as a periscope. The following factors led to this arrangement:

- The first lens collimates the excitation light, and the second focuses it onto the sample. The logic of using two lenses instead of one as follows: The probe laser is firmly mounted to the table. It cannot be translated because adding a translation stage under the laser introduces unacceptable noise. The position of the sample surface is fixed at a specific distance relative to the probe beam. Therefore, to focus the excitation light, the entire excitation system (source, monochromator, and

lens) would have to be moved. Introducing a second lens adds a needed degree of freedom to the system. The source and monochromator can remain fixed. Movement of the second lens focuses the excitation light.

- With two lenses the distance allowed between the monochromator and sample is greatly expanded. Practical optics are limited to 50 mm diameter. With the $f/3.5$ monochromator, the maximum distance between monochromator and a 50 mm diameter lens is 175 mm. The image of the slit should be demagnified to increase the intensity of the excitation light. Therefore, the distance between lens and sample must be less than 175 mm. For a single lens and an image size ratio of 2:1, the total distance from monochromator to sample is 260 mm. This is a difficult space in which to accommodate a chopper, mirror, and photodiode.
- The focusing lens is arranged so that its translations are relative to the position of the translation stage under the cell. With this arrangement, movement of the cell also moves the focusing lens. Because the input beam to the focusing lens is collimated, focus remains constant when the cell is moved. This allows the probe offset to change without changing the focus.
- The exit slit of the monochromator is a vertical slit. The two mirrors rotate the image 90° to form a horizontal image on the sample. The alternative is to rotate the monochromator. The height of the entrance slit of the monochromator would be increased. Two mirrors would still be required to lower the optical axis to that of the probe beam.
- The mechanical stability of the probe beam, cell holder, and detector is improved by keeping them close to the surface of the table. Using the two

mirrors allows each part of the system to be kept at its minimum distance from the table surface.

- To implement our eventual goal of extending the excitation wavelength into the mid IR, the lenses and mirrors would be replaced by off-axis paraboloid mirrors. Therefore, the right-angle bend in the excitation beam path is required.

The use of two lenses and two mirror increases the losses. The lenses have anti-reflection coatings, but still lose 1-2% due to first surface reflections. The mirrors are coated to be 98% reflective. A one-lens system would lose 2%; our system loses 8%. We think the benefits outweigh this small loss.

Modulation

The most common device for modulating the excitation light is a mechanical chopper, which is typically a spinning disk with two slots cut into it. For the 2-slot wheel, the motor spins at half the modulation frequency. We believe that noise is produced at harmonics of the motor frequency, especially at 2 times the motor speed. To reduce this noise, we use a chopper wheel with 5 slots rather than the typical 2-slot wheel. By switching to a 5-slot wheel, the motor speed is greatly slowed. The first harmonic at 2 times the motor speed is still $2/5$ of the modulation frequency. There is the possibility that slower motor speeds will be less stable. We periodically confirm the stability of the chopper speed. The slots in the 5-slot wheel are smaller than those in the 2-slot wheel. The size of these slots approaches the size of the excitation beam. The result is that the modulation waveform is not square.

Effect of Modulation Waveform

In laser-based spectroscopies, the excitation beam is small compared to the size of the chopper slots and the excitation waveform is close to a pure square wave. The use of a continuous source results in a larger excitation beam. The result is that the excitation waveform is no longer square. Figure 3-2 shows how the modulation waveform changes as the size of the excitation

Figure 3-2. As the excitation beam size approaches that of the chopper slot, the modulation waveform becomes a triangular wave.

beam approaches that of the chopper slots. This waveform we call an "equal energy triangle." Even as the slope of the sides of the waveform increases, the energy in the excitation light remains constant. Various waveforms were analyzed to determine their effect on the PDS signal. Figure 3-3 shows several other waveforms we studied. The first three waveforms can be created with a mechanical chopper. The two sinusoidal waveforms would require an electro-optic modulator or a complex, graded neutral-density filter.

Lockin detection measures the response of the system at one frequency, the modulation frequency.¹ A square wave is equivalent to the

¹ This is only true if the lockin implements sine wave correlation. Older lockins were limited to square wave correlation which measures the response at mostly the modulation frequency.

sum of a sine wave and all its odd harmonics. The other waveforms will have their energy distributed among different frequencies. The system is being excited at multiple frequencies and responding at multiple frequencies, but we only measure the response to one frequency. There are no non-linear effects—processes which allow an excitation at one frequency to produce a response at a different frequency. Therefore, only the energy in the waveform at the modulation frequency is important. We can use a Fourier transform to determine this component, or in our case, we used the numerical lockin model discussed in Chapter 2, to measure the sine component of the modulation waveforms.

Figure 3-3. Various hypothetical waveforms. All of these are made from a source of unit intensity. For the triangle waveforms, the slope was 80% of maximum. The pulse has a duty cycle of 20%.

Table 3-1 shows the signal-producing component of the modulation, S , for various waveforms shown in Figure 3-3. The energy, E , and signal to energy ratio, SER are discussed in the next section.. An interesting result is that the pure square wave has a larger signal component than the pure sine wave, 0.637 vs. 0.5. From the same excitation source, a 27% larger signal is achieved from the square wave. Of the waveforms shown in the table, the square wave has the largest signal component, S .

Using the results in the equal energy triangle column, we can determine the effect of the size of the chopper slots. A moderate slope of 0.3 only results in a signal loss of 4%, and a severe slope of 0.5 loses 10%. We typically experience slopes of 0.1 to 0.2, therefore we conclude that the losses are not severe.

Table 3-1. For an excitation source of unit intensity, the signal amplitude, S , energy, E , and ratio, SER, are given. The fraction in the left column is the degree of slope or duty cycle of the waveform. The triangles have a slope of 1 when no plateau remains in the waveform.

slope or duty	equal E triangle			unequal E triangle			pulse		
	S	E	SER	S	E	SER	S	E	SER
0	0.637	0.5	1.27	0.637	0.5	1.27			
.1	0.634	"	1.27	0.634	0.475	1.34	0.197	0.1	1.97
.2	0.626	"	1.25	0.626	0.45	1.39	0.374	0.2	1.87
.3	0.613	"	1.23	0.613	0.425	1.44	0.515	0.3	1.72
.4	0.596	"	1.19	0.596	.4	1.49	0.605	0.4	1.51
.5	0.573	"	1.15	0.573	0.375	1.53	0.637	0.5	1.27
.6	0.547	"	1.10	0.547	0.35	1.56	0.605	0.6	1.01
.7	0.516	"	1.03	0.516	0.325	1.59	0.515	0.7	0.736
.8	0.482	"	0.964	0.482	0.3	1.61	0.374	0.8	0.468
.9	0.445	"	0.890	0.445	0.275	1.62	0.197	0.9	0.219
.99	0.409	0.5	0.818	0.409	0.25	1.64			

	S	E	SER
pure sine	0.5	0.5	1
pure square	0.637	0.5	1.27
half-wave rectified sine	0.5	0.318	1.57
unequal energy triangle	0.409	0.25	1.64
impulse			2

Optimization of Signal to Energy Ratio

Table 3-1 also lists the energy, E , and signal to energy ratio, SER, of the various waveforms. The energy is the time average of the power. In some systems it would be beneficial to reduce the amount of energy being introduced into the system. Figure 3-4 shows model results for three waveforms: square wave, half-wave rectified sine, and 20% pulse (in order of increasing SER). The intensity of the excitation has been adjusted so that equal signal magnitude would be measured by the lockin for each waveform. The temperature profiles show that using the higher SER waveform reduces the temperature throughout the system about 33%. The probe beam deflections each are imposed upon a baseline caused by the steady state heat input of the excitation light. This baseline is also reduced 33% by using the higher SER waveform.

An example makes the benefits of modulation waveform optimization clear: consider a situation of square-wave modulation, and we desire to reduce the energy input to the system by $1/3$. Two choices are available: 1) retain the square-wave modulation and reduce the excitation intensity 33% with a neutral-density filter, and thereby reduce the signal 33%, or 2) change to the 20% pulse modulation with the same excitation intensity and lose no signal.

Figure 3-4. The temperature profile and probe beam deflection for three modulation waveforms as calculated by the model. The temperature profile is for the beginning of cycle 7. The electrolyte was transparent and the surface was 30% absorbing. The probe offset was 150 μm and the modulation frequency was 20 Hz. The intensity of the excitation, I , has been adjusted so that the same signal magnitude results from each waveform. (A) is the pure square wave, $\text{SER}=1.27$, $I=139 \text{ W m}^{-2}$ (B) is the half-wave rectified sine, $\text{SER}=1.57$, $I=177 \text{ W m}^{-2}$ and (C) is a 20% pulse, $\text{SER}=1.87$, $I=237 \text{ W m}^{-2}$.

Detection of Deflections

The probe deflections are measured with silicon photodiode devices and a position monitor. Two types of position detectors are shown in Figure 3-5. The bicell contains two photodiodes separated by a narrow divider. Part of the beam hits each photodiode, generating two currents. The position monitor calculates the position by

$$\text{position} = \frac{i_A - i_B}{i_A + i_B} \quad [3-1]$$

The denominator of this equation makes the measurement insensitive to intensity fluctuations of the probe beam. The bicell position detector is linear

over only a small range. The linear position detector (LPD) is a single photodiode with an anode on each end, and a common cathode. Current generated travels to each anode. The anode closer to the beam centroid will receive more current. The position monitor uses the same formula (Equation 3-1) to calculate the position. The LPD is so named because it is linear over its entire length. The bicell is more sensitive than the LPD. We use the bicell detector when interested in small AC deflections. When measuring the relatively large DC deflections, the LPD is better.

Other types of position detectors have special applications. Probe deflections can be measured in 2 dimensions with a 2D position detector. Weaver has used this detector to measure 2-dimensional concentration gradients [41 - 43]. A pinhole detector has a frequency response that is flat up to several megahertz (the above devices have a flat frequency response to about 10 kHz). The pinhole detector is used to measure probe beam deflections caused by impulses and steps [68].

Figure 3-5. Two position detectors (A) bicell, and (B) 1D linear. The probe beam strikes from the left.

Electrical and Control

Figure 3-6. Block diagram of the instrumentation.

The instrumentation is shown in Figure 3-6. The deflection signal is fed to two bandpass amplifiers. One is adjusted to be a low-pass filter for the DC. This amplifier removes the AC deflection and amplifies the signal. The other amplifier is adjusted to be a bandpass filter for the AC. The AC

amplifier removes the DC baseline from the AC signal. The AC signal is processed by the lockin, which sends the in-phase and out-phase components to the computer. The photodiode provides the reference signal to the lockin. While most choppers provide a reference signal, the phase of this reference signal is not accurate.

The DC amplifier is required so that the DC signal can be resolved by the 10 V bipolar 12-bit AD converter in the computer (which has a resolution of 5 mV). The AC signal does not have to be amplified, because the lockin can measure nanovolt signals. Instead, we use an AC amplifier to eliminate DC fluctuations from the AC signal. These DC fluctuations can cause the lockin to overload. Setting the bandpass of the AC amplifier too narrow risks introducing phase shift into the AC signal. In our experience, shifts as large as 40° occur. The phase shift and frequency response of any filter should be tested.

Vector Tracking Modes

Lockins offer a vector track mode. In this mode, the instrument displays the magnitude and phase of the signal. Our experience is that this mode is more noisy than the standard two-phase mode. Internally, the lockin is using a phase-locked loop to rotate the reference signals until the out-phase channel is nulled. This operation is difficult at low SNR's. We prefer to measure the two phases and calculate the magnitude and phase afterwards

$$S = \sqrt{A^2 + B^2} \text{ and } \phi = \arctan(B/A) \quad [3-2]$$

Some lockins offer these calculated values.

Which Correlation Mode Is Best?

Considered in the frequency domain, a square wave is the sum of sines at odd harmonics. Most lockins perform square wave correlation², which means that the lockin responds at the primary modulation frequency and all odd harmonics. Because PDS uses square-wave excitation we initially considered this correlation mode to be the most suitable.

Two considerations led us to reverse this decision. The frequency response of the PDS signal is not uniform. The signal decreases with $1/\sqrt{f}$. There will be only small probe deflections produced at the higher frequencies. There is often much noise in the frequency range 50-80 Hz. With typical

² The trend is moving away from square-wave correlation. Newer lockins offer sine-wave correlation.

modulation frequencies of 10-40 Hz, square-wave correlation will let in more noise than signal, at the higher frequencies. Our experience is that sine wave correlation is a better choice.

Computer Control

The computer records the signals and controls the potentiostat and monochromator. Two types of experiments are common. One is the measurement of the absorption spectrum of the surface while the electrode is held at constant potential. The other type of experiment is to conduct a potentiodynamic program while the excitation wavelength is held constant. Both experiments require averaging to achieve an acceptable SNR.

During the acquisition of spectra, the wavelength of the monochromator is stepped, not scanned. The monochromator stops at a series of wavelengths. At each wavelength, the computer waits a predefined time, and then reads the values from the lockin. The outputs from the lockin are an average over a length of time characterized by the time constant, t_c . The average is weighted by $\exp[-t/t_c]$ (the common 6 dB/octave slope of an RC filter). If the computer waits 3 time constants, 95% of the signal will be due to the present wavelength step; at 4 time constants 98%, etc. We typically use time constants of 300 ms or 1 s and wait for 4 to 5 times this value. The stepper motor produces some noise while the monochromator is changing the wavelength. The lockin has a signal gating input which allows the computer to block the signal from entering the lockin. The computer controls the gating input to prevent noise from entering the lockin while the monochromator is changing the wavelength. The computer repeats the spectral scan several times and averages the results. Depending on the signal quality desired, the process takes 5-30 minutes. What has been

acquired at this point is a raw spectrum. The methods of correcting the spectrum are described later in this chapter.

The second type of experiment is a potentiodynamic program. In order to average the results, a pretreatment must be applied before each potential program. The potentiostat is programmed to perform two potential programs: the pretreatment, and the experiment, *e.g.*, triangle sweep, or potential steps. During the experimental program, the computer records all the signals. This process is repeated many times and the results are averaged. To get monolayer sensitivity during platinum cyclic voltammetry, for example, the experiment was repeated between 25 and 50 times. This repetition is a minor limitation: the electrochemistry must be reproducible through the use of some program of pretreatment and experiment.

B. Cells

PDS requires the electrochemical cell to have three windows: entrance and exit windows for the probe beam, and a window for the excitation light. The cell is mounted on a translation stage and rotation stage to allow the electrode surface to be aligned with the probe beam. The electrode must be held rigidly; movements of more than a few micrometers will create noise. Bubbling a purge gas through the electrolyte during the experiments creates convection currents which cause unacceptable noise. During the experiment, we only pass the purge gas above the electrolyte. Other than these requirements, the cells are common electrochemical cells.

Two electrochemical cells we have used are pictured in Figure 3-7. Both assemblies are placed in 10x10x40 mm fluorimeter cuvettes, which

provide the three windows needed. The double-sided cell allows the probe beam to pass on the front or back of the electrode. The symmetric counter electrodes assure that the potential distribution and concentration gradients will be the same on both sides.

Figure 3-7. Diagram of single-sided and double-sided electrochemical cells. The working electrodes are 10x10 mm platinum foils 125 μm thick. The shaded region on the electrode shows the area illuminated by the excitation light. The purge gas and reference electrode are connected with small tubes. Platinum screens are used as counter electrodes.

The cell shown in Figure 3-8 is the best general purpose cell we have designed. The placement of the electrode at the end of a small channel ensures that all the physical processes are 1-dimensional: the current distribution is uniform over the electrode surface, mass transport is linear within the region the probe beam senses, and because the plastic supporting material has a low thermal conductivity, thermal conduction occurs mostly into the electrolyte. The large electrolyte volume outside the channel and a small electrode ensure that electrochemical reactions do not significantly change the bulk concentration of the electrolyte species during the course of an experiment.

Figure 3-8. Two views of a general purpose electrochemical cell. The assembly is constructed of Kel-f (a halogenated polymer with superior dimensional stability and strength compared to Teflon) and placed in a 10x40x40 mm fluorimeter cuvette. The counter and reference electrodes are contained in separate compartments, which are linked with small tubes.

Surface of the Sample

In general, PDS places few restrictions on the sample, only that it should be planar. Polished or unpolished electrodes can be studied. Rough samples can be studied, as long as the roughness is small compared to the thermal diffusion length. Even a curved sample can be used. The only reason to use planar geometries is to be able to apply theoretical developments found in the literature. If one is willing to accept some uncertainty or develop new models, there is no reason to avoid deviating from a planar sample.

A curved sample eliminates the problem of making the probe beam and sample parallel. We recommend this technique only when one is willing to lose some precision in measuring the signal magnitude and phase. When the sample is very wide (several centimeters), it is impossible to focus the probe beam and place the beam waist close to the sample surface. In this situation, a curved sample is necessary. It is very easy to achieve good signals with a slightly curved sample, as long as the curvature is convex. A very slightly concave sample can make the signal impossible to detect. One hundred micrometers of curvature is significant with respect to the probe beam, but may be insignificant to physical processes. If the curvature is not great, the transport processes may be modeled as one-dimensional.

When the roughness of the surface approaches the thermal diffusion length, problems will occur (see Figure 3-9). Locations in the

Figure 3-9. Side view of the probe beam passing a very rough sample. Different points on the surface are different distances from the probe beam.

valleys will be so far from the probe beam (when scaled by the thermal diffusion length) compared to the peaks, that their contribution to the signal will disappear. Concentration gradients are characterized by much longer lengths and will not be as strongly affected by surface roughness.

Thin-Layer Cell

A thin-layer cell is shown in Figures 3-10 and 3-11. This cell creates a thin layer of electrolyte on the front of the electrode. The working electrode is mounted on a piston which moves within a cylindrical cell body. The piston fits tightly within the body at the top and bottom to maintain alignment. Two flats are cut into the sides of the piston to provide electrolyte access to the working electrode.

Because the electrolyte layer thickness can be smaller than the diameter of the probe beam, the probe beam measures the thermal gradient at the back of the electrode. This technique is called the secondary gradient technique and is described in the next section. This cell was designed for use with infrared excitation. Because aqueous electrolytes strongly absorb in the infrared, a thin layer of electrolyte must be used. Cells of similar design are used in infrared reflection spectroscopy. Because of the small electrolyte volume near the electrode, depletion of electrolyte species can occur. References 69 and 70 discuss the effects of depletion of the thin electrolyte layer.

Figure 3-10. Cross-section diagram of a thin-layer cell for use with the secondary gradient technique. The cell body is cylindrical. The working electrode, WE, is mounted on a piston. The thickness of the electrolyte layer between the electrode and window is controlled with a micrometer stage with $0.2\ \mu\text{m}$ resolution. The reference electrode compartment is contained in the cell wall. The counter electrodes, CE, are at the top. The probe beam travels normal to the page through windows in the cell body.

Figure 3-11. The bottom view of the thin-layer cell. The working electrode is mounted on the center of the piston. The piston has two sides cut flat to provide an electrolyte channel. The D-shaped channels help to control the current distribution. The other sides fit tightly. A slot allows the probe beam to pass behind the electrode.

C. Secondary Gradient Technique

Figure 3-12. Side view of primary and secondary gradients for a thermally thin electrode.

The probe beam does not have to be at the front of the sample. If the sample is thermally thin, the heat absorbed at the front of the sample will conduct through the sample and into the backing material, which we call the secondary phase (see Figure 3-12).

(The thermal diffusion length is large in metals (see Table V-2). The result is that the PDS signal in the secondary phase is close in magnitude to the signal in the primary phase. Solids, liquids, or gasses can be used as the secondary phase.³

There are several situations where such an arrangement is beneficial or even necessary. Thin-layer cells do not have room for the probe beam to pass in front of the electrode. Our major motivation for developing the secondary gradient technique was for infrared spectroscopy, which requires a thin-layer cell. Other situations can also benefit from this technique. A gas-evolving electrode could not have the probe beam on the front; the bubbles

³ PDS in gaseous phases and PDS in liquid phases are so different from each other as to be almost indistinguishable with respect to theoretical treatment. In general, PDS signals in gases are small. We have not investigated using a gas as a secondary phase, however it is an interesting possibility.

would cause random deflections of the probe beam. An electrode surface which was very rough or non-planar, could be mounted on a smooth substrate. Because the thermal diffusion length is long in solids, the surface would "appear" smooth from the back (see Figure 3-9). In these situations we do not have the ability to measure concentration gradients simultaneously with the surface absorption.

For electrochemical systems, the use of a solid backing has advantages. The back of the electrode becomes completely isolated electrochemically. This allows the Peltier heats to be isolated from the concentration gradients. Because the Peltier heats will be small, it is important that the second interface of the electrode be completely isolated. Small leakage currents would cause concentration gradients that would likely dominate the beam deflection. In some systems we have studied, the concentration gradients can cause large beam deflections of the order of milliradians. These deflections are capable of moving the probe beam large distances away from or toward the electrode. A 1 mrad deflection will move the probe beam 10 μm away from a 10 mm wide electrode. Such a deflection would cause the AC PDS signal to increase or decrease significantly. This effect would be impossible to separate from changes in the surface absorption coefficient. Here again, complete isolation of the back of the electrode will remove the effect of the concentration gradients.

The design of a secondary-gradient cell is not easily optimized. The sample should be thermally thin. The thermal diffusion length varies from 100 to 30 μm in water (see Table V-2). To keep a thin sample flat within that distance scale requires that the sample be supported. One solution is to

support a thin sample on a solid material that is transparent to the probe beam. The probe beam will then pass through the support.

Because quartz is a stable material and can be precisely machined, it was evaluated as a secondary material. The thermal diffusivity of quartz is about 6 times that of water, and it performs acceptably in a thermal sense. The probe deflection is $\theta = \frac{L}{n} \frac{\partial T}{\partial x} \frac{\partial n}{\partial T}$. While the thermal gradient would be satisfactory, the thermal refractivity, $\partial n / \partial T$, is very small for quartz (see Table V-3). When evaluating solid materials, the thermal expansivity can be used as the main indicator of the thermal refractivity, and is approximated by

$$\frac{\partial n}{\partial T} \equiv \frac{-\alpha}{6n} (n^2 - 1)(n^2 + 2) \quad [3-3]$$

where α is the volumetric thermal expansivity and n is the refractive index [71]. Because glasses in general have low thermal expansivities, they can be excluded as the secondary material.

Plastics offer good prospects for secondary materials [71]. The thermal diffusivity and the thermal expansivity of acrylic are close to those of water. Acrylic is transparent and machinable. In our experience the two difficulties with acrylic are machining and thermal bonding to the sample. Because the probe beam will sense the thermal gradient in the region within 100 μm of the sample, the surface must not be stressed. The machining must be done carefully so that stresses are not created in the surface. The problem of bonding is complicated by the need to avoid introducing soluble impurities into the electrochemical system. The general problem we have experienced with epoxy bonding materials is poor thermal conductivity and excessive

thickness. The most promising technique appears to be sputtering the desired metal directly onto the acrylic. Sputtering eliminates the thermal resistance of the bond between sample and acrylic, and does not appear to chemically or mechanically stress the interface.

Because the thermal diffusion length in metals is long, the secondary signal is close in magnitude to the primary signal. Table 3-2 shows the primary and secondary signals for various sample thicknesses. Acrylic and water have similar signals. Because the heat capacity of acrylic is less than that of water, the temperature changes for acrylic-backed samples are larger than for water. A larger signal is the result. The secondary signal magnitude is more than 80% of the primary signal magnitude.

Table 3-2. Comparison of model calculations of two signals (in μrad) for various thicknesses of platinum samples when water and acrylic are the secondary medium.

sample thickness	water:Pt:water		water:Pt:acrylic	
	primary	secondary	primary	secondary
500 μm	0.40	0.21	0.39	0.21
125 μm	0.82	0.71	0.90	0.78
25 μm	1.7	1.5	2.2	1.9

The surface absorption was 20%, the excitation intensity is 139 W m^{-2} , the frequency is 45 Hz and the probe offset is 50 μm .

Although quartz is a poor secondary medium, it has desirable mechanical properties. To make use of these properties, we explored the possibility of mounting the electrode on a thin substrate of quartz where water is the secondary medium, as shown in Figure 3-13. This

Figure 3-13. An electrode can be mounted on a thin quartz substrate. Water is used as the secondary medium.

arrangement takes advantage of the desirable mechanical and thermal properties of quartz but avoids the low thermal refractivity. Table 3-3 contains the PDS signal for a variety of sample and substrate thicknesses. We see that the quartz must be kept very thin to avoid signal loss. Microscope cover glass slides are 125 μm thick and are easily handled without breaking. It seems feasible that a thinner glass substrate could be used and still have adequate durability. Sputtering is an ideal method of bonding the electrode to the substrate.

Table 3-3. Comparison of model calculations of secondary signals (in μrad) for various thickness of electrode and quartz substrate as calculated by the model. The electrode was platinum and water was the primary and secondary medium.

electrode thickness	quartz substrate thickness		
	100 μm	50 μm	25 μm
10 μm	0.50	0.97	1.34
5 μm	0.51	0.99	1.37
2.5 μm	0.52	1.00	1.39

The surface absorption was 20%, the excitation intensity is 139 W m^{-2} , the frequency is 45 Hz and the probe offset is 50 μm .

Absorbing Electrolytes

When the electrolyte is optically absorbing, the secondary signal is superior to the primary signal. Figure 3-14 shows model calculations of the primary and secondary signals versus the absorption coefficient of the surface. The calculations were performed for electrolytes of various absorption coefficients. In each case we would desire that the signal vs. absorption relation be a straight line. The primary signal shows significant distortion at 50% absorption and becomes completely unresponsive at 90% absorption. The secondary signal is well behaved. The secondary signal decreases as the electrolyte absorption increases because less light reaches the surface. The small secondary signal seen at zero surface absorption is the effect of heat generated in the electrolyte being conducted through the sample to the probe beam. This causes a small baseline value to be added to the 50% and 90% lines.

The cause of the distortion in the primary signals is made evident in Figure 3-15. The left pane shows model calculation of the temperature profile of the system at one point in time. Curve A in Figure 3-15 represents 90% electrolyte absorption, the other curves are discussed shortly. The strongly absorbing electrolyte causes heating in the electrolyte. Because the intensity of the excitation light is reduced as it travels towards the electrode, the amount of heating is a maximum near the windows and decreases closer to the electrode. Because the window is assumed to be isothermal, the temperature profile exhibits a maximum. The temperature profile produced by electrolyte heating causes a probe deflection towards the electrode which opposes the normal probe deflection away from the electrode (see Figure 3-4 on page 57 for how the temperature profile appears with no electrolyte

heating). The opposition of the probe deflections caused by electrolyte heating and surface heating results in the poor behavior of the primary signal demonstrated in Figure 3-14. The 50% curve shows a situation where these two effects are closely balanced: At low surface absorptions, the electrolyte signal is dominant. As the surface absorption increases, the surface signal eventually dominates.⁴

Figure 3-15 also demonstrates how increasing the SER with different modulation waveforms can decrease the average temperature of the system without any loss in signal. The excitation intensity has been adjusted so that each of the temperature profiles produces the same signal magnitude, yet case C, the 20% pulse modulation waveform, reduces the temperature of the system about 1/3 compared to case A, the pure square wave.

⁴ Since the signal magnitude is plotted there are no negative values. Instead the phase of the signal is varying greatly to account for the opposing direction of the electrolyte and surface signal.

Figure 3-14. The primary and secondary signal magnitude are plotted vs. the surface absorption coefficient for various electrolyte absorptions. The electrolyte absorptions indicate how much light is absorbed before the excitation reaches the surface.

Figure 3-15. The temperature profile and probe beam deflection for three modulation waveforms as calculated by the model. The conditions are the same as Figure 3-4, except that 90% of the excitation light is absorbed before reaching the surface ($L=1$ mm, $\beta=2.306$ mm $^{-1}$). Node 850 is the window, and the electrode extends from nodes 400 to 450. The temperature profile is at the beginning of cycle 7. The surface was 30% absorbing. The probe offset was 150 μ m and the modulation frequency was 20 Hz. The intensity of the excitation, I , has been adjusted so that the same signal magnitude results from each waveform. (A) is the pure square wave, SER=1.27, $I=139$ W m $^{-2}$ (B) is the half-wave rectified sine, SER=1.57, $I=177$ W m $^{-2}$ and (C) is a 20% pulse, SER=1.87, $I=237$ W m $^{-2}$.

D. Correction of Spectra

The raw signals recorded during any given experiment are not directly usable. The power of the excitation light varies with wavelength. This variation is caused by the spectral characteristics of the source, the grating efficiency of the monochromator, and the optics. To obtain the correct absorption spectrum of a sample, the effect of the excitation light variation must be removed.

Correction for Source Intensity

The data can be corrected by several methods. We have explored several real-time normalization techniques, which use the data from a single experiment to produce the corrected result. None of these techniques were satisfactory. We prefer using the results of two experiments to produce the corrected result. A discussion of each class of technique follows.

Single-Experiment Normalization

PDS is the equivalent of a single-beam spectrometer. A dual-beam PDS spectrometer would be a complex device, which uses two samples (one a reference) and two probe beams to achieve a corrected spectrum with one experiment. Because the alignment between probe beam and sample is critical, two samples would present us with more than twice the problems. Both samples would have to be aligned exactly the same. As we discuss in the next chapter, aligning one sample is not easy. The effort required to align two samples identically is too large to be practical.

Another real-time method of correcting the spectrum is to use a photodiode to measure the power of the excitation light. A mathematical signal divider is then used to divide the output from the lockin by the signal from the photodiode. This process is excessively noisy in our experience.

If the photodiode signal was recorded during the experiment, the process would be improved, because the photodiode signal could be averaged. The computer would then divide the lockin signals by the photodiode signal after the experiment. But even this process would be subject to errors. The reference signal should be of greater quality than the surface signal. Slight noise in the reference will be magnified in the "corrected" spectrum and result in artifacts. The route we prefer is to acquire a high quality reference signal with a separate experiment.

Dual-Experiment Correction

To obtain a quiet reference signal, we prefer post-acquisition normalization. A great number of averages can be used to acquire the reference spectrum, using either the direct output from a photodiode or pyroelectric, or the PDS signal from a black sample.

We correct experiments using the PDS signal from a reference sample. The first experiment is to measure the unknown sample, which produces a PDS signal that can be represented as:

$$S(\lambda) = \eta \alpha(\lambda) P(\lambda) \quad [3-4]$$

In this equation, $P(\lambda)$ is the power spectrum of the excitation light, η is the collection efficiency of the signal, and $\alpha(\lambda)$ is the surface absorption coefficient. The second experiment is to measure the reference sample. Any

sample with a constant absorption coefficient is a suitable reference. White, gray or black materials are suitable, but black samples are likely to be the most accurate. The reference experiment produces a signal

$$S^{REF}(\lambda) = \eta' \alpha^{REF} P(\lambda) \quad [3-5]$$

where the collection efficiency has been changed to allow for different alignment of the sample with the probe beam. Dividing the sample signal by the reference signal yields the desired result

$$\frac{S(\lambda)}{S^{REF}(\lambda)} = \left(\frac{\eta}{\eta' \alpha^{REF}} \right) \alpha(\lambda) . \quad [3-6]$$

This result shows that the sample absorption coefficient is determined to within an arbitrary constant. Determination of this constant is what prevents PDS from being a quantitative technique. If the probe beam could be reproducibly aligned with any sample surface, the collection efficiencies would both be equal (Chapter 4 discusses this issue of quantitative alignment of the probe beam and sample surface). Use of a calibrated reference sample would determine α^{REF} . These two factors would eliminate the constant term from Equation 3-6.

We require that α^{REF} in Equation 3-6 is not a function of wavelength. This means that the sample is neutral white, gray, or black. But finding a neutral reference sample is not so easy as might be expected. Figure 3-16 shows the relative absorption spectrum of several candidate black reference samples. The samples were carbons and graphite held in place by wax or double-sided tape, and an "ultrablack" paint applied to assorted substrates. All the samples appear black in color. One candidate was defined as black as a basis for this comparison. The other samples deviate by up to 20 % from

the basis. This difficulty has been experienced by others [72, 73]. Correction for source intensity is one of the problems of any single-beam spectrometer.

Figure 3-16. The relative spectra of several candidate reference samples. The blackness of the samples deviates significantly from 1.

Cross Plotting

It is desirable to obtain surface spectra during potential programs such as cyclic voltammetry. Acquisition of an absorption spectrum can take 10-20 minutes. Given that the potential program might only last 1-2 minutes, this acquisition time is not acceptable. We might consider stopping the potential program at various points and collecting a spectrum. This method would require that the electrode surface be stable once the potential program was halted. This is a difficult requirement. The solution is to acquire the data in the opposite order.

The spectrum can be quickly acquired by reversing the order in which the data are acquired. A potential program is applied to the electrode while the excitation wavelength is held constant. This program is repeated at several wavelengths. The data can then be rearranged, plotting the signal *vs.* wavelength at any given potential. An absorption spectrum acquired by this method is effectively instantaneously acquired. We typically use a lockin time constant of 1 s. This would mean that 86% of the signal was acquired in the previous 2 s and 95% in the previous 3 s. This fast acquisition time allows the detection of dynamic processes.

The correction of a spectrum acquired by this technique is more difficult than the correction of regular spectra. Each experiment is performed at one excitation wavelength while the electrode potential is varied. A slight variation in lamp power over time is common when using an arc lamp [74]. These variations may cause each experiment to be performed with a different source power. When the variations in surface absorption with potential are small the variation in the source power can be overwhelming, *e.g.*, during cyclic voltammetry of platinum, the signal only changes 2% due to the change in surface absorption. The desired effect may be buried beneath the source variation. To correct such an experiment, the excitation power must be precisely measured during the experiment, using either a photodiode or pyroelectric detector. The excitation power can be averaged over the entire length of the experiment and used afterward to correct the spectra.

Copper Example

We have performed the above procedure while studying the electrochemistry of copper in alkaline solutions. Figure 3-17 (figures are at

the end of this section starting on page 85) shows the PDS signal for several experiments at different wavelengths. These experiments were performed under the same conditions as in Figure 1-3. Each experiment was cyclic voltammetry of copper in 0.1 M KOH. The sweep rate was 20 mV s^{-1} and the potentials refer to a DHE in the same electrolyte. Figure 3-18 shows the cross-plotted absorption spectra at several potentials during the anodic scan. Each spectrum was effectively acquired in a few seconds. Because the lockin time constant was 1 s, 63% of the signal was from the last second, 86% from the last 2 seconds, and 95% from the last 3 seconds. This fast acquisition time allowed us to use the moderate sweep rate of 20 mV s^{-1} .

The spectra in Figure 3-18 are not very useful, because small oxidation films are forming on the surface that change the absorption spectra slightly. To better see the changes, we plot the difference of one spectrum from the spectrum at a reference potential. Figure 3-19 shows difference spectra relative to the spectrum at 100 mV. At this potential the surface is reduced copper. To interpret the difference spectra, Figure 3-20 shows the absorption spectra of four possible copper species. Copper is orange, cuprous oxide (Cu_2O) is red, cupric hydroxide is blue, and cupric oxide is black. Figure 3-21 shows the difference spectra for the three oxidized species relative to pure copper. These difference spectra can help us qualitatively interpret the experiment, within the constraint that these reference standards only consider the differences between pure species. During the experiment, thin films are being formed on the copper, which are partially transmitting and partially reflective. Also, the film morphology changes the optical properties of the surface. We do not attempt to account for these parameters, and

therefore cannot predict precisely how the difference spectra of certain films will appear.

Using the curves in Figure 3-21 we can interpret the results. The difference spectra in Figure 3-19, begin to change at lower potentials than might be expected from the voltammogram. Miller has shown that Cu(I) begins to dissolve from the surface at 400 mV [61]. The difference spectra in Figure 3-19 for 400, 600 and 800 mV do not strongly show the characteristic shape of the difference spectrum of Cu_2O . Because the charge during the first oxidation peak is small (peak AI in Figure 1-3), it would be unlikely that the formation of a small amount of Cu_2O would be detectable. The increase for 400, 600 and 800 mV across all wavelengths in the difference spectrum can be explained by a roughening of the surface. Because the DC deflection of the probe beam does not indicate a strong gradient (see Figure 1-3), we conclude that any Cu(I) dissolved is immediately precipitated to the surface as Cu_2O .

The difference spectrum changes noticeably at 900 mV. The difference spectrum shows a characteristic shape that indicates that $\text{Cu}(\text{OH})_2$ is formed. In order for the difference spectrum to decrease in the blue wavelengths, a film must be formed which reflects some blue light. The formation of $\text{Cu}(\text{OH})_2$ continues to shift the difference spectra downward, until 1000 mV. As the potential increases past 1000 mV on the anodic scan, the difference spectra shift upward.

There are two plausible explanations for the observed change in the difference spectra from 1000 to 1500 mV. One is that the $\text{Cu}(\text{OH})_2$ is being converted to CuO . Another is that the $\text{Cu}(\text{OH})_2$ layer is becoming very

absorbing. If the $\text{Cu}(\text{OH})_2$ layer is formed by precipitation as others suggest, it is likely that the surface will be very rough [61, 75]. The absorption cross section of such a surface would be greater than that of the initially smooth surface. If a sufficiently thick film was formed the surface would appear black. Therefore, it is plausible that the difference spectrum of an unreflective $\text{Cu}(\text{OH})_2$ surface would appear be similar to that of a surface covered with a CuO film. These experiments are not precise enough to determine which of the postulates is correct. The two difference spectra for $\text{Cu}(\text{OH})_2$ and CuO can be discerned by carefully locating the position and slope of the edge in the two spectra. More-precise experiments would answer this question.

There was not enough information in the cross-plotted spectra during the cathodic scan to draw firm conclusions. We can, however, make one speculation. In Figure 3-17 there is an increase in the signal at the end of the cathodic scan before the final reduction for the 500 and 550 nm experiments. There is no corresponding increase in the 600 and 650 nm experiments. This bump in Figure 3-17, is located between the two cathodic peaks in the voltammogram (see Figure 1-3). This increase in the blue absorption is evidence that $\text{Cu}(\text{OH})_2$ is being reduced to Cu_2O . Reduction of CuO to Cu_2O would not cause the absorption to increase in the blue (see Figure 3-20); it would cause the absorption to decrease in the red. This lends support to the postulate that $\text{Cu}(\text{OH})_2$ is not converted to CuO at the end of the anodic scan. This also agrees with the Raman evidence from Schwartz and Muller showing that the $\text{Cu}(\text{OH})_2$ formed during the anodic scan is present until the second reduction peak (peak CII in Figure 1-3) [76].

Figure 3-17. Cyclic voltammetry of copper is repeated at 4 wavelengths. This staggered plot shows each experiment after it has been corrected for the excitation intensity. The conditions are the same as those in Figure 1-3.

Figure 3-18. The cross-plotted spectra at four potentials on the anodic scan. The key shows the potential in mV vs. DHE. The absorption spectrum of the copper substrate dominates the spectra. Difference spectra allow the changes to be more easily observed.

Figure 3-19. Cross plotted difference spectra for the anodic scan of the copper cyclic voltammetry experiment. The data are split among two graphs. The top pane shows the progression from 200 to 900 mV. The bottom shows the progression from 900 to 1500 mV. The arrows show the order of progression. Both are the difference from the spectra at 100 mV.

Figure 3-20. Measured absorption spectra of four pure copper species as measured by PDS. The copper was a bright electrochemically reduced copper electrode. The two oxides were AR grade powders. The cupric hydroxide was prepared by mixing cupric sulfate and potassium hydroxide. The insoluble hydroxide precipitates from solution.

Figure 3-21. For each of the oxidized species, the difference from pure copper is shown. These standards are used to interpret the difference spectra in Figure 3-19.

Conclusion

The components required for a PDS system are commonly available research equipment. Nothing we have used would be considered exotic—most components are available off-the-shelf. The only custom-built component is the electrochemical cell and its holder. The simplicity of the components of PDS is a distinct advantage.

There are two design considerations to emphasize: To maximize the signal magnitude the modulation waveform should be a square wave. But when this is not practical, the best option is to let the modulation waveform degrade into either type of triangular waveform. The best general purpose cell is shown in Figure 3-8. This cell design controls the physical processes such that they can be modelled as 1-dimensional processes.

The secondary gradient technique solves many problems. The beam deflections caused by Peltier heats can be separated from the concentration gradients. The cross effect between DC and AC discussed in Chapter 1 is eliminated by using this technique. The technique also allows us to study rough surfaces, thin-film cells, and other difficult systems.

The copper cross-plotting example clearly demonstrates that PDS can acquire spectra very quickly. The effective acquisition time of a spectrum was a few seconds. Even spectroscopic systems equipped with photodiode array detectors cannot acquire spectra this fast. The cross-plotting technique is applicable to other spectroscopic techniques.

The copper experiments were done before the computer data acquisition system was in place. The results could be made more precise by using averaging methods. But even at this low resolution, we see clear evidence for the formation of $\text{Cu}(\text{OH})_2$ on the electrode surface. These experiments need to be performed with a smaller wavelength interval to reach more-quantitative conclusions.

Chapter 4:

The Probe Beam

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The probe beam deflection is the basis of the PDS technique. In theoretical discussions the spatial relation between the probe beam and the sample surface is assumed to be accurately known. In practice we have found the precise determination of this relation to be a troublesome problem. The uncertainty in the determination of the spatial relation between probe and sample is the limiting factor that prevents PDS from being a quantitative technique. This chapter is devoted to the characterization of this relation.

The basic difficulty is the establishment of a method to reproducibly fix the position between a light beam and a solid surface. Precision of better

than 10 μm is required. The problem is compounded by the Gaussian profile of laser beams.¹ This profile lacks distinct edges. Without a distinct edge, one cannot say whether or not the beam is touching a surface. In theory the beam is always touching the surface no matter how far away. The relevant question is how much of the beam is touching the surface. Although we have examined many methods, we have not found a satisfactory mechanical method for making this determination. Instead, we have looked to information contained in the PDS signal itself. Methods based on the PDS signal appear to be the most precise methods available.

Here we discuss three parameters: the angle between the probe beam and the sample, the offset of the probe beam centerline from the sample, and the diameter of the probe beam. Methods which can determine and fix the angle and offset are discussed in Sections A and B. Unfortunately, the probe beam cannot be constricted to an infinitely thin ray. In practice it is a large beam compared to the thermal diffusion length and mass transport boundary layers. Section C discusses the effect of the finite beam diameter. The shape of the probe beam is a practical consideration that is often overlooked. Section D examines how the probe beam is shaped after passing the sample.

A. Angle

The procedure of aligning the probe beam with the sample should begin by making the two parallel. The methods for determining the offset

¹ The intensity profile is discussed in Section C.

(discussed in the next section) require that the probe beam be parallel to the sample. It appears to be a tacit assumption that the AC PDS signal is maximized when the probe beam is parallel to the sample surface. A few theoretical studies have suggested that the AC signal is maximized when the surface and probe beam are parallel, but under some unusual conditions the maximum signal may be slightly away from parallel [9, 10]. Experimentally it is observed that the signal is maximized as the sample is rotated, and it appears that the maximum signal occurs when the sample surface and probe beam are parallel. Our theoretical studies show that the signal is not maximized at zero angle.

If one accepts the assumption that the signal is maximized at zero angle, the obvious alignment method is to rotate the sample until the AC signal is maximized. In practice this method has poor precision. The maximum tends to be broad. Also the enclosure must be removed, the surface rotated, and the enclosure replaced. This process introduces much noise and is tedious. In the search for alignment methods many procedures were explored. The useful procedures are discussed first. Because none of these methods was completely satisfactory, the use of the AC signal itself was explored. But before discussing that method, another important factor must be addressed: The rotation axis of the cell is not precisely known. After dealing with this parameter, analytic solutions and numerical solutions of the effect of angle are discussed.

Physical Techniques

Several techniques were developed to make the probe beam parallel with the sample surface. All have been used with some degree of success.

- Our thin-gap cells allow a precise, quick method for alignment: The gap is progressively narrowed. At each gap thickness, the cell is rotated until the probe beam passes through the gap undistorted. As the gap thickness approaches the diameter of the beam, the beam and surface quickly become aligned. The precision of this method is better than 10 min arc.
- Typically the probe beam is focused to a waist at the sample surface. If the probe beam is perfectly aligned, then it would graze only the edges of the surface when the surface is moved close to the beam (see Figure 4-1). For a 10 mm wide surface, this observation would not be very precise. A 150 mm machinist's parallel bar can be clamped into the cell holder [77]. Now when the probe beam is parallel to the bar, both ends of the bar will be illuminated when the bar is moved close to the beam. If the beam diameter is 0.25 mm at the ends of the bar, then the bar can be no more than 6 min arc from parallel.

Figure 4-1. Alignment of a focused probe beam with a flat bar. The maximum error (in radians) is the diameter of the probe beam divided by the length of the bar.

- If the probe beam is not focused the method above is not applicable. Also, some cell holders may not allow the sample surface to be reproducibly positioned. In such cases we can use the sample surface in a method similar to the gap method, except that we only have half the gap. The probe beam is moved close to the surface so that part of the beam

grazes the surface. The cell is rotated until the power of the probe beam which passes by the surface is maximized. The power of the probe beam is measured with a photodiode. This method is somewhat empirical. When the beam grazes the surface, the light is diffracted, reflected and scattered, and these effects are not easily calculated. In practice, we have found the maximum in the power of the probe beam is reproducible to about 10 min arc.

- The phase of the AC signal is a function of the distance between the sample surface and probe beam. With only one edge of the surface illuminated by excitation light, we measure the AC signal phase. Then the trailing edge of the surface is illuminated and the signal phase measured. When the two phases are equal the surface will be parallel to the probe beam.

This principle leads to a simple automated method for alignment. An excitation beam system can be setup to alternately illuminate each edge of the surface, as shown in Figure 4-2. The power of the beam impinging on each edge of the surface will be equal. Because the excitation light on each edge will be 180° out of phase, the AC signals generated will be 180° out of phase. The probe deflection

Figure 4-2. An automated alignment system. A mirror chopper is a rotating mirror with two quadrants cut out. The excitation beam is alternately directed to each edge of the sample. The signal measured by the probe beam will be nulled when the sample is parallel to the probe beam.

will sum these two signals resulting in null only when the surface is precisely aligned.

These methods all allow the surface to be aligned with the probe beam, with adequate precision. But none of these allow one to determine a numerical value for the angle between the probe beam and surface.

Center of Rotation

Another practical problem, which is easily overlooked, must be considered. Where is the rotation axis of the cell? Figure 4-3 indicates several possible locations for the rotation axis. As a cell is rotated, the offset of the probe beam will change. Because the PDS signal is a strong function of offset, the rotation effect is complex. The mathematical relations between probe offset and angle are developed here. These relations will be used in both the analytic approximation and numerical model to make predictions of what happens in a **real** PDS system when the cell is rotated.

Figure 4-3. Several possible locations for the rotation axis of the cell. Point A is on the center of the sample surface.

The most obvious rotation axis to consider is point A in Figure 4-3, which is centered on the surface of the sample. The leading-edge and trailing-edge probe offsets, x_o and x_e , are given by

$$x_o = \frac{x_1 - \frac{L}{2} \sin \beta}{\cos \beta} \text{ and } x_e = L \tan \beta + x_o \quad [4-1]$$

where x_1 is the probe offset when the beam is parallel, L is the length of the sample and β is the angle of cell rotation. The limits of cell rotation are defined when the probe beam centerline hits the sample at the leading or trailing edge. From the above equation the limits are

$$\beta_{x_o=0} = \arcsin\left[\frac{2x_1}{L}\right] \text{ and } \beta_{x_e=0} = \arcsin\left[\frac{-2x_1}{L}\right]. \quad [4-2]$$

We now consider a rotation axis moved in the x -direction. For rotation axis B (Figure 4-3) the probe offsets are

$$x_o = \frac{x_1 - \frac{L}{2} \sin \beta - x_r + x_r \cos \beta}{\cos \beta} \text{ and } x_e = L \tan \beta + x_o \quad [4-3]$$

where x_r is the distance from the sample surface to point B. The limits of rotation are found by solving

$$\frac{L}{2} \sin \beta_{x_o=0} - x_r \cos \beta_{x_o=0} - x_1 + x_r = 0 \quad [4-4]$$

numerically for $\beta_{x_o=0}$. Because point B is centered, the cell can be rotated between $\pm \beta_{x_o=0}$.

A comparison of Equations 4-1 and 4-3 indicates that the probe offsets for points A and B are similar. As the cell is rotated about axis B, the sample center translates toward or away from the probe beam. The amount of this translation, Δx , is

$$\Delta x = x_r (1 - \cos \beta). \quad [4-5]$$

Even if point B is 50 mm from the sample surface, a 1° rotation causes only a $7.6 \mu\text{m}$ translation of the sample center. We can conclude that the location of the rotation axis along the x axis is unimportant.

In contrast, the difference as the axis moves in the y-direction is significant. For a rotation axis along $\overline{DAE}$ the probe offsets are

$$x_o = \frac{x_1 - \left(\frac{L}{2} - y_r\right) \sin \beta}{\cos \beta} \quad \text{and} \quad x_e = x_o + L \tan \beta \quad [4-6]$$

where y_r is positive for shifts of the rotation axis toward the leading edge. This equation is valid for both positive and negative y_r . The limits of rotation are

$$\beta_{x_o=0} = \arcsin \left[\frac{2x_1}{L - 2y_r} \right] \quad \text{and} \quad \beta_{x_e=0} = \arcsin \left[\frac{-2x_1}{L + 2y_r} \right]. \quad [4-7]$$

The shift of the sample center with rotation is

$$\Delta x = y_r \sin \beta. \quad [4-8]$$

For a rotation axis 0.5 mm from the sample center in the y-direction, a 1° rotation causes the sample to shift 8.7 μm closer to the probe. This shift is 100 times larger than the shift caused by moving the rotation axis an equal amount in the x-direction.

The first observation we can make from these equations is the range through which the cell can be rotated without the beam hitting the sample. The values in Table 4-1 show that the sample surface must be very nearly parallel to the probe beam, or much of the probe beam will strike the sample surface. Experience indicates that aligning the cell within 1° is difficult.

Analytic Approximation

The effect of the probe angle has not been deeply explored in the literature. The probable reason is that it is assumed that everything is best

Table 4-1. The limits of rotation are shown for various rotation axes and probe offsets.

Rotation Axis (see Figure 4-3)	x_1	β when $x_0=0$	β when $x_e=0$
A	100 μm	1° 16'	-1° 16'
	200 μm	2° 32'	-2° 32'
B($x_f=5000 \mu\text{m}$)	100 μm	1° 15'	-1° 15'
D($y_f=4500 \mu\text{m}$)	100 μm	n/a *	-34°
	200 μm	n/a *	-1° 16'
D($y_f=500 \mu\text{m}$)	100 μm	1° 26'	-1° 15'
	200 μm	2° 52'	-2° 18'

Calculations made for $L=9 \text{ mm}$.

* For this rotation axis, the leading edge of the sample will never cross the probe beam centerline.

when the probe beam is parallel to the sample surface. References 9 and 10 briefly discuss the effect of probe angle. Both papers demonstrate that the AC signal can be maximized, minimized or unaffected by changing the probe angle. Because both papers discuss the AC signal for a system with air as the deflection medium, the results are not directly applicable to our work. We studied the effect of the sample angle using an analytic approximation and the model. We discovered that the AC signal is not maximized, in theory, when the probe and sample are parallel.

With two approximations, the effect of the probe angle can be easily calculated in closed form. First we assume that the AC signal varies exponentially with distance according to the simple predictions discussed in Chapter 1.

$$\frac{S(x)}{S_0} = \exp\left[-\frac{x}{\mu}\right] \quad [4-9]$$

where $S(x)/S_0$ is the relative AC signal magnitude and μ is the thermal diffusion length. If the probe beam travels at an angle to the sample, it will experience a varying signal. The net AC signal is the simple average over the path of the probe beam

$$S^{\text{total}} = \int_{y=0}^L \exp\left[\frac{-x}{\mu}\right] dy \quad [4-10]$$

where L is the length of the sample. Small angles are assumed, so that the difference between dy and the true path, ds , can be neglected. The offset of the probe beam is a function of y

$$x = x_0 + y \tan \beta \quad [4-11]$$

where x_0 is the leading edge probe offset, and β is the probe angle.

Combining Equations 4-10 and 4-11 leads to a general expression for the total signal.

$$S^{\text{total}} = \int_{y=0}^L \exp\left[\frac{-1}{\mu}(x_0 + y \tan \beta)\right] dy \quad [4-12]$$

This integral is solved to yield the final expression that depends only on the leading edge probe offset, x_0 , the sample angle, β , and sample length, L .

$$S^{\text{total}} = \frac{-\mu}{\tan \beta} \left\{ \exp\left[\frac{-1}{\mu}(x_0 - L \tan \beta)\right] - \exp\left[\frac{-x_0}{\mu}\right] \right\} \quad [4-13]$$

Using the relations between β and x_0 derived in the previous section, the effect of rotation of the sample can be evaluated. We are only interested in moving the rotation axis in the y -direction, therefore Equation 4-6 is substituted into Equation 4-13 to calculate the signal magnitude as a function of angle. Figure 4-4 shows the signal as a function of angle,

calculated by this equation. The thermal diffusion length was $68\text{ }\mu\text{m}$, which corresponds to a modulation frequency of 10 Hz and the thermal properties of water (see Table V-2). Figure 4-4 shows the signal variation for a rotation axis at the sample center, and moved $\pm 1\text{ mm}$ off center. The path of the probe beam is shown in Figure 4-5 for a rotation axis moved -1 mm off center. When the rotation axis is centered on the sample surface, the signal is **minimized**. When the rotation axis is $+1\text{ mm}$ off center, the theory predicts the signal is minimized at about 20 min arc . A -1 mm shift causes a symmetric shift in the signal minimum. These results disagree with the experimental observation that the PDS signal is maximized when the sample surface and probe beam are parallel.

Figure 4-4. The PDS signal versus angle is shown for three rotation axes. One is at the center of the sample surface. The other two are 1 mm to the left and right of the center of the sample surface.

Figure 4-5. The path of the probe beam is shown for different angles of the sample. The rotation axis (R) is 1 mm to the left of the sample center (C). The sample is 9 mm wide.

If the rotation axis is moved to the leading edge of the sample, the results are as shown in Figure 4-6: No maximum or minimum is seen. The value at negative angles is limited by the maximum rotation. Positive angles will cause the signal to decrease indefinitely.

Figure 4-6. The PDS signal versus angle for a rotation axis at the leading edge of the sample. No minimum or maximum occurs.

Equation 4-10 considers an infinitely thin ray. Changing the probe offset, x_1 , only causes the curves in Figures 4-4 and 4-6 to change by a multiplicative factor. A consideration of the finite size of the beam would sum the effects of many thin rays. Because each thin ray predicts a minimum at the same angle, the sum will predict the same minimum.

The integral in Equation 4-10 does not account for the change in signal phase as the probe offset changes. The signal phase changes through 360° over several thermal diffusion lengths. The phase difference over the path of the probe beam will not be large. We can use the numerical model to obtain a more accurate result.

Results of the Numerical Model

The thermal model will calculate a probe beam deflection that will account for both the phase of the PDS signal and other thermal effects not considered in the simple 1-D model that is the basis of Equation 4-9.

Figure 4-7 demonstrates the agreement between the numerical and analytic results. The rotation axis in this figure was at the leading edge of the sample. The two curves have been normalized to a value of 1 at zero angle. The agreement is good. It would be expected that the model result would be smaller than the analytic result, because the magnitude of the sum of two sine waves with different phases is less than the simple sum of the magnitudes (derived in Appendix II). Therefore, the change in phase over the probe path should cause the summation of the signal to be lessened.

Figure 4-8 shows the comparison when the rotation axis is 500 μm off center. Both predict that the minimum is at positive angles. The numerical result predicts a much weaker minimum that is almost 1° from zero.

Discussion

The above results were surprising. Both the numerical and analytic

Figure 4-7. Comparison of numerical and analytic predictions of the effect of sample angle on signal. The rotation axis was at the leading edge of the sample. The dotted curve is the analytic result.

Figure 4-8. Comparison of numerical and analytic predictions of the effect of sample angle on the signal. The rotation axis was 500 μm off center. The dotted curve is the analytic result.

result lead us to conclude that the electrode cannot be aligned by simply rotating the sample and observing the signal. Even if a minimum was found experimentally, a slight misposition of or uncertainty in the rotation axis would result in the cell being out of alignment.

The reason the signal is minimized at or near zero angle is clear—at least in retrospect. Consider Equation 4-9 and a sample rotated about its center. Half the beam moves closer to the sample and half moves an equal distance away from the sample. The beam that moves closer to the sample will sense a signal increase. The symmetric portion of the beam which moves farther from the sample will sense a signal decrease. The exponential dependence of the signal magnitude on distance from the sample surface causes the increase to be larger than the decrease. Table 4-2 demonstrates this change. The result is that the average signal sensed by the probe beam will increase.

Table 4-2. The change in relative signal for symmetric changes in beam offset. Positive changes are away from the sample.

Δx	$\Delta(S/S_0)$
+10 μm	-0.0350
-10 μm	+0.0387
+20 μm	-0.0667
-20 μm	+0.0815

From Equation 4-9 with $\mu=100 \mu\text{m}$.

Figure 4-9. Rotation of the sample causes the part of the probe beam closest to the sample to be scattered away. The remaining beam is farther away causing the PDS signal to decrease.

As stated previously, it is an experimental observation that the PDS signal is maximized when the sample appears to be parallel to the probe beam. In light of the above theoretical discussion, the basis of this experimental observation is not clear. It is possible that the blocking of the

probe beam as it passes the sample is the basis. Figure 4-9 shows that rotating the sample blocks the part of the probe beam closest to the sample. The remaining beam is farther from the sample surface causing a decrease in signal magnitude.

The combination of the two conflicting results, beam blocking and PDS signal, leads to a confusing behavior. The signal can be either maximized or minimized at zero angle. Reference 10 presents a theory that includes the effect of the sample edge blocking the probe beam. The results show three behaviors: 1) the signal is maximized at zero angle, 2) the signal is unchanged by angle, and 3) the signal is a minimum at zero angle, increases to a maximum at intermediate angles, and then decreases to zero at large angles. These results were calculated in air with a large beam, large probe offsets, and large angles. Because the thermal diffusion length in air is much larger than in water, the results in air are not directly applicable to our situation. But these results support our conclusion that simply rotating the sample cannot be used to precisely align the sample with the probe beam.

B. Offset

If in practice the surface can be made substantially parallel to the probe beam, then the next step is to determine the offset of the probe beam. No physical methods have been found to reliably determine the offset of the probe beam from the surface. One technique suggested by Gastieger [52] is to monitor the intensity of the probe beam as it passes by the sample. The sample is continuously moved closer to the probe beam by a constant speed motor driving the translation stage under the sample. The intensity of the probe beam passing the electrode should decrease to zero as the probe beam

becomes progressively blocked. When the intensity is at half the maximum, the beam is at zero offset. Because of diffraction and scattering from the sample, and other experimental difficulties, the precision of this technique is not high.

Theoretical studies of the PDS signal suggest that the offset can be determined from the signal itself. The simple model suggests the relations

$$S \propto \exp\left[-x_o \sqrt{\frac{v\pi}{\alpha}}\right] \text{ and } \phi \propto -x_o \sqrt{\frac{v\pi}{\alpha}} \quad [4-14]$$

These relations suggest that by varying the modulation frequency, v , the probe offset, x_o , could be determined. Plots of $\ln S$ vs. $\sqrt{v}$ and ϕ vs. $\sqrt{v}$ would both yield straight lines with slopes of m . The offset of the beam would then be calculated with

$$x_o = -m \sqrt{\frac{\alpha}{\pi}} \quad [4-15]$$

where α is the thermal diffusivity.

The validity of these relations was tested with the thermal model. Model calculations were made at a series of modulation frequencies. The result of one of these simulated experiments is shown in Figure 4-10. While the signal magnitude is linear, the signal phase is best fitted with a quadratic polynomial. The calculated value of the probe beam offset, x_o^{calc} , was determined from the slope of the signal magnitude data by Equation 4-15. The simulation in Figure 4-10 was repeated at several probe offsets. The calculated value of the probe offset, x_o^{calc} , for each simulated experiment

is compared with the true value in Figure 4-11. It is seen that the calculated probe offsets did not agree with the true values.

Disagreement between the calculated and true values can be caused by the large diameter of the probe beam or the geometry. We first discuss the probe diameter which can explain much of the difference. Then the geometry, which also causes some difference, is discussed.

Figure 4-10. Results of one of the simulated signal versus phase experiments. The probe beam offset was $160\text{ }\mu\text{m}$. The $1/e^2$ probe beam diameter was $270\text{ }\mu\text{m}$. The calculations were performed for water as the primary fluid, a $125\text{ }\mu\text{m}$ thick platinum sample, and a PFA backing.

Figure 4-11. The signal versus frequency simulated experiment is repeated at several probe offsets. The calculated probe offset versus the true offset is shown for each experiment. The dotted line is the simple theory of Equation 4-14.

Figure 4-12. The calculated relation between the true probe offset and the calculated value is shown for various probe beam diameters. The dotted line is the simple theory represented by Equation 4-15.

Effect of Probe Diameter

Figure 4-12 shows the calculated values *vs.* the true values for a series of probe beam diameters. The figure indicates that as the probe diameter gets smaller, the model comes into closer agreement with Equation 4-15. As the beam gets bigger, significant deviation from ideal develops. Coincidentally, at 95 μm there is good agreement between the model and ideal.

At zero diameter, the results do not exactly agree with the simple theory. The slope of the 0 and 20 μm lines in Figure 4-12 is 1, but there is an intercept of 30 μm . The origin of this remaining discrepancy lies in the geometry.

Effect of Geometry

At a probe offset of zero, an infinitely thin probe beam should sense only the boundary condition at the interface

$$k_{\text{primary}} \frac{\partial T_{\text{primary}}}{\partial x} + k_{\text{sample}} \frac{\partial T_{\text{sample}}}{\partial x} = q . \quad [4-16]$$

This relation is unaffected by modulation frequency. Thereby the slope of the $\ln S$ *vs.* $\sqrt{\nu}$ line should be zero and the intercepts of the lines in Figure 4-12 should be zero. Because the intercepts of the lines are non-zero, another process that depends on the modulation frequency must be influencing the probe deflection.

The source of this effect can be explained as a reflection from the secondary interface of the sample. Similar to partial reflections at glass-air interfaces, there are reflections at discontinuities in thermal properties. The

reflected wave must travel the length of the sample twice. The time of travel is a function of the thermal diffusion length in the sample, which depends on the modulation frequency. We can test this hypothesis by changing the thickness of the sample.

Figures 4-13 A and B show the calculated *vs.* true offset for various sample thicknesses. The model predicts that the 250 μm sample gives the largest discrepancy from the simple theory expressed by Equation 4-15. Making the sample thinner reduces the discrepancy. As the primary and secondary interfaces become closer, the signals between the two interfaces become indistinguishable. The discrepancy is also reduced by making the sample thicker. The secondary interface becomes sufficiently far away that the thermal reflection is attenuated before reaching the probe beam.

The reflection can be eliminated by changing the thermal properties of the backing. Figure 4-14 shows that as the thermal diffusivity of the backing is increased, the discrepancy decreases. As the thermal diffusivity of the backing becomes closer to that of the sample, the thermal reflection is decreased. The line for the copper backing has a negative intercept. This indicates that slope of the signal magnitude *vs.* modulation frequency line is negative, which means the signal magnitude increases with increasing modulation frequency.

Figure 4-13. The effect of the thickness of the sample is shown in the above two figures. Figure A shows thicknesses from 25 to 250 μm and Figure B shows thicknesses from 250 to 1250 μm . The dotted line is the simple theory.

This is a curious result, because normally the signal magnitude decreases. The high thermal conductivity of copper causes any energy that reaches the secondary interface to be quickly conducted away to the constant temperature boundary. As the modulation frequency is increased, the thermal diffusion length in the sample decreases and less energy is conducted to the secondary interface. Thereby more energy is available at the primary interface to produce a signal as the modulation frequency increases.²

² This effect cannot be used to allow the use of higher modulation frequencies. The effect only occurs if an infinitely thin probe beam is at zero distance from the sample surface.

Figure 4-14. The effect of various backing materials. PFA, water, a material with 20 times the thermal conductivity of PFA, and copper were tested.

Discussion

One conclusion that can be drawn is that there is enough information in the signal *vs.* frequency experiment to determine the probe offset. In all of the calculated *vs.* true probe offset graphs, the data have been well represented by straight lines! This is fortuitous and useful. Lasalle, *et al.* have explored particular systems which exhibit "catastrophic" behavior [14]. They demonstrated both experimentally and theoretically that the relation between signal and modulation frequency can exhibit cusps, and invariance. Given a system like theirs, the signal *vs.* frequency experiment would be useless.

Within the range of parameters we have explored, the model can be used to derive useful relations between probe offset, x_0 , and m , the slope of the signal magnitude *vs.* frequency experiment. Each relation would be of the form

$$x_0^{\text{expt}} = a - b m . \quad [4-17]$$

Each of these can be considered to be a calibration curve. Table 4-3 contains the values of a and b for the conditions discussed in this section. For any other set of conditions, a series of computer runs could determine a corresponding relation.

Table 4-3 also contains a representative signal magnitude for each set of parameters. As will be discussed further in the next section, changing the probe radius has little effect on the signal magnitude. The sample thickness and backing material have significant effects on the signal magnitude. When designing a cell, these effects must be considered.

The results of this section suggest two design considerations. First, the probe beam diameter should be kept to a minimum. Large beams decrease the precision with which the probe offset can be determined. Second, the sample should be very thin and mounted on an insulating material. A sample less than 25 μm thick will result in a large signal and will not need the calibration curve.

Table 4-3. Values of constants for use in Equation 4-17 for the conditions in the figures in this section. A representative signal magnitude, S , is given for each line for the conditions $x_0=100$ μm and $f=5$ Hz.

conditions	$a(\mu\text{m})$	$b(\mu\text{m} \sqrt{\text{Hz}})$	S
Figure 4-12 - probe radius			
0 mm	24.5	1.0757	2.94
20	29.5	1.0440	2.94
70	13.6	1.0764	2.89
95	14.6	0.9220	2.75
107	29.3	0.7313	2.68
120	47.7	0.5383	2.59
132	53.2	0.4354	2.47
145	67.8	0.3014	2.36
157	69.0	0.2598	2.28
Figure 4-13 - sample thickness			
25 mm	6.43	1.0405	4.5
62	16.64	1.0524	3.8
125	24.54	1.0757	2.9
250	26.64	1.1216	2.0
500	11.96	1.1661	1.2
750	-2.79	1.1202	0.88
1000	-13.79	1.1036	0.73
1250	-15.18	1.0804	0.67
Figure 4-14 - backing material			
PFA	24.5	1.0757	2.9
water	20.7	1.0619	2.4
PFA*20	15.5	1.0464	1.9
copper	-12.0	1.0000	0.38

These results were calculated by least square linear regressions.

C. Diameter

The diameter of the probe beam is typically large compared to the length scale of the temperature and concentration gradients being measured. In this section we will briefly explain why we use large-diameter probe beams and discuss the effect the diameter has on the probe deflections.

Limitations on Beam Size

To achieve high spatial resolution it would be desirable to have a probe beam with a diameter of 1 μm . Unfortunately, light does not always behave as most of us were taught in basic physics and a 1 μm collimated beam cannot be achieved. When dimensions are on the order of tens of micrometers, diffraction effects become important. Figure 4-15 (at the end of this section, page 117) shows the calculated $1/e^2$ diameter of a probe beam as it is focused near a sample. The laser beam size is originally 630 μm and the lens has a 150 mm focal length. The beam does not reach zero diameter at any point. Instead it reaches a waist and then diverges again. The waist is not located at the focal length of the lens.

A simplified form of the equation which describes the propagation of Gaussian beams, *i.e.* a laser, is

$$2w_0 = \frac{4\lambda}{\pi} \cdot \frac{1}{\theta} \quad [4-18]$$

where $2w_0$ is the diameter of the beam at its narrowest, the waist, and θ is the divergence of the beam. The divergence is a measure of how the diameter of the beam changes as it propagates. What is evident from Equation 4-18 is that the waist diameter of the beam and the divergence of the beam are not

independent. Decreasing the diameter increases the divergence. The path in Figure 4-15 was calculated using the more precise equation known as the ABCD law [78, 79].

The interdependence of the probe diameter and divergence presents an optimization problem. The change in diameter of the probe beam as it passes the sample must be maintained at a minimum. The sample must be kept wide, or edge effects may invalidate the assumption of one-dimensional refractive index profiles. For samples with a 10 mm width, we have concluded that the minimum practical diameter of the probe beam is 80 to 100 μm .

There are several considerations which have led us to this conclusion. Table 4-4 shows the change in the beam diameter as it traverses a 10 mm sample. A change in diameter of 20% is the maximum we accept. The alignment of the sample with the beam waist in the direction parallel to the probe beam becomes more difficult as the divergence increases, see Figure 4-16. For the 184 μm diameter beam, if the sample is moved 10 mm to either side of the waist, the diameter of the beam changes about 10 μm . For the 76 μm beam, the same movement causes a 40 μm change. The diameter of the probe beam when it reaches the position detector also must be considered. Table 4-4 has values of the beam diameters for two typical locations of the position detector. The most sensitive position detectors have small dimensions.³ Appendix IV lists the dimensions of detectors we have used.

³ The dark current noise of a the photodiode-based position detectors increases with the area of the detector. The signal does not increase, therefore the SNR decreases.

The 60 mm lens produces a spot size which approaches the size of the position detector.

Table 4-4. Calculated $1/e^2$ beam diameter at the beam waist and the relative change of the beam diameter at locations 5 mm from the beam waist (in the direction parallel to the beam). The diameter at two distances from the lens shows predicted spot sizes on the position detector.

lens focal length	@ beam waist	change	distance after lens	
			@ 250 mm	@ 500 mm
150 mm	184	0.7%	530	1600
80 mm	100	8%	1400	3400
60 mm	76	20%	2000	4700

All diameters are in μm .

An option is to decrease the wavelength of the probe beam. A He-Ne laser has a wavelength of 632.8 nm. If we used a laser with a shorter wavelength, the diameter of beam could be decreased without increasing the divergence, see Equation 4-18. Argon lasers operate at 415 nm and He-Cd at 442 nm. Either would allow the beam diameter to be decreased by about 1/3. While this seems an attractive possibility, practical problems prevent their use. The lasers that are commercially available do not have favorable properties. The beams at the laser exit tend to be bigger and more divergent. Also, their pointing stability is less than that of the best He-Ne lasers. There is no reason that an Ar or He-Cd laser could not be made to similar specifications of the He-Ne lasers commonly available. It is only the lack of demand which leaves us with the conclusion that the He-Ne lasers we use are optimum.

Figure 4-15. Calculated diameter of the probe beam as it passes the sample. The initial beam size is 630 μm and the lens has a 150 mm focal length. This figure is drawn to an unequal scale.

Figure 4-16. Calculated diameter of the probe beam as it passes the sample. The initial beam size is 630 μm and the lens has a 60 mm focal length. This figure is drawn to an unequal scale.

The Effect of the Beam Diameter

To test the accuracy of the numerical models, several analytic solutions were developed to calculate probe deflections. The linear position detector (LPD) outputs a signal proportional to the position of the intensity centroid of the light striking its surface. The laser beam has a Gaussian intensity profile:

$$I(x, y) = I_0 \exp \left[\frac{-(x - x_0)^2 - (y - y_0)^2}{r^2} \right] \quad [4-19]$$

One-dimensional gradients will be considered. The probe beam is considered as differential ribbons, each with a different power. The deflection of a beam is the sum of the deflection of each ribbon, weighted by its power.

$$\theta = \frac{\frac{L}{n_0} \int_{-\infty}^{\infty} P'(x) \frac{dn(x)}{dx} dx}{\int_{-\infty}^{\infty} P'(x) dx} \quad [4-20]$$

$$\text{where } P'(x) = I_0 r \sqrt{\pi} \exp \left[\frac{-(x - x_0)^2}{r^2} \right]$$

This equation is a power weighted average. $P'(x)$ is the linear power density in W m^{-1} , which is obtained by integrating Equation 4-19 in the y -direction.

As a test profile consider $n = n_0 + bx + cx^2$ which yields a refractive index gradient $dn/dx = b + 2cx$. When this profile is substituted into Equation 4-20, the resulting beam deflection as measured by the LPD is

$$\theta = \frac{L}{n_0} (b + 2cx_0) . \quad [4-21]$$

There is no contribution of the probe radius, r , in this solution. For a cubic refractive index profile, $n = n_o + bx + cx^2 + dx^3$, the same procedure yields

$$\theta = \frac{L}{n_o} \left(b + 2cx_o + 3dx_o^2 + \frac{3}{2}dr^2 \right). \quad [4-22]$$

Only when the refractive index profile exhibits third order character, is there any effect of the probe beam diameter. This is a significant characteristic. Though the beam cannot be focused to a small diameter, the change in the beam deflection caused by a large beam is not drastic. The main effect of the large beam is that the center, x_o , cannot be placed close to the sample surface. The effect of placing the beam too close to the surface is the topic of the next section.

D. Shape

We assume that the probe beam has a Gaussian profile. But, the probe beam does not necessarily maintain its Gaussian profile as it passes by the sample. Figure 4-17 shows an actual probe beam profile after the probe beam passes the sample. The sample was aligned by eye by rotating the sample until the signal was maximized and moving the beam until it appeared to graze the sample surface. The profile in Figure 4-17 is a harsh reality. Figure 4-18 shows probe beam profiles as the sample is moved progressively closer to the beam. By comparing the two figures, we see that the probe beam should have been moved about 300 μm farther away to correct the beam profile.

Other than the inability to model the processes which produce the profiles in these figures, the response of the position detectors is of concern.

The LPD measures the movement of the intensity centroid. If only the main peak at $12450\text{ }\mu\text{m}$ in Figure 4-17 was deflecting, the LPD would still respond. The response would be diluted by the other peaks which may not be deflected.

The response of the bicell position detector is not as reliable when the intensity profile of the probe beam is distorted. Normal practice would suggest that the probe beam spot would be centered on the bicell during an experiment. This is accomplished by moving the bicell until the output from the position monitor is zero, which indicates that half of the probe strikes each side of the bicell. The vertical line in Figure 4-17 indicates where the bicell would read zero. The main peak at $12450\text{ }\mu\text{m}$ is $140\text{ }\mu\text{m}$ from the bicell divider. Typical PDS signals will not produce deflections with magnitudes of $100\text{ }\mu\text{m}$. If only the main peak was moving, the bicell would register no signal. This occurs because the bicell will detect only those parts of the probe beam that move to the left or right of the divider; if light already on the right of the divider moves farther to the right, no signal change will occur.

If significant diffraction or scattering is present, a different approach is suggested. The bicell should be moved until the AC signal is maximized. The full range of the position detector can easily be scanned by attaching a constant-speed motor to the translation stage under the detector. But, if during an experiment a DC probe deflection moves the main peak off the bicell divider, the AC signal will disappear. The safest practice is not to allow the probe beam to graze the sample when a bicell is being used, or use the LPD.

There is some suggestion in the literature that a probe beam can be passed by a sample and be cleanly "cut", leaving a beam that is part of the Gaussian profile [80 - 82]. Reference 80 contains probe beam profiles which show that 25% of a 600 μm beam can be cleanly removed. Both references consider beams with diameters similar to the 630 μm beam in Figures 4-17 and 4-18. It may be that misalignment of the waist of the probe beam with the sample produces our results. The angle with the electrode is also likely to be important.

Figure 4-17. Typical probe beam profile when the sample is aligned by eye. The vertical line divides the profile into two equal-energy parts. *Position* is the reading of the translation stage micrometer; the absolute value is unimportant.

Figure 4-18. Profiles of an unfocused 630 μm probe beam after grazing the sample surface at four probe offsets. The curves are labeled with the distance in micrometers that the sample has been moved into the path of the probe beam. As the sample is moved into to the probe beam, diffraction and scattering form a tail. The sample approaches from the right.

Conclusion

In this chapter we have emphasized the problems of aligning the probe beam. The values in Table 4-1 are severe limits because they were calculated for the sample edge hitting the centerline of the probe beam. Blocking half of the probe beam will cause an intolerable amount of diffraction. Therefore, the range through which the cell can be rotated is very small. The best way of making the sample parallel with the probe is to use the phase of the AC PDS signal. The phase of the signal varies through 360° as the probe offset moves from 0 μm to about 700 μm ; about 1° per 2 μm . Given that lockin amplifiers are commonly precise to better than 1° , we should be able to align the probe beam and sample to less than 2 μm from

parallel. Only the low SNR of the AC signal prevents this precision from being attained. The only method of determining the probe offset is the method which relies on the model. The sample should be carefully aligned with the beam waist. This can be accomplished with calculation of the location of the beam waist, but it would be better to measure the location of the waist with a beam profilometer (Appendix IV describes the simple inexpensive profilometer we developed). Accomplishment of these three alignments allows for a reproducible quantitative technique.

There are several warnings to be taken from this chapter. First, we cannot assume that the simplified descriptions of signal magnitude and phase will describe any given system. As we have shown here, apparently minor deviations in geometry result in large deviations from simple theory. Large deviations in geometry can place the operating conditions near discontinuities, resulting in "catastrophic" behavior [14]. Modelling is required to certify that a given geometry "works." Second, the beam shape should be monitored and not allowed to deviate far from Gaussian. What appears to the eye as a small distortion, can be in fact quite severe. If the beam becomes excessively distorted, the model results will not be comparable to experiments. As we will see in Chapter 6, when interpreting DC probe beam deflections caused by concentration gradients, comparison of model and experimental data becomes necessary. Lastly, the spatial relation between the probe beam and sample is of central importance, and corresponding attention should be given. It is too easy to neglect this non-trivial detail.

Chapter 5:

Noise

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PDS is an extremely sensitive technique. The theoretical limitation for beam deflections is on the order of 1 nrad [9, 83]. The deflections we measure approach this limit. Despite the layers of insulation surrounding the system and the isolation provided by the optical bench, many problems we have faced during the development of PDS were results of experimental noise. For example, the *clunk* caused by closing the door to the laboratory would send the oscilloscope trace of the probe deflection off the screen. Waving a sheet of paper near an exposed probe beam would cause the amplifier to overload.

Because of this extreme sensitivity, much effort went into diagnosis and eradication of noise sources. The detection scheme of PDS is very different from that of conventional spectroscopies. Conventional spectrometers are based on sensitive optical detectors that are limited by electrical noise and stray light. The noise sources in a PDS system are mechanical, *i.e.*, parts of the system are moving.

A spectrum analyzer was the main instrument used to characterize the noise. We record both the frequency spectrum of the probe deflection signal and the acoustic spectrum. As we will see, the noise is not simple white noise (noise equally spread among all frequencies), instead the frequency spectrum has distinct peaks and valleys. This distinct "fingerprint" makes studying the noise somewhat easier.

In this chapter we present comparative studies. The noise changes a small amount from day to day and changes greatly when the components used in the PDS system change. The studies presented here were accumulated over a period of years. The results in a single figure are comparable, however the reader should be aware that the results in different figures may have been recorded for very different setups that are not comparable.

A. Detection Limits

Figure 5-1. One nanoradian would produce a 1/2 mm deflection on a card held 500 km away!

Before using the term *nanoradian* further, an idea of the size of a nanoradian is helpful. One nanoradian is $1/18,000,000$ of a degree, but one might ask "how big is that?" Figure 5-1 demonstrates.

A researcher stands at the University of California at Berkeley and is **very** steadily holding a probe beam pointed at Los Angeles. A second researcher stands 500 km away in Los Angeles holding up a

white card on which the laser is directed. If the researcher at Berkeley twists the laser 1 nanoradian, the spot on the card will move 1/2 mm. Indeed a nanoradian is a small angle!

The laser beam is not a perfectly collimated beam, but instead has a divergence (the divergence of our probe beam is 2 mrad). This divergence would result in the beam having a diameter of 1 km by the time it had reached the card in Los Angeles. This attests to the sensitivity of the position detectors, which can detect incredibly small movements of comparatively large spots of light. The sensitivity of position detectors is also the basis of the atomic force microscope [84].

Because the angular deflection of the probe beam is measured as a linear displacement along the face of the position detector, it may seem advantageous to place the position detector far away. Two facts make this

approach inappropriate. First, moving the LPD twice as far away from the cell will double the signal, but it will also double the noise produced by movement of the cell and instability in the probe beam. Therefore, the SNR will not be increased. Second, moving a bicell position detector twice as far away from the cell does not increase the signal. The bicell position detector outputs a signal proportional to the movement of the probe spot relative to the diameter of the probe spot. The probe beam diverges after passing the cell. With the detector twice the distance from the cell, the probe diameter will double and the movement of the spot will double. The result is that the signal will remain the same. The practical distance of the position detector from the cell is limited by the size of the position detector element; the probe beam spot can only be as large as the detector element. While position detectors are available in a wide range of sizes, larger detectors will have a larger dark current, which is an intrinsic noise source. Therefore, it is beneficial to use small position detectors. The position detectors we use are placed 0.25 to 0.5 m from the cell (see Appendix IV for dimensions of position detector).

The sensitivity of PDS is a desirable aspect, but it is also the root of our mechanical vibration problems. It doesn't take much force to cause parts of the PDS system to move a distance that would deflect the probe beam by a few nanoradians. Noise diagnosis is required to determine the source and reduce mechanical noise.

B. Noise Measurement

A schematic diagram of the spectrum analyzer is shown in Figure 5-2. The function generator synthesizes a square wave that is used as the

reference signal for the lockin. The function generator is programmed to ramp the frequency of the square wave with time as shown in the figure. The signal from the position detector or the microphone is connected to the signal input of the lockin. The sine wave correlation mode of the lockin is used. The computer records the magnitude output from the lockin (the magnitude output is $\sqrt{A^2 + B^2}$ where A and B are the in-phase and out-phase signals of the two-phase lockin). A synchronization output from the function generator indicates the beginning of each frequency ramp.

Figure 5-2. Schematic of the spectrum analyzer used to characterize the noise in the PDS system.

This setup forms a spectrum analyzer and avoids the need of obtaining and using the more-expensive integrated device. We typically average the results from 3 to 5 scans of the frequency range. The rate at which the reference frequency can be swept is limited by the lockin. We sweep the

range 100 - 5 Hz over 200 s.¹ The lockin time constants are set at 1 s. Therefore the spectrum will be averaged over about a 2 Hz window (4 time constants).

SNR Determination

Figure 5-3 shows two frequency spectra of the probe deflection signal. One is gathered with 40 Hz excitation light and the other is the background, which is recorded without cell in place. The sharp peak at 40 Hz is the AC PDS signal; everything else is noise. The sharp peaks at 60 and 180 Hz are the effect of stray fluorescent room light reaching the position detector. The broad noise between 60 and 80 Hz and around 120 Hz are characteristic of the cell. The small peak at 18 Hz is pointing instability inherent in the probe laser. These characteristic peaks allow noise sources to be analyzed. If all sources caused featureless regions of noise, tracking down individual sources would be very difficult.

The signal-to-noise ratio (SNR) is the quantity to be maximized. In Figure 5-3 we see that the SNR is quite high at 40 Hz, but if we tried to perform this experiment at 75 Hz, the SNR would fall below 1:1. The frequency spectrum also indicates that we should avoid 18 Hz. The

¹ It is better to scan the frequency downward to allow the low frequency range to be measured. When the reference frequency jumps, the lockin loses the reference. The lockin needs several seconds to reacquire the reference at the new frequency. By scanning downward, the lost data are at the high-frequency end of the spectrum, which is less interesting.

frequency spectrum allows one to intelligently choose modulation frequencies that maximize the SNR.

Figure 5-3. Two frequency spectra of the probe deflection signal. One is recorded with 40 Hz excitation light. The other is a background experiment with no cell. This spectrum was recorded with an increasing frequency sweep causing the tail on the signal peak to extend to higher frequencies.

C. Noise Sources

We have tried to identify the sources of the noise shown in Figure 5-3 and the figures in the remainder of this chapter. We believe that the signal path is free from electrical noise. Other than the absence of characteristic mains interference at 60 Hz, there are two factors that indicate the noise is not electrical in origin. First, the signal produced by the position detector is 4 orders of magnitude above the lockin's sensitivity limit. Second, we removed all the equipment between the laser and position detector and observed that most of the noise disappears. Excluding electrical effects, the remaining noise sources are due to movements of the probe beam. A few electrical noise sources are discussed below.

Electrical

It took several years, but the ubiquitous ground loop was eventually eliminated. This accomplishment is evidenced by the lack of a 60 Hz peak in the frequency spectra (except Figure 5-3 which was effected by room light). This was not always so; early spectra showed huge peaks at 60 Hz. Strict adherence to the rules [47], and some luck was required. Reference 47 states "Such problems [grounding] are often difficult to assess and their elimination remains somewhat of an art." We agree.

Strong RF fields often plagued our experiments. ICP's and pulsed laser power supplies were used in neighboring labs. We believe the mechanism of these effects is through the power supplied to the probe beam. The pointing stability of the probe beam is sensitive to small static charges. Touching the cable leading to the laser head causes large beam deflections.

Because the cable is securely bolted to the table, the mechanism is not mechanical. Shielding of the power supply and the cable to the laser head helps to reduce these effects. Waiting until your neighbors leave their laboratories is also an effective solution.

Mechanical or Acoustic

Bulk movement of air has a large effect on the probe beam. Waving one's hands can deflect an exposed probe beam. It is hard to believe, but the slight pressure gradient moving the air, causes relatively large refractive index gradients. Fortunately, this noise source is easily removed. The PDS system is protected by two enclosures. An inner enclosure minimizes dead space, and an outer enclosure keeps air currents away from the entire system. Each enclosure is closely fitted to prevent air currents.

Our conclusion is that most of the noise is due to movement of the cell. Two possibilities exist for moving the cell: mechanical vibrations directly moving the cell through the table and cell holder, and acoustic waves moving the cell. We have focused more attention on acoustic sources, but the evidence is not complete that this is the major mechanism. The optical table is mounted on vibration-isolation legs that have a resonant frequency at 5 Hz. Above the resonant frequency, vibrations should be strongly attenuated. Dropping a lead brick on the floor causes a spike in the probe deflection. That observation might lead us to believe that there is significant mechanical coupling of the noise source to the cell, but clapping one's hands also causes similar noise. The measurements of the acoustic noise profiles in a following section lends some evidence that the major cause of noise is acoustic.

D. Laser Stability

The noise can be no less than the inherent instability in the probe laser. Our experience has been that the probe beam pointing stability far exceeds the manufacturer's specifications, and how far can vary greatly between similar lasers. Figure 5-4 (page 135) shows the pointing stability of two essentially identical lasers manufactured by Uni-phase, Inc. The only difference is that one is contained in a 1 inch diameter body and the other is contained in a 1.5 inch diameter body. The larger-body laser is far worse than its smaller relative. The specification of both lasers is 0.01 milliradian.

We advise researchers to carefully critique manufacturers' specifications. The pointing stability of a laser is considered by some to be the DC shift over several hours of operation. Few manufacturers test lasers as shown in Figure 5-4. Stability is sometimes rated in terms of frequency and intensity stability. As an example, we tested a laser with active frequency and intensity stabilization that had very poor pointing stability.

Figure 5-5 shows that the instability of the laser is not equal in all directions. The laser head is a cylindrical body, and the figure shows the result of rotating the head 45 and 90 degrees from its original orientation (the identity of the three curves in Figure 5-5 is not important). What we note is that the characteristic peaks do change. The peaks at 25 Hz or 120 Hz can be reduced by simply rotating the laser head (the angle that was best at 25 Hz was not best at 120 Hz). This characteristic will be different for every laser and probably varies with the age of the laser.

The probe beam can become very unstable if part of the beam is reflected back into the laser cavity (sometimes referred to as retroreflection). Partial reflections of 5% will occur from every uncoated glass surface. There are many of these partial reflections: both surfaces of the focusing lens, one each at the entrance and exit windows of the cell, two from an interference filter, two from the window of the position detector, and one 50% reflection from the surface of the silicon element of the position detector. The number of reflections is greatly increased because partial reflection of the partial reflections occurs. Even a 0.25% retroreflection can cause significant instability of the probe beam. These instabilities appear as large amplitude (mrad) low frequency oscillations (<5 Hz) of the probe beam. Retroreflections are eliminated by skewing optical components slightly from perpendicular to the probe beam and using small irises to block stray beams.

Figure 5-4. Comparison of the pointing stability of two lasers with identical specifications. Both lasers were from the same manufacturer, and have the same power and stability specifications. One laser is contained in a larger body.

Figure 5-5. The frequency spectra of the laser instability with the laser head rotated to 0, 45 and 90 degrees.

E. Acoustic Profiles

Our attempts to determine the noise sources finally concentrated on acoustic sources. The deciding experiment was performed late one night. Some helpful building engineers (who shall remain anonymous) turned off the building ventilation for a very short period. Once the ventilation fans stopped, it became obvious: Laboratories are noisy places.

We began exploring the acoustic spectra of different rooms. The results were surprising. Because the frequencies of greatest interest approach sub-audible, the ear is not a reliable gauge. Some of the more interesting results are shown here.

Incorrect Perceptions

The typical acoustic profile in our lab is shown in Figure 5-6. The spectra for four consecutive days show stable characteristic peaks at 12, 25, 37, 52, and 72 Hz. Figure 5-7 shows the acoustic spectrum near ventilation ducts in the corner of the room. Clearly these are a major noise source. All the component frequencies in Figure 5-7 do not appear in Figure 5-6. Resonance of the room can be factor. Our room is 12.6 m long by 7.4 m wide by 4.6 m high. The speed of sound at 20 °C and 30% relative humidity is 344 m s⁻¹ [57]. A 27 Hz acoustic wave has a wavelength of 12.6 m ($\lambda v = v$) [85]. The acoustic peaks at 12, 25 and 37 Hz could be $1/2 \lambda$, $2/2 \lambda$, and $3/2 \lambda$ resonances along the length of the room. The height and width of the room resonate at frequencies of 74 and 46 Hz.

Figure 5-8 shows the acoustic spectrum measured in an apparently quiet hallway. This demonstrates that building designers only account for

audible acoustic noise. What sounds like a good place to perform experiments is worse than our current location.

We also investigated other rooms in search of a quiet location. Every room had distinct acoustic peaks. The best room (acoustically) lacked ventilation and was very small. Its spectrum is shown in Figure 5-9. Besides the distinct peak at 27 Hz, this room would be a better site for experiments. Except this room, no room offered a significant advantage to the current laboratory.

Figure 5-6. The acoustic spectra for four consecutive days. The scale is in millivolts as measured by the lockin. These values can be quantitatively compared with the remaining acoustic spectrums.

Figure 5-7. The acoustic spectrum near the ventilations ducts that are suspected being the major acoustic source.

Figure 5-8. Acoustic spectrum of a 'quiet' hallway.

Figure 5-9. The acoustic spectrum of this room is very quiet except for the one peak.

F. Approaches to Noise Control

There are three approaches to reducing the noise: eliminate the source, eliminate the transmission path, or prevent the system from moving. The conclusion of the previous section is that no specific location available to us is much better than the current one. Because ventilation is required in all laboratories, we don't consider removing building ventilation to be a solution. Our other options are to reduce the transmission of noise to our system, and to improve the system so that it cannot move. Neither of these is very easy.

Unstoppable Low Frequency Noise

Figure 5-10 shows the acoustic spectrum outside and inside the enclosure of our system. There is no significant difference between the two spectra. The outer enclosure is 2 inch closed-cell polystyrene foam. The inner enclosure is 1 inch open-cell foam with a lead backing. While these enclosures effectively prevent air currents, they have no acoustic isolation value at low frequencies.

Handbooks recommend that attenuating low-frequency sound can be accomplished by viscous dissipation in the small pores of an open cell foam or other porous material [86 - 88]. But 1 foot of foam has no effect. Figure 5-11 shows the acoustic spectra outside and inside a large box (3 feet on each side) filled with foam and wrapped in blankets; both spectra are essentially the same. Other than viscous dissipation the next option is mass. The attenuation of a wall at low frequencies increases with mass [86 - 89]. If the optical table can support the weight, a brick or lead wall can be constructed around the system. Reference 86 notes that the enclosure must be airtight, because much sound can travel through small openings. While this approach might reduce transmission of the sound, it makes access to the experiment difficult.

Figure 5-10. The acoustic spectrum inside and outside of the system enclosure are very similar, which indicates that the enclosure offers no acoustic isolation.

Figure 5-11. The acoustic spectrum inside a huge box of foam is little changed from that on the outside.

Why Dust Is Unlikely

If we can't stop the sound from reaching the cell, perhaps we can stop the cell from moving. The cell construction is rather sturdy. There is the possibility that particulates in the electrolyte can cause noise in the probe deflection. Particles in the path of the beam would cause a shadow on the position detector. The position detector only measures the intensity centroid and would incorrectly indicate that the beam had moved (both the LPD and bicell detector would behave this way). There are two observations that led us to suspect dust. First, when the probe beam is focused the deflection signal seems more noisy. The particles become relatively larger as the beam becomes smaller. Second, if the cell was allowed to sit overnight, the beam deflection seemed to become quieter. This evidence is anecdotal so two experiments were performed.

Figures 5-13 and 5-14 (page 144) contain the results of two experiments which discount the role of particulates. The first experiment compares the acoustic spectrum with the probe deflection spectrum. The particles are freely supported in the electrolyte and should be free to respond to any acoustic wave imposed upon them. Figure 5-13 shows that the probe deflection spectrum only contains one of the four major peaks present in the acoustic spectrum. The second experiment was to allow the cell to sit for several days, and then stir up the electrolyte. Figure 5-14 shows the probe deflection spectrum before and after this experiment. Aside from a slight increase in the peak at 20 Hz, the two spectra are similar. If dust does play a role, it is not significant.

Figure 5-12. When the beam passes the sample, the sample surface is touching the edges of the beam.

The two observations that made us suspect dust remain to be explained. The observed effect of focusing the probe beam can be explained by movement of the sample surface. Figure 5-12 shows

how a probe beam is shaped when passing the sample surface. However, the probe beam does not have sharp limits as shown in the figure. The Gaussian intensity profile of laser beams means that some of the laser is always grazing the sample surface. As the sample moves slightly, more or less of the beam will be blocked by the edge of the sample. When part of the beam is blocked, the position detector will indicate movement. The same movement of the sample will affect a small beam more than a large one.

The tendency of the system to become more quiet overnight remains unexplained. The cell assembly is a rigid mechanical system with little damping. The constant adjustments made during the day can be considered as energy input to the mechanical vibrations. The vibrations would be slowly dissipated overnight. If the small amount of floor vibrations coupled through the legs of the optical table are the source, we would expect the floor to be more stable in the morning before foot traffic begins to excite the vibrations of the building.

Figure 5-13. The acoustic spectrum and probe deflection are compared. The acoustic spectrum has distinct peak at 12, 25, 35, and 52 Hz. The probe deflection signal only shows a distinct peak at 25 Hz.

Figure 5-14. The spectrum of the beam deflection is shown when the electrolyte has been undisturbed for 2 days and after it is stirred. The probe beam passed through a cell, but was not near the electrode. This experiment cannot be compared with Figure 5-13 because they were performed three months apart.

Conclusion

The noise levels reported here become a severe problem only when the excitation wavelength is moved into the mid-infrared. The IR glowbar reduces the excitation power to microWatt levels. To increase the sensitivity of PDS, the noise must be controlled. There is not much ability to increase the signal using spectrally continuous light sources. The IR glowbar operates at 1900 K and has an emissivity of 0.7. New broadband continuous and pseudo continuous lasers may provide more power, but this is not necessarily a good direction. One of the advantages of PDS is that it uses low excitation power.

With the experiments shown in this chapter, we can conclude that the pointing stability of the laser is not the limiting factor; suitable lasers can be found. The main noise source is acoustic in origin. In our case, ventilation is the culprit, and it is not possible to eliminate this source.

Attenuation of the noise should be possible, however building an airtight brick wall around the system is a less-than-ideal solution. Preliminary investigations indicated that specially-engineered materials may provide a suitable enclosure. The enclosure is an aspect of the system that can be greatly improved. Both the AC and DC signals will benefit from an improved enclosure.

The cell design can be improved. Simple theory suggests that increasing the weight of a system will decrease the oscillation frequency and that increasing the stiffness of a system will increase the oscillation frequency. We have observed both these behaviors. Reinforcing plates added

to the cell holder moved the broad noise band at 60 to 80 Hz in Figure 5-3 to its present location; previously it was located 10 Hz lower.

Our current approach is to avoid the noise problem. The frequency spectrum indicates quiet valleys. The bandpass of the lockin is narrow, so one only needs a few Hertz wide valley to perform an experiment (so long as the sides are stable). This approach is not courageous, but it works. If we can't increase the signal or decrease the noise, there is still one option: Advanced signal processing and transform techniques applicable to PDS, which are discussed in the concluding chapter.

Chapter 6:

Oxidation of Platinum

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Platinum is a good candidate to be studied with PDS. The electrochemistry is very reproducible allowing signal averaging to be used. Using the average of many experiments, we have been able to achieve the submonolayer sensitivity necessary to study the electrochemistry on the platinum electrode surface. Cyclic voltammetry of platinum presented us with results which were not immediately understandable in the terms of current theories and thereby served as the motivation for the work discussed in this chapter. Also, platinum is commonly used as a catalyst in fuel cell electrodes and there is a strong incentive to better understand its reaction mechanisms. The long-term goal of this type of investigation is to improve the utilization of platinum.

To explain the PDS results, we developed numerical models that simulate the electrolyte concentration gradients produced by various reaction mechanisms. By comparing the simulated results with the experimental data, we can exclude certain mechanisms and provide support for others.

A. The Experiment

Cyclic voltammetry of platinum in 0.1 M sulfuric acid is shown in Figure 6-2. The three graphs in this figure are all plotted versus electrode potential (which refers to a DHE in the same electrolyte). The top pane is the current; the middle pane is the concentration gradient as measured by the DC probe deflection; and the bottom pane is the surface absorption as measured by the AC probe deflection. The excitation light wavelength was 650 nm. All three signals were recorded simultaneously and are the average of 25 sweeps. The current response was recorded on paper during all 25 sweeps and confirmed that the electrochemistry was closely reproduced for each sweep. The potential program of each sweep is shown in Figure 6-1. The pretreatment is two oxidation/reduction steps, followed by a triangular sweep between 50 and 1600 mV at 50 mV s⁻¹. The PDS signals are recorded only during the triangular sweep. The same data as in Figure 6-2 are also plotted versus charge in Figure 6-3. The charge is derived by integration of the current data.

Figure 6-1. Potential program for experiment in Figure 6-2. The arrow shows where data acquisition begins for each sweep.

Figure 6-2. Cyclic voltammetry of platinum in 0.1 M sulfuric acid. Positive currents are anodic. Downward deflections of the probe beam are towards the electrode.

Figure 6-3. The same data in Figure 6-2 are plotted versus charge. The top curve is the potential, the middle curve is the DC deflection, and the bottom curve is the AC signal. The vertical bar is a reference point drawn through the double layer region of the voltammogram. Oxidation of the platinum begins to the right of this line.

Moderate agreement about the electrochemistry of platinum exists in the literature [90 - 94]. As a starting point for discussion, we consider typically-proposed reactions in acid electrolyte:

The reactions are the reduction of the platinum to platinum hydride and the oxidation of the platinum to an oxide. Reaction 6-2 and 6-3 are "placeholders" for a multistep mechanism which will be discussed below.

The cyclic voltammogram describes a process wherein the electrode surface is oxidized during the anodic scan (left to right in Figures 6-2 and 6-3) and then reduced during the cathodic scan. To describe this process, it is convenient to start at A on the anodic sweep (see Figure 6-2). At this potential the platinum surface is free of hydrogen and oxygen. Formation of an oxide layer occurs by either Reaction 6-2 or 6-3 during the anodic sweep from A to C. Due to the irreversibility of platinum oxidation, little change occurs during the cathodic sweep from C to D. As the potential is decreased further, reduction of the oxide layer by the reverse of Reaction 6-3 occurs during the cathodic sweep from D to E. From E to F a platinum hydride layer is formed by Reaction 6-1. The oxidation of the hydride layer occurs during the anodic sweep from F to A, after which the platinum surface is again free of hydrogen and oxygen.

Both PDS signals demonstrate that PDS is capable of submonolayer sensitivity. The AC signal demonstrates submonolayer sensitivity to the

absorption of light at the electrode surface. The DC signal demonstrates that the concentration gradients produced by submonolayer reactions can be measured. Each signal is discussed separately below.

Surface Signal

The AC signal detects the formation of the oxide film. The AC signal increases as the oxide film is formed from A to C. The oxide film remains fairly stable during the cathodic sweep from C to D. The AC signal then quickly decreases as the oxide film is reduced, from D to E. No change in the optical absorption at visible wavelengths has been seen due to the hydride film. A similar signal associated with the surface absorption coefficient has been observed with photoacoustic spectroscopy (PAS) [92]. Note that the surface absorption signal contains a large background and is only changing approximately 2% during this experiment.

A plot of the AC signal versus charge is shown in Figure 6-3. The significance of this method of presenting the data is that it shows that the optical absorption of the surface is linearly related to the charge during the formation of the oxide layer. The optical absorption of the surface is therefore linearly related to the surface coverage by the oxide. The charge consumed during oxidation of the platinum surface from A to C is about 3 mC (from 800 to 1500 mV), which is twice the charge consumed to oxidize the PtH film from F to A. This confirms that the signal change from A to C is due to the formation of a single monolayer of platinum oxide, because the formation of PtO requires twice the number of electrons as to oxidize PtH. The AC signals for anodic and cathodic scans have the same shape, but are

slightly shifted apart from each another. The hysteresis is due to the time constant of the lockin.

This experiment has been performed at different excitation light wavelengths. Because platinum is gray and the oxide is black, the change in surface spectrum as the platinum surface is oxidized is not useful. Also, because the change in the AC signal from its reduced state to its oxidized state is only a few percent, correcting this experiment is difficult. As shown in Chapter 3, finding an accurate black reference is difficult. In order to cross plot the data as was done for copper in Chapter 3, we would require a very precise reference spectrum.

Concentration Gradient

The DC deflection signal provides interesting insight into the electrochemistry. To interpret this curve one must keep in mind that the refractive index of sulfuric acid increases as the acid concentration increases and that the probe beam is deflected towards the region of higher refractive index. Again, starting from A in Figure 6-2, a deflection towards the electrode is seen from A to B. This is qualitatively consistent with either Reaction 6-2 or 6-3, each of which consume water and release protons, resulting in an increased acid concentration near the electrode. Ignore for a moment the change from B to C; this is discussed subsequently. From C to D a slow relaxation of the gradient by diffusion is seen. From D to E, the reverse of either Reaction 6-2 or 6-3 causes the beam to be deflected towards the electrode. Small effects are seen due to the hydrogen reaction at F.

There are two characteristics of the DC deflection which are not explained by the simple reactions discussed so far:

- The DC deflection shows a reversal at B. Because the anodic current is constant, there is no reason to expect the magnitude of the concentration gradient to decrease. As is discussed in the next section, it should (according to a simple mechanism) continue to increase for about 100 s before approaching an asymptotic value.
- The DC deflection from F to A is much smaller than the deflection from A to C. Because the current at F to A is similar to that at A to C, the concentration gradients should have similar magnitudes. The charge plot shows this discrepancy very clearly. The hydrogen region from F to A in Figure 6-3 consumes about 1.5 mC. Yet the DC deflection produced by this 1.5 mC is much smaller than the deflection produced during the first 1.5 mC of oxide formation from A to B.

These features force us to discard the simple theory. To account for the inflection in the DC deflection, we looked to multistep mechanisms. The DC deflection size difference between the hydrogen region and oxide region will be explained in a following section.

Of interest is the location of the zero value of the DC deflection in Figure 6-2. The scale shown is only relative. Theoretically, by measuring the position of the probe beam while the cell is at open circuit, the rest position of the probe beam would be determined. We measured the beam position before the experiment began, but the results were random. Either charging of the double layer, drift of the probe beam, or movement of the electrode when the electrical circuit is made could be the source of the random behavior. Despite this problem, it is very probable that the flat region near A where no electrochemical reaction occurs is the rest position of

the probe beam. Better methods need to be developed to determine the rest position of the probe beam.

The experiment in Figure 6-2 has been performed more than 100 times. Other than for the electrochemical data, we used this experiment as a benchmark of the PDS system's performance. The data shown in Figure 6-2 are one of the best sets of results with respect to noise. The data shown for this experiment are repeatable.

B. Current Step Response

The oxidation current from A to C in Figure 6-2 can be approximated as a current step. We can derive an analytic solution for this simple case and compare it with the experimental data. We assume that only the cation (H^+) is being consumed or produced at the electrode surface. Using dilute solution theory for a binary electrolyte, the diffusion equation and boundary conditions are [53]:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad [6-4]$$

$$\frac{-D}{1-t_+} \left. \frac{\partial c}{\partial x} \right|_{x=0} = \frac{i}{z_+ v_+ F} \quad \text{Boundary Condition 1}$$

$$c(\infty, t) = c^0 \quad \text{Boundary Condition 2}$$

$$c(x, 0) = c^0 \quad \text{Initial Condition}$$

In these equations, c is the concentration of the electrolyte, which is assumed to be a binary electrolyte which dissociates into v_+ cations with charge z_+ and v_- anions with charge z_- . ($A_{v_+} B_{v_-} \rightarrow v_+ A^{z_+} + v_- B^{z_-}$). The sign of the current, i , is determined by its direction; thereby, anodic reactions have a positive current. The diffusion coefficient is an effective diffusion coefficient, defined as:

$$D = \frac{D_+ D_- (z_+ - z_-)}{z_+ D_+ - z_- D_-} \quad [6-5]$$

The transference number, t_+ , is defined as:

$$t_+ = \frac{z_+ D_+}{z_+ D_+ - z_- D_-} \quad [6-6]$$

The differential equation is solved to yield the expression for the concentration.

$$c(x,t) = c^o + \frac{i(1-t_+)}{z_+v_+FD} \left[2\sqrt{\frac{Dt}{\pi}} \exp\left(\frac{-x^2}{4Dt}\right) - x \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \right] \quad [6-7]$$

Differentiation of this expression results in the electrolyte concentration gradient, which is directly proportional to the probe deflection.

$$\frac{\partial c(x,t)}{\partial x} = \frac{-i(1-t_+)}{z_+v_+FD} \operatorname{erfc}\left[\frac{x}{2\sqrt{Dt}}\right] \quad [6-8]$$

Equation 6-8 shows that the beam deflection increases asymptotically to a steady state value. The error function term in the above equation approaches one as time approaches infinity, therefore the steady state value of Equation 6-8 is equal to Boundary Condition 1 of Equation 6-4. Not only does Equation 6-8 not predict an inflection in the probe response, it also predicts that the probe deflection should increase for long times.

In the table at the right, we have calculated the time required for the magnitude of the concentration gradient to

reach 90% of its steady state value at several distances from the electrode surface. These distances are within the

range of practical probe offsets. Even if the probe offset was 50 μm , the probe

deflection would not approach its

asymptote for 26 s. Figure 6-2 shows that the concentration gradient

abruptly stops increasing after only 3 seconds (150 mV equals 3 s at a sweep

Table 6-1. Time for the probe response to a current step to reach 90% of the steady state value.

x_0	time
50 μm	26 s
100 μm	110 s
150 μm	240 s
200 μm	420 s

$$D = 3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

rate of 50 mV s^{-1}). Clearly, the current step model cannot explain the data. A more-complex reaction mechanism must be occurring.

C. Consumption of Water

We propose that the difference between the size of the DC deflection for the platinum hydrogen reactions and oxidation reactions must be due to the consumption of water. Cyclic voltammetry of platinum in alkaline electrolyte proves this hypothesis. Figure 6-4 shows the current and DC deflection for the same potential program (see Figure 6-1) as was used in the acid experiment shown in Figure 6-2, except that the electrolyte has been changed to 0.1 M KOH . The hydrogen and oxide reactions in a hydroxide electrolyte are:

The role of water in these three reactions is reversed from that in the analogous reactions for acidic electrolytes (Reactions 6-1, 6-2, and 6-3). The reactions also cause a probe deflection in the opposite direction to their acid analogs. Reactions 6-10 and 6-11 and the reverse of Reaction 6-9 consume hydroxide, thereby causing a probe deflection away from the electrode.

The DC deflection in Figure 6-4 shows that the beam deflection in the hydrogen region is much larger than for the case of acidic electrolyte. During the anodic sweep, the probe deflection in the hydrogen region is of similar height to that in the platinum oxidation region. These data prove our

hypothesis that the consumption of water has a significant role in the beam deflection.

Figure 6-4. Cyclic voltammetry of platinum in 0.1 M potassium hydroxide.

D. Reaction Mechanism Studies

Given that simple theories cannot explain the beam deflection in Figure 6-2, we developed a numerical model to explore different reaction mechanisms. This model allowed us to study complex mechanisms with time-varying boundary conditions and to account for the consumption or production of water.

The model solves the one-dimensional diffusion equation for two species.

$$\frac{\partial c_j}{\partial t} = D \frac{\partial^2 c_j}{\partial x^2} \quad [6-12]$$

$$c_j(x, 0) = c_j^o \quad \text{Initial Condition}$$

$$\left. \frac{\partial c_j}{\partial x} \right|_{x=0} = \text{flux}_j(t) \quad \text{Boundary Condition 1}$$

$$c_j(L^\infty, t) = c_j^o \quad \text{Boundary Condition 2}$$

For the electrolyte, the diffusion coefficient is defined by Equation 6-5 (see page 156). For water, the self-diffusion coefficient for the movement of water through water is used. Values for the self-diffusion coefficient are reported in References 95 & 96 and listed in Table V-5.

The boundary conditions at the electrode are flux boundary conditions. Boundary Condition 1 in Equation 6-4 (page 156) is used for the electrolyte, and for the solvent a simple flux boundary condition is used.

$$D \left. \frac{\partial c}{\partial x} \right|_{x=0} = \text{flux} \quad [6-13]$$

The mass transport equation is solved for both the electrolyte and water independently. In effect we have linearized the problem, by assuming that the water concentration and electrolyte concentration change independently. Because the concentration changes are on the order of μM for the monolayer reactions involved, such linearization is a reasonable approximation. The refractive index gradient is the summation of the contributions by each of the species

$$\frac{dn}{dx} = \sum_j \frac{\partial n}{\partial c_j} \cdot \frac{\partial c_j}{\partial x} \quad [6-14]$$

Concentrative refractivities, $\partial n/\partial c$, are listed in Table V-4.

The implementation of the model is extremely similar to that for the thermal model. The code for the concentration model was derived from the thermal model code with only a few modifications, and the probe deflection was calculated with the same modules described in the thermal model. Because the concentration gradients have a larger boundary layer thickness than the thermal gradients, the size and angle of the probe beam have a smaller effect on the probe deflection. The model results we show are all for a parallel probe beam with an offset of $75 \mu\text{m}$ and a radius of $65 \mu\text{m}$ ($180 \mu\text{m}$ $1/e^2$ diameter).

Candidate Reactions

With the model, we could test various reaction mechanisms. Candidate reactions include:

The process we expect to cause the inflection in the DC response is an initial high rate of water consumption followed by sudden reduction in the rate of water consumption. A consistent mechanism is the initial formation of platinum dihydroxide followed by the formation of the oxide. The formation of the dihydroxide by Reaction 6-15 consumes twice as much water as the formation of the oxide by Reaction 6-16. If we assume that these two reactions proceed simultaneously, the total electrochemical current must be divided between the two reactions. The methods of dividing the current are somewhat arbitrary and require many adjustable parameters. Also, these two electrochemical reactions do not allow dihydroxide to be converted into oxide. By using a combination of Reactions 6-15 and 6-18 we were able to solve these problems.

We have also considered Reaction 6-17, which is proposed mainly by Burke, *et al.* [97 - 101]. This reaction is reported to begin occurring at about 200 mV on the anodic scan (between the two platinum hydride oxidation peaks). Reaction 6-17 consumes water and releases acid which would cause a deflection of the probe beam towards the electrode. We see no evidence of such a reaction occurring in Figure 6-2 (page 149). Because this reaction produces deflections in the same direction as the hydrogen reaction, the effect of the formation of the hexahydroxy species could be masked. Reaction 6-17 consumes three times the water of Reaction 6-15 and six times the water of Reaction 6-16. We cannot exclude the occurrence of this reaction, but if the

hexahydroxy platinum species is formed, the DC deflection data indicate that only a very small amount is formed.

Proposed Mechanism

We propose that all the electrochemical current is used to form platinum dihydroxide by Reaction 6-15 and that the dihydroxide is dehydrated by the non-electrochemical Reaction 6-18. The rate of the dehydration is controlled by a simple expression.

$$\text{rate} = k \Gamma_{\text{OH}}^* \left(\frac{\Gamma_{\text{OH}}}{\Gamma_{\text{OH}}^*} \right)^m \quad [6-19]$$

In this expression k is the rate constant (s^{-1}), m is the reaction order, Γ_{OH} is the macroscopic surface concentration of dihydroxide (mol mm^{-2}), and Γ_{OH}^* is the macroscopic surface concentration for a complete monolayer, which is equal to the roughness factor of the electrode surface times the concentration of a monolayer on a perfectly smooth electrode. The expression in the parentheses is the fractional surface coverage, sometimes termed θ . By using the fractional surface coverage and including an extra Γ_{OH}^* in Equation 6-19, the rate constant and reaction order are independent of the surface roughness. If the roughness of the electrode surface is doubled, Γ_{OH}^* will double to compensate, and the same k and m can be used.

The boundary conditions for this mechanism in acidic electrolyte are:

$$\left. \frac{-D_e}{1-t_+} \cdot \frac{\partial c_e}{\partial x} \right|_{x=0} = \frac{i(t)}{z_+ v_+ F}, \text{ and} \quad [6-20]$$

$$-D_w \left. \frac{\partial c_w}{\partial x} \right|_{x=0} = \frac{-i(t)s_w}{nF} + k \Gamma_{OH}^* \left(\frac{\Gamma_{OH}}{\Gamma_{OH}^*} \right)^m \quad [6-21]$$

where s_w is the stoichiometric coefficient of water and n is the number of electrons in Reaction 6-15 (both are 2). The current, $i(t)$, is allowed to vary with time (positive currents are anodic). The surface concentrations of dihydroxide and oxide change according to:

$$\frac{d\Gamma_{OH}}{dt} = \frac{i(t)s_{OH}}{nF} - k \Gamma_{OH}^* \left(\frac{\Gamma_{OH}}{\Gamma_{OH}^*} \right)^m \quad [6-22]$$

$$\frac{d\Gamma_O}{dt} = k \Gamma_{OH}^* \left(\frac{\Gamma_{OH}}{\Gamma_{OH}^*} \right)^m \quad [6-23]$$

where s_{OH} is the stoichiometric coefficient of $Pt(OH)_2$ (which is 1 in this case).

Results

The simulated probe deflections for several dehydration orders are shown in Figure 6-5. The first-order dehydration shows the continuously increasing shape similar to what the current step would predict. The higher orders for the dehydration reaction can produce the reversal in the probe deflection, which is observed experimentally. With $m=2$, the simulated beam deflection has a shape similar to that of the experimental probe deflection. The higher dehydration order allows the oxidation to initially proceed solely by the formation of dihydroxide. When a sufficient concentration of dihydroxide is formed, the rate of the dehydration becomes significant. Once dehydration begins, the rate of water consumption decreases and thereby causes the probe deflection to decrease.

For the best fitting curve in Figure 6-5, the magnitude of the model deflection is about 1.5 times as large as the experimental data. Uncertainty in the true probe offset and the roughness factor of the electrode contribute to the magnitude difference between the experiment and model. The model used a roughness factor of 4 to produce the results in this chapter. The electrochemical cell used was the double-sided cell shown in Figure 3-7. With this cell, the electrode cannot be polished to a uniform finish, and the supporting wires, which have an unknown roughness factor, are exposed to the electrolyte. Because of this poor design (with respect to the ability to determine the roughness factor) the uncertainty in the roughness factor is about ± 2 . Different roughness factors cause model deflections that have the same shape but vary in magnitude. Because our main intent is to demonstrate that the model predicts the characteristics we observe experimentally, the magnitude difference between model and experiment is not significant.

Figure 6-6 shows the predictions by the model of the complete anodic scan. The boundary conditions for the hydrogen region is Equation 6-20, and the water flux is zero in the hydrogen region. The current used is an idealization of the experimental current. The model shows the effect of water is as we observe. The simulated probe deflections in the hydrogen region are about 6 times smaller than those in the oxidation region, which is the experimental observation.

Figure 6-5 shows that the best fit is obtained for a reaction order of 2. The other adjustable parameter is the rate constant. Figure 6-7 shows the simulated probe deflections for various rate constants. When the rate of dehydration is fast, the probe response is essentially that which would be

produced by Reaction 6-16. When the rate of dehydration is slow, the response is governed by Reaction 6-15. The intermediate values produce the reversal in the probe deflection seen in the experimental data.

The model surface concentrations of dihydroxide and hydroxide are shown in Figure 6-8. This figure offers some added insight into the AC signal in Figure 6-3 (page 150). The AC signal plotted versus charge shows a slight curvature. A slight difference in the optical constants of platinum dihydroxide and platinum oxide can explain this curvature. Figure 6-8 shows that during the first half of the oxidation, mostly dihydroxide is formed. During the second half of the oxidation, mostly oxide is formed. If the optical absorption of the oxide were smaller than that for the hydroxide, we would expect to see the curvature in Figure 6-3.

The experiments described in this chapter were performed before accurate methods of determining the offset of the probe beam were developed. Figure 6-9 shows the effect of the probe beam offset on the model deflection. The values of probe offsets are within the range where we estimate that the probe was actually located. The calculations were for a reaction order of 2 and a rate constant of 0.3 s^{-1} . The probe offset of $75 \text{ }\mu\text{m}$ provides the best fit to the experimental data. The larger offsets produce a deflection which shows little or no reversal. The simulations in Figure 6-9 demonstrate two points. First, the probe beam must be placed very close to the electrode surface or important features will be lost. If the probe offset in our experiments was $125 \text{ }\mu\text{m}$ or more, the reversal in the beam deflection would not have been observed. Second, the position of the probe beam must be precisely known to quantitatively compare experimental data with model calculations.

Figure 6-5. The model probe deflection is shown for reaction orders of 1 to 4 for the dehydration reaction. The solid lines are the model calculations plotted against the left axis. The circles are the experimental data plotted against the right axis; this is the same data as in Figure 6-2. The rate constant was 0.3, the probe offset was $75\ \mu\text{m}$, and the probe diameter was $180\ \mu\text{m}$. The electrolyte is sulfuric acid and the current used is shown in Figure 6-6.

Figure 6-6. The model probe deflection during the anodic sweep for platinum cyclic voltammetry is shown in the top pane. The idealized current used by the model is shown in the bottom pane; the units are $\mu\text{A mm}^{-2}$. This current corresponds to an electrode roughness factor of 4. The model simulates a sweep rate of 50 mV s^{-1} from 50 to 1550 mV. The rate constant was 0.3 s^{-1} and the reaction order was 2. The probe offset was $75 \mu\text{m}$ and the probe diameter was $180 \mu\text{m}$. The monolayer concentration, Γ_{OH}^* , is $1.04 \times 10^{-10} \text{ mol mm}^{-2}$.

Figure 6-7. The model probe deflection is shown for several rate constants and a reaction order of two. The model deflections are plotted against the left axis and the experimental data shown as circles are plotted against the right axis. The dotted lines represent $k = 0.5, 0.4, 0.3, 0.2$, and 0.15 s^{-1} ; the other rates are indicated in the graph. The probe offset was $75 \text{ }\mu\text{m}$ and the probe diameter was $180 \text{ }\mu\text{m}$.

Figure 6-8. Model predictions of the surface coverage of dihydroxide and oxide are shown for the anodic scan. The concentrations are expressed as fractions of a monolayer. The monolayer concentration is $1.04 \times 10^{-10} \text{ mol mm}^{-2}$, which corresponds to an electrode surface with a roughness factor of 4. The rate constant was 0.3 s^{-1} and the reaction order was 2.

Figure 6-9. The model probe deflection is shown for four probe offsets (labeled in micrometers). The rate constant was 0.3 s^{-1} and the reaction order was 2.

E. Different Acids

Cyclic voltammetry experiments for platinum in perchloric, sulfuric and phosphoric acid are shown in Figures 6-10, 6-11, and 6-12 (see pages 175 to 177 at the end of this section). Two trends are evident in the DC deflection: small deflections are seen at 330 mV on the anodic scan and 220 mV on the cathodic scan for sulfuric and phosphoric acid, and the reversal in the probe deflection is largest in perchloric acid and smallest in phosphoric acid. A likely explanation for these trends lies in the specific adsorption of anions on the platinum surface. The ranking of the strength of specific anion adsorption on platinum is:

which is the order in which the three figures are presented (weakest to strongest.)

The possibility that the small deflections centered at 270 mV in Figures 6-11 and 6-12 are caused by impurities is small. Metals are typical electrolyte impurities, and many metals can form monolayer films on platinum at potentials above the reversible potential listed in thermodynamic tables.¹ Such a film would be formed on the cathodic sweep

¹ These films are termed underpotentially deposited (UPD) films. The qualification *under* derives from the lack of a universal sign convention for potential.

and removed from the surface on the anodic scan. The anodic reaction for oxidation of a metal is:

This reaction releases metal cations into the electrolyte, which almost certainly increases the refractive index. Therefore, the oxidation of a metal film causes a probe deflection toward the electrode surface and the reduction causes a deflection away. Contamination by a metal impurity is not possible because the direction of the two small peaks in the figures is the opposite: the anodic deflection is away from the electrode, and the cathodic deflection is toward the electrode. Contamination by organic impurities is also unlikely. Organic electrochemical reactions are typically irreversible. The separation between the two peaks in the Figures 6-11 and 6-12 is only about 100 mV. This small separation between the anodic and cathodic peaks is strong evidence against an organic impurity. The coincidence between the magnitude of the small peaks in the DC deflection and the order of anion adsorption is too strong to ignore.

Specific adsorption of the anion is a process that can explain the experimental data. Adsorption of the anion causes the electrolyte concentration to decrease near the electrode resulting in a deflection away from the electrode. This direction agrees with the experimental probe deflections. The potential at which the small probe deflections occur agrees with the potential of zero charge (pzc) for platinum, which is about 400 mV [102]. At potentials below the pzc, the electrode surface is negatively charged and the anion is repelled. At potentials above the pzc, the electrode surface

is positively charged and the anion is attracted. Specific adsorption refers to a chemical force which binds the anion to the electrode surface in addition to the electrostatic forces [53, 102, 103]. Specific adsorption results in the anion being adsorbed on the electrode surface while the electrode is at potentials negative of the pzc. The probe deflection on the anodic sweep is centered at 330 mV, which is a realistic potential for adsorption of the anion to begin.

The deflection data in Figures 6-10, 6-11, and 6-12 are different in the oxidation region. The perchloric acid shows a strong reversal while the phosphoric acid shows none. This suggests that the order of the dehydration reaction is affected by the adsorption of the anion. The strong reversal in perchloric acid agrees with a higher-order dehydration (see Figure 6-5 on page 167). The phosphoric acid deflection levels off and agrees with a first-order dehydration. The trend in the data shows that the more strongly adsorbed anions reduce the dehydration order: an order of 3 or 4 for perchloric acid, 2 for sulfuric acid, and 1 for phosphoric acid.

Figure 6-10. The DC signal is shown during cyclic voltammetry of platinum in 0.1 M perchloric acid. The potential sweep rate is 75 mV s^{-1} . The signal is the average of 40 scans.

Figure 6-11. The DC signal is shown during cyclic voltammetry of platinum in 0.1 M sulfuric acid. The potential sweep rate is 75 mV s^{-1} . The signal is the average of 25 scans. This experiment and the next used a different cell than the previous experiments, which changes the electrode surface area.

Figure 6-12. The DC signal is shown during cyclic voltammetry of platinum in 0.1 M phosphoric acid. The potential sweep rate is 75 mV s^{-1} . The signal is the average of 7 scans.

Conclusion

The dihydroxide formation / dehydration mechanism we propose is consistent with the experimental data. Except that the mechanism involves both an electrochemical and non-electrochemical reaction, the mechanism is not unusual. The mechanism can predict the experimentally observed reversal of the probe deflection with only two adjustable parameters. The predicted response is close in magnitude to the experimental data.

The reaction order of two for platinum dehydration in sulfuric acid suggests that adjacent hydroxides react to form a bridge bonded oxide layer (as shown below). The comparison of the oxidation in different electrolytes suggests that the anion facilitates the dehydration of the hydroxide. The higher reaction order suggested for the platinum oxidation in perchloric acid suggests that steric crowding is required before the dehydration occurs at a significant rate. The first-order dehydration in phosphoric acid suggests that the dehydration can occur on a single platinum atom. The first-order reaction forms $\text{Pt}=\text{O}$ instead of the bridge-bonded oxide. The dehydration between adjacent groups leads to the interesting possibility that the surface cannot be fully dehydrated. Isolated hydroxide groups could remain on the surface.

The formation of oxygen-containing films on platinum is important to the study of the electrochemical oxidation of methanol on platinum. The electrochemical oxidation of methanol requires the addition of one oxygen atom to the methanol molecule. The oxidation reactions discussed in this chapter are the first step in getting an oxygen atom to the methanol molecule. Cyclic voltammetry of platinum in the presence of methanol shows that methanol oxidation is hindered on platinum oxide surfaces. The data here shows a mechanism by which different electrolytes affect the electro-oxidation rate of methanol on platinum. The dehydration of the hydroxide leaves oxygen on the platinum surface that is less reactive toward methanol. Anion adsorption facilitates the dehydration reaction and thereby reduces the methanol oxidation rate.

The model discussed here can be improved. Solution of the continuity equation, the Navier-Stokes equation, and concentrated solution theory will yield a more-accurate prediction [53]. Without the ability to accurately determine the probe offset, improvement of the model was not warranted. With the techniques discussed in Chapter 4, one should be able to accurately determine the probe offset. With this parameter better known, we can make more-quantitative comparisons between the model and data.

Conclusion

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This work has demonstrated the applicability and usefulness of PDS to electrochemical systems. We have proved that PDS is not "impossible" nor is it "interesting but not useful" as has been suggested by some. We feel that PDS is well beyond the initial stages of development and that the theoretical foundations are stable. It seems unlikely that any unexplored areas remain which could upset the soundness of the technique. As more researchers apply PDS to electrochemical systems this hypothesis will be tested. Currently, PDS is an easily applied technique which has a unique position among other *in situ* techniques. PDS has been developed sufficiently that

most researchers should be able to apply the technique to electrochemical systems and be able to devote most of their efforts to electrochemical problems rather than experimental problems. At the end of this chapter, we discuss some promising routes for advancing PDS.

A. Current Status

The state of PDS has advanced considerably over the last several years, but it does appear that the development is past the initial rapid changes characteristic of new techniques. The several effects present in the PDS signal are well understood and can be separated. The basis of the technique, the characteristics of the technique and the analysis of the data are considered below. In the next section, we will compare PDS with other techniques.

Signals

PDS measures one thing: the deflection of a probe beam as it passes through a refractive index gradient near an electrode surface. Many effects are contained in the refractive index gradient. The gradient can measure the absorption of light at the electrode surface, concentration gradients, absorption of light in the electrolyte, and heats of reaction. Each of these effects can be separated from the others through instrumental or physical techniques. Because the excitation light is modulated in PDS, absorption of light results in a periodic probe beam deflection signal. The separation in frequency space allows the probe deflections caused by concentration gradients and heats of reaction to be separated from the probe deflection caused by the absorption of light. The heats of reaction can be separated

from the concentration gradients by using the secondary gradient technique. The absorption of light in the electrolyte and at the surface can be separated based on their phase difference. The number of processes that cause probe deflections is an advantage.

Optical Absorption

PDS can measure the absorption of light in the electrolyte and at the electrode surface. Because these two absorption processes occur at different locations, the AC PDS signal caused by each process has a different phase. This phase difference provides an inherent basis for separating the absorption of light at the electrode surface from the absorption in the electrolyte. Reflection-based spectroscopies cannot differentiate these two types of absorption.

Concentration Gradients

We and others have found the measurement of concentration gradients in the electrolyte to be a useful tool for discerning reaction mechanisms. The potentiostat at best only measures the mass transfer boundary condition at the electrode surface. The concentration gradient response to dynamic experiments has a distinct characteristic shape. Matching the experimental data with the experimental response easily allows mechanisms to be rejected or supported. The shape of the concentration gradient responses is far more unique than the current response to potential step experiments, which to most people would appear to be a simple spike followed by exponential decay. Given the successes in fitting theoretical reaction mechanisms to potential step experiments, matching theoretical models with experimental concentration gradients should be very successful. In a sense, the

concentration gradient experiment gives us two data points to which we must fit the model: the boundary condition (derived from the current), and one point in the electrolyte.

The concentration gradients have advantages of a less quantitative nature. The concentration gradient can provide answers to fundamental questions. An ideal example is the electrochemical oxidation and reduction of various thin films. During an oxidation current, either the anion is being transported into the film or the cation is being transported out of the film. The two processes are indiscernible to a potentiostat, yet they have a huge impact on the reaction mechanism. Simple observation of the direction of the beam deflection has answered this fundamental question for charging and discharging of thin films [30, 31, 36, 37].

Just the shape of the concentration gradient response can indicate a lot about reaction mechanisms. In every system we have studied, the concentration gradients did not behave as simply as anticipated. Even in an extremely ideal system, the ferri/ferrocyanide redox couple, the probe deflection shows an unexpected feature. The probe deflection is initially in one direction for a very short time followed by a large deflection in the opposite direction. This small feature required that the mass transfer model be updated. During the oxidation of platinum the probe beam deflection also increased initially and then began to decrease. This unexpected change led to the development of the mechanism discussed in Chapter 6. The unexpected behavior of the concentration gradients force us to discard simple mechanisms and lead to the development of new theories.

When chromophores are present in the electrolyte, the ability to measure absorption of light in the electrolyte can be used to selectively measure concentration gradients. The DC probe deflection measures a net effect of all species, but the AC signal caused by absorption of the excitation light is linked to the absorption spectrum of each species. If the species in the electrolyte have distinct absorption spectra, the AC signal will allow us to separate the contribution of each species to the concentration gradient. By choosing excitation wavelength, the concentration gradient of specific species can be "illuminated" to produce a thermal gradient proportional to the concentration gradient of only that species. This type of measurement is not generally applicable, but is very useful when possible [25].

Detection of Non-electrochemical Processes

It is incorrect to assume that only electrochemistry occurs in an electrochemical system. As we have seen, regular chemical reactions and processes can occur simultaneously with the electrochemistry. Without *in situ* techniques, non-electrochemical processes cannot be detected. As an example, during copper cyclic voltammetry, the concentration gradients detect the dissolution of a species from the electrode surface. The platinum oxidation reaction has been discussed much in the literature [93] but the mechanism we proposed in Chapter 6 is unique because it includes a non-electrochemical step. Because PDS can detect non-electrochemical processes undetectable to the potentiostat, a wider range of electrochemical systems can be studied.

System Strengths and Weaknesses

The PDS system is relatively simple. The components are commonly available and well established. The total cost of a PDS system is moderate; a whole PDS system could cost less than one large laser used in laser spectroscopies. The operation and assembly is also simple.

The technique is suited to electrochemical systems. The system places little restriction on the electrochemical cell and is probably the least intrusive compared to other techniques. The main shortfall of the technique is its inability to study dynamic processes in the millisecond and microsecond time domains.

Excitation Intensity

Our implementation of PDS does not use the high intensities used by laser based spectroscopies, *e.g.*, Raman spectroscopy and second harmonic generation. These techniques require excitation intensities of 10^2 to 10^6 W cm⁻². PDS uses low intensities of 10^{-2} W cm⁻² and less.¹ These low intensities are the result of using spectrally continuous broadband sources. New continuously tunable and semi-continuously tunable broadband lasers are becoming available in visible and infrared wavelengths. We might be tempted to use these sources for their higher intensities, but restricting ourselves to low intensity sources has advantages.

¹ This is a limit imposed by the intensity of spectrally continuous sources. We would gladly use higher intensities to increase the SNR.

Some electrochemical systems of interest are photochemically active. Copper corrosion is an example of a photoelectrochemically active system [61, 76]. Cuprous oxide, Cu_2O , and cupric oxide, CuO , are semiconductors. During our studies of copper, the area of the electrode under the excitation light was slightly discolored after several hours of experiments. It is evident that the excitation light is changing the chemistry we were trying to study.

Other systems will be sensitive to thermal effects. The temperature changes of the surface induced during PDS experiments are on the order of milliKelvins. The laser techniques will induce significantly larger temperature increases. While the biggest advantage of laser spectroscopies is the high intensity excitation light the laser provides, we must not allow the measurement process to change the system we are attempting to measure.

Design Considerations for Cells

PDS only requires that the electrode surface is planar. The surface can be rough, as long as the roughness does not approach the boundary layer thickness of the process under study. For concentration gradients, the boundary layers can be on the order of millimeters, allowing very rough electrode surfaces to be studied. The thermal diffusion length is much shorter, so measuring the absorption of light at the surface requires a smoother electrode. But, by using the secondary gradient technique, the surface absorption of even rough surfaces (relative to the thermal diffusion length) can be studied. Most electrode surfaces can be studied with PDS.

PDS only requires three windows to be incorporated into the design of the electrochemical cell. Because many electrochemical experiments are performed in glass, optical cuvettes can be used for most situations. For

more difficult situations, two windows must be transparent to the probe beam, and one window must be transparent to the excitation light. The windows may be difficult for design for high temperature cells, *e.g.*, molten sodium-sulfur cells. Although the window requirements may exclude some systems from being studied by PDS, other spectroscopies are similarly excluded.

The geometry of the cell should be such that heat and mass transport can be modelled as one-dimensional (except of course, if the goal is to study two dimensional concentration gradients). This restriction simplifies the analysis of the data and the development of models. This restriction also implies that the current distribution will be uniform, which is a good feature for an electrochemical cell anyway.

Speed

The speed at which PDS can measure the surface absorption signal is relatively slow. Useful modulation frequencies are below 200 Hz. Assuming this as a limit, events shorter than 5 ms cannot be detected. Assuming a more typical modulation frequency of 20 Hz and a lockin time constant of 300 ms, the practical time resolution is about 1 s. Other optical spectroscopies that do not rely on modulation are much faster. State of the art laser spectroscopies can achieve femtosecond time resolution — fast enough to measure molecular rotations. Compared to this state of the art benchmark, PDS is very slow. But PDS is not as slow relative to more the usual techniques. Reflection spectroscopies also use modulation techniques, although at higher frequencies. The cross plotting technique we have discussed allows PDS to effectively acquire surface spectra in a few seconds (although the entire process may take hours). We do not foresee any method

which could reduce the acquisition time into the millisecond or microsecond domain necessary to study detailed chemical kinetics. Therefore, PDS is confined to studying dynamic systems with characteristic times on the order of seconds.

The speed at which PDS can measure concentration gradients is only limited by the frequency response of the detector. The detector and amplifier we use have a 10 kHz frequency response. This is more than sufficient to measure most diffusion processes in electrolytes. If necessary, faster position detectors offer 1 MHz frequency response, *e.g.*, the pinhole detector.

Probe Alignment

The alignment of the probe beam with the sample remains a critical detail. The methods used only a few years ago were very crude. Despite this, the qualitative results are still valid. Only when we attempt to quantitatively compare the models with experiment does the alignment difficulty impede progress.

Two levels of alignment are desirable. The first level is reproducible alignment. This level does not require that one know the offset and angle of the probe beam. We only imply that when the electrochemical cell is removed and replaced, that the electrode surface should be repositioned to the same position with 10 μm and 5' angle. This is not a trivial mechanical problem, but is the minimum workable level of alignment. The second level of alignment is to be able to measure and set the position of the electrode surface within 10 μm and 5' of parallel.

Continued effort to meet this second level of alignment is required if PDS is to become a quantitative technique. In Chapter 4, we developed dry-lab based empirical relations that allow the probe beam offset to be determined from the frequency response of the AC PDS signal. These techniques reduce to simple analytical-based relations if the sample is very thin and mounted on a thermal insulator. This is a troublesome requirement for electrochemical systems. Bonding with epoxies or other adhesives of the thin electrode to another material often introduces unwanted impurities into the electrolyte. To avoid this, self-supporting electrodes should be used along with the empirical relations.

Modelling Requirements

The data from a PDS experiment is directly usable. A model is not required to interpret the data. Although some basic information can be learned directly from the data in most cases the best evidence will be formed from comparison of a model with the experimental data. Although the thermal and mass transport equations can be very similar, the models required by each are different.

Thermal Gradients

The thermal models are required to learn the behavior of the PDS signals in geometries which vary from ideal. Analytic solutions have been derived for many geometries. If systems are used which stay in within the established literature base, there is little need for a new model. The PDS signal for the absorption of light at the surface is extremely well behaved. Even when the excitation light is applied in a non-uniform manner, the PDS signal maintains one essential characteristic: the signal is directly

proportional to the absorption coefficient of the surface.² To measure the absorption spectrum of the surface, this is the only required characteristic. Modelling is required to measure the absolute value of the absorption coefficient, or determine other characteristics of the signal, e.g., how the signal varies with modulation frequency.

The thermal model we have used is not complex. One dimensional transient heat transfer is a well explored numerical problem. A useful model is easily developed which is capable of running on personal computers in acceptable time. The best plan is to design the experimental cell so that the one-dimensional model is accurate. If this design limitation is unacceptable, two and three dimensional models are not significantly more difficult.

Concentration Gradients

The refractive index gradient contains the summation of the effect of the concentration gradient of each species:

$$\frac{\partial n}{\partial x} = \sum_i \frac{\partial n}{\partial c_i} \cdot \frac{\partial c_i}{\partial x}$$

The measurement of concentration gradients is non-selective because there is no method to calculate the concentration gradient of each species from the single measurement of the refractive index. For electrolytes more complex than binary solutions, models become necessary. The model will calculate

² We assume in this statement that the electrode is opaque. Transparent, or semi-transparent samples are more complex to treat. Since very few electrodes are transparent, we have not considered them.

the concentration gradient of each species and thereby simulate the beam deflection. Comparison of the model simulation with the experimental data allows some hypotheses to be rejected and others to be supported. Models are also required when complex mechanisms are being hypothesized.

The theory used in concentration gradient models have evolved several times during our researches. The first models in the literature only considered the concentration gradient of the reactant, ignoring the effect of the product and supporting electrolyte. Later work has become more sophisticated. The transport of water is a difficult boundary condition, especially when water is consumed in monolayer quantities. Approximations when dealing with monolayer quantities of species will always be questionable. We have not seen mass transport problems before which require such precise theory. Given this, more complex models lurk on the horizon.

Because a relatively large effort will be required to build these models, we must consider what value the PDS experiment is. In our experiences, the PDS experiment has sufficient qualitative information to direct the search for mechanisms. The model developed in Chapter 6 for platinum oxidation, was not the result of a large amount of trial and error. The experimental results provided a direction to search for the mechanism.

The mass transport models require some data which might not be available or easily determined. Other than the mass transport data, the refractive index data must be acquired. For multicomponent systems this is a tedious but straight-forward process. But for some systems it may prove

impossible *e.g.*, how can we determine the concentrative refractivity of supersaturated zincate, or a medium-lived free radical?

B. Relation to Other Techniques

Among the vast number of spectroscopic techniques, we may wonder why we need another technique. The variety of techniques almost form a continuum, resulting in a huge number of acronyms. In this section PDS is compared with other photothermal techniques, variations on PDS, and competing techniques which try to obtain similar information. We only discuss a few of the nearest neighbors to give some picture of where PDS lies.

Other Photothermal Techniques

There are several techniques similar to PDS which measure the absorption of light at an interface. The difference is the method of detection. When light is absorbed, the temperature changes, thereby the refractive index changes, the gradient of the refractive index changes, and the curvature of the refractive index changes. Also, an acoustic wave is produced. A technique exists to measure each of these five different effects.

Photothermal spectroscopy (PTS) measures the temperature changes of the surface directly. A sensitive temperature sensor is bonded to the back of the sample. The modulated temperature signal replaces the probe beam deflections [13]. This technique is similar to the secondary gradient technique we have explored — both measure the heat conducted to the back of the electrode. The main advantage of PTS is that the type of noise encountered is electrical, not the difficult acoustic noise we have faced.

Photothermal interferometric spectroscopy (PI) measures the refractive index as opposed to the gradient of the refractive index. The probe beam is split into two beams; one passes near the sample, and the other through the bulk. As the refractive index changes near the sample, the phase of the two beams changes. Interference of the two beams is used to measure the absolute value of the refractive index at the probe beam near the sample. This technique offers the advantage of the sensitivity of interferometry. Because the thermal gradients are much smaller than the diameter of the probe beam, the phase of the probe beam does not change in a simple manner.

Thermal lensing spectroscopy (TLS) measures the curvature, *i.e.* the second derivative, of the refractive index. The curvature causes a probe beam to distort. To the author's knowledge this technique has only been applied to homogeneous phases. It is unlikely that the technique is sensitive enough to be applied to surfaces. The theoretical basis of TLS at surfaces has been explored in Reference 26 (in this reference, the source of the curvature is a concentration gradient, but the theory would be little different for a temperature gradient).

Photoacoustic spectroscopy (PAS) measures the acoustic wave caused by the heating of the surface. This technique has been used to study electrochemical systems [92]. In general, PDS is considered more sensitive than PAS for solid surfaces immersed in liquids.

Similar Forms

Measuring the refraction of light as it passes through refractive index gradients is not a new technique by any scale. The Schlieren effect has been

known since long. Shadowgrams and interferometry have used this effect. The availability of lasers and position detectors has changed the method only slightly. Now the difference is we are able to measure a small region with precision.

Probe beam deflection (PBD) is PDS where we only measure the concentration gradients, and no excitation light is used. PBD has been used in several forms. Some researchers have modulated the concentration gradients by applying a sinusoidal current to the electrode [28]. Lockin detection is used to process the signal. The goal of this method is to increase the sensitivity. In our opinion, this is an unnecessary complication. Concentration gradients can be measured for mono-layer reactions with only a x-y recorder. A small amount of signal averaging is a better method than modulation to increase sensitivity. Also, the modulation frequencies used are typically <1 Hz. The lockin time constant would have to be 5 to 10 s. The result is that fast events can not be monitored. Modulation of the concentration gradients decreases the time resolution to excessively long times. The effects that we observed during platinum oxidation occur over the first three seconds of the oxidation step. If we had employed a modulation technique, the effects would not have been observed. Also, modulation is not applicable to chemically irreversible systems.

Tamor, *et al.* have used a scanning PBD technique. Their system scans the probe beam through the concentration gradient, from the surface to the bulk electrolyte and thereby measures the gradient at all distances from the electrode surface. Integration of the gradient yields the concentration profile [44]. Similar to concentration modulation (this is spatial modulation),

this technique reduces the time resolution of the concentration gradient measurement.

Other Techniques

There are a few other competing *in situ* techniques of note. Most of them are surface techniques, but there is one technique of note for measuring concentration gradients. If electrolyte species are absorbing (chromophores) the techniques discussed by McCreery, *et al.* in References 80, 81, 82, and 104 are useful. A laser beam is collimated and passes parallel to the electrode through the concentration gradient. Absorption of light by the species forming the concentration gradient causes the intensity profile of the laser beam to be modified. A photodiode array measures the intensity profile of the laser beam. The spatial resolution of this technique is on the order of 10 μm , which is much higher than PDS or PBD. It also measures the whole concentration gradient simultaneously. This technique is limited to systems with absorbing electrolyte species. The other *in situ* techniques of interest are all surface techniques.

Secondary harmonic generation (SHG) is a promising addition to the *in situ* club [105, 106], which has monolayer sensitivity. Because modulation is not required, this technique is fast. The fundamentals have not been developed sufficiently to identify surface species. Raman spectroscopy is another promising technique. Unfortunately for electrochemists, Raman only has sufficient sensitivity to detect surface layers when the surface enhancement mechanism is operable (SERS), and this enhancement only occurs on a small set of metals (the most notable being silver). Most of the catalytically interesting metals, including platinum, cannot be studied.

While the non-linear spectroscopies became very popular with the increasing availability of lasers, the interest in conventional spectroscopies was reduced. But the failure of Raman to achieve monolayer sensitivity, and the development of Fourier transform spectrometers led to a renewed interest in simple reflection spectroscopies. *In situ* IR reflectance has been applied to electrochemical interfaces by Bewick and Pons, *et al.* [107 - 113] and many others [114 - 124].³ *In situ* reflectance spectroscopy has also been performed in the visible region [125 - 128], but more attention has been given to IR spectroscopy, which provides vibrational information. Because water is highly absorbing in the infrared, thin layers of electrolyte on the order of micrometers are required.

The main advent that allowed IR spectroscopies of surfaces in aqueous electrolytes, was the use of a thin layer electrochemical cell. PDS has the promise of being able to use the thin layer cell with two advantages. First, in PDS the excitation light only has to get to the electrode surface; it does not have to reflect and exit the cell. Because >90% of the excitation light is absorbed traveling through a few microns of water, less than 1% of the excitation light which is directed at the electrode will exit the cell. Second, PDS does not require an electrode polished to a mirror finish. Instead PDS will perform better as the electrode surface becomes more absorbing. Thereby more electrodes can be studied with PDS.

³ These IR spectroscopies are an example of acronyms gone mad: SNIFTIRS, EMIRS, EMFTIRS, NNIRS, etc.

The table below summarizes the techniques we have discussed. PDS has the necessary monolayer sensitivity to study electrochemical reactions. The types of surfaces which can be studied fills an important gap: PDS makes dark surfaces accessible to spectroscopy. Reflection techniques require highly reflective electrodes. The PDS signal increases as the electrode surface becomes more absorbing (the opposite of reflection based spectroscopies). Therefore, PDS can be applied to dark or diffusive surfaces, such as carbon, which are inaccessible with reflection based spectroscopies. The ability to simultaneously measure concentration gradients and the surface absorption is a benefit built into the PDS system. These two signals make PDS a more general technique for studying electrochemical systems.

technique	monolayer sensitivity	usable surfaces	identify species	speed	concentration gradients	cost
PDS	y	reflective & dark	y	slow	y	\$\$
PBD	y	n/a	n	fast	y	\$
PTS	?	dark	y	slow	n	\$\$
PAS	?	dark	y	fast	n	\$\$
PI	?		y	fast	y	\$\$
IR reflectance	y	reflective	y	slow	n	\$\$
Raman	y	very few	y	fast	n	\$\$\$
SHG	y	all	?	fast	n	\$\$\$

C. Future Research

Within the electrochemical community, PDS and PBD are applied by only a small number of researchers. As the technique is applied to new electrochemical systems the usefulness of the technique will be advanced.

Advancement of the spectral range into the mid-infrared will greatly increase the ability to identify surface species. This advancement requires increasing the SNR from its present state. The most direct route for improving the SNR of PDS and thereby increasing its speed and sensitivity is through reduction of noise. Promising techniques also exist by processing the signal in the frequency domain and through the use of transform sources.

There are many electrochemical systems waiting to be studied with PDS. PDS makes it possible to measure the surface spectrum of electrodes in more realistic states, *i.e.* dark surfaces and those which are not polished to a mirror finish. The ability to measure concentration gradients in 1 and 2 dimensions is an important tool. Much effort has been put into developing 2 dimensional ternary current distribution models (models that account for the primary current distribution, kinetics and mass transfer). PDS is an excellent tool for testing these models against experimental data.

With the broadband continuous sources we currently use, there is no simple technique to increase the signal. The main route to increasing SNR is to reduce the noise, most of which is acoustic in origin. Acoustic noise in this frequency domain is difficult to control, partly because the literature contains little information, but mostly because low frequency waves cannot be easily absorbed. Building designers have no interest in controlling noise which cannot be heard, and many researchers using PDS will be confronted with acoustic problems. A system for noise isolation is the main component of the PDS system which needs further development.

There are exciting possibilities for extension of PDS. In Chapter 4, we discussed a technique for automatically aligning the probe beam parallel to the electrode surface. The determination of the offset of the probe beam can

be automated by analyzing the signal in the frequency domain. The excitation light already contains the primary modulation frequency and all its odd harmonics. Therefore, comparison of the Fourier transform of the PDS signal and the transform of the excitation light, will yield the frequency response of the system (at odd harmonics of the modulation frequency). Chapter 4 demonstrated that the slope of the frequency response can be used to determine the probe offset. Thereby, the experiment is greatly simplified. No longer would the user have to vary the modulation frequency across a range of values and record the signal at each. With this method the computer take the Fourier transform of the PDS signal and compute the probe offset.

Another route for advancing the technique is the use of transform sources. The Fourier transform infrared spectrometer is a common instrument, but the Fourier source is not well suited to PDS. The excitation light from a Fourier source is mixed such that each wavelength is present at a different modulation frequency. Because the PDS signal varies strongly with frequency, the deconvolution of spectra obtained with a Fourier source becomes greatly complicated. Also the effective modulation frequencies in a Fourier source are too high, $>1\text{kHz}$, for PDS in liquids. There are two routes to avoid the problems of the Fourier source, while still gaining the advantages of transform sources. The first is step-scan Fourier sources. This technique modifies a standard FTIR source so that the scanning mirror advances by steps, instead of continuously scanning. An optical chopper modulates the excitation light resulting in the same modulation frequency for all wavelengths. This route would be very attractive except for the great cost required to modify the standard FTIR. The scanning mirror must be made to

accurately move in sub-micrometer steps. The most attractive route is an old transform technique: the Hadamard transform, which is a discrete transform. The excitation light is discretized into several ranges and each range is either on or off. This technique allows that each wavelength range is modulated at the same frequency and is easily implemented through mechanical means. The inversion of the Hadamard transform signal only involves one matrix inversion, thereby the processing of the signal can be performed very quickly. The cost of the Hadamard source should be comparable to that of the Fourier source, but the signal processing section should be far less expensive.

These developments can be seen to lead to a much improved system. The automatic alignment frees the user from the most difficult part of the experiment, allowing efforts to concentrate on the design of experiments and analysis of data. The transform source reduces the length of the experiments, some of which can take an hour. With some development effort, it is conceivable that PDS instruments can become a commercially available.

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Appendix I: Thermal Model Details

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The PDS model consists of three modules. The first solves for the temperature profile. Common implicit finite difference equations are used to solve the one-dimensional transient heat conduction equation. The second module solves for the deflection of the probe beam as it passes through the temperature gradient. Simple numerical integration is used to solve for the probe deflection. The equations are described in Chapter 1. The third module simulates the response of the lockin to the probe deflection signal and is described in the Appendix II.

A. Equations

Explicit finite difference equations were not suitable for this problem. Especially when the 'M' parameter ($M = (\Delta x)^2 / (\alpha \Delta t)$) assumed the common value 2, severe oscillations occurred in the calculated probe deflection in

addition to the desired AC deflections at the modulation frequency. The use of implicit techniques eliminated the oscillations.

The equation to be solved for one-dimensional transient heat transfer (with a generation term) is

$$\dot{q}'' + kT_{xx} = \rho c T_t \quad [I-1]$$

where $\dot{q}''$ is the heat input ($J s^{-1} m^{-3}$), k is the thermal conductivity ($W m^{-2} K^{-1}$), ρ is the density ($kg m^{-3}$), and c is the heat capacity ($J K^{-1} kg^{-1}$). T_{xx} is the second spatial derivative and T_t is the time derivative of temperature. In these models only the excess temperature is solved, defined by

$$T(x, t) \equiv T^E(x, t) - T_o \quad [I-2]$$

where T_o is the initial temperature of the system. When this relation is substituted into Equation I-1, the resulting differential equation is

$$\dot{q}'' + kT_{xx}^E = \rho c T_t^E \quad [I-3]$$

We see that the differential equation can be solved equivalently for temperature or excess temperature. The temperature changes are small, and only the gradient of temperature is required. A more-precise result is achieved if the model solves for excess temperatures, because round-off errors are avoided. In the remainder of this appendix when we refer to T we imply T^E .

Implicit Finite Difference Equations

The finite difference equations are well known (References A1 and A2 among many others, describe the method). At each node an equation is written that has the form:

$$A_s T_{r+1,s-1} + B_s T_{r+1,s} + C_s T_{r+1,s+1} = D_s \quad [I-4]$$

The T 's are the temperatures at the next time step, the A 's, B 's, and C 's are constants, and the D_i 's are dependent on the values of T at the current time step. The time index is r and the spatial index is s . The equations for all of the nodes form a tridiagonal matrix:

$$\begin{bmatrix} B_0 & C_0 & & & & \\ A_1 & B_1 & C_1 & & & \\ & \ddots & \ddots & \ddots & & \\ & & A_s & B_s & C_s & \\ & & & \ddots & \ddots & \ddots \\ & & & & A_{n-1} & B_{n-1} & C_{n-1} \\ & & & & & A_n & B_n \end{bmatrix} \begin{bmatrix} T_{r+1,0} \\ T_{r+1,1} \\ \vdots \\ T_{r+1,s} \\ \vdots \\ T_{r+1,n-1} \\ T_{r+1,n} \end{bmatrix} = \begin{bmatrix} D_0 \\ D_1 \\ \vdots \\ D_s \\ \vdots \\ D_{n-1} \\ D_n \end{bmatrix} \quad [I-5]$$

which is easily solved for the values of T at the next time step. The fast algorithm to invert the tridiagonal matrix is described in Reference A1.

Figure I-1. An equation is written at each node that uses 6 adjacent nodes.

Six nodes are involved in each equation. The pattern shown in Figure I-1 is the Crank-Nicolson method. One node on each side, at $s+1$ and $s-1$, of the center node is

used to evaluate the spatial derivative at both the current time index and the next time index. The average of the two spatial derivatives is used to approximate T_{xx} . Because the thermal gradient decays quickly, a variable spatial mesh was used. A modified form of the Crank-Nicolson equations for a variable mesh was derived.

The entire region solved by the model was treated as a single medium with variable properties. There are three classes of equations used. The

interior nodes are the primary, sample, and secondary phases. The physical properties are constant for the interior nodes. There are two interfacial nodes and two boundary nodes. The constants for Equation I-4 (A , B , C , and D) are derived for each class of node.

Interior Nodes

The interior nodes are derived by substituting the following approximations into Equation I-1.

$$\begin{aligned}
 T_t &\cong \frac{1}{\Delta t} [T_{r,s} - T_{r,s}] \\
 T_{xx} &\cong \frac{1}{2} [T_{xx}|_{r+1,s} + T_{xx}|_{r,s}] \text{ where} \\
 T_{xx}|_{r,s} &\cong \frac{1}{\Delta \bar{x}_s} \left[\frac{T_{r,s+1} - T_{r,s}}{\Delta x_{s+1}} - \frac{T_{r,s} - T_{r,s-1}}{\Delta x_s} \right] \\
 T_{xx}|_{r+1,s} &\cong \frac{1}{\Delta \bar{x}_s} \left[\frac{T_{r+1,s+1} - T_{r+1,s}}{\Delta x_{s+1}} - \frac{T_{r+1,s} - T_{r+1,s-1}}{\Delta x_s} \right] \\
 \text{where } \Delta \bar{x}_s &\cong 1/2 (\Delta x_{s+1} + \Delta x_s)
 \end{aligned} \tag{I-6}$$

These approximations state that the time derivative is a forward difference, and that the spatial derivative is the average of the derivative at the current time step and the next time step (the Crank-Nicolson approximation).

Equations I-6 are substituted into Equation I-1, and the result is rearranged to combine like T 's, and yield the coefficients for Equation I-4:

$$\begin{aligned}
 A_i &= \frac{-\alpha \Delta t}{2\Delta x_i \Delta \bar{x}_i} & C_i &= \frac{-\alpha \Delta t}{2\Delta x_{i+1} \Delta \bar{x}_i} \\
 B_i &= 1 + \frac{\alpha \Delta t}{2\Delta \bar{x}_i} \left(\frac{1}{\Delta x_i} + \frac{1}{\Delta x_{i+1}} \right) \\
 D_i &= \frac{q_{r,i} \Delta t}{c\rho} + \left(\frac{\alpha \Delta t}{2\Delta x_i \Delta \bar{x}_i} \right) T_{r,i-1} \\
 &+ \left[1 - \frac{\alpha \Delta t}{2\Delta \bar{x}_i} \left(\frac{1}{\Delta x_i} + \frac{1}{\Delta x_{i+1}} \right) \right] T_{r,i} + \left(\frac{\alpha \Delta t}{2\Delta x_{i+1} \Delta \bar{x}_i} \right) T_{r,i+1}
 \end{aligned} \tag{I-7}$$

The thermal properties have been combined into the thermal diffusivity, $\alpha = k/\rho c$. To save computation time, D_i can be simplified to

$$D_i = -A_i T_{r,i-1} - (2 - B_i) T_{r,i} - C_i T_{r,i+1} \tag{I-8}$$

Since A , B , and C , are constants, they need only be calculated once at the beginning of the program.

Interface Nodes

The interfacial nodes were developed as a combination of half of each adjacent node. Figure I-2 shows the primary/sample interface. The thermal conductivity on each side of the node is different. The heat flux passing through each side of the interfacial node is evaluated with the corresponding thermal conductivity. The approximations substituted into Equation I-1 are:

Figure I-2. The interfacial node consists of half of each adjacent phase.

$$\begin{aligned}
T_i &\equiv \frac{1}{\Delta t} [T_{r+1,s} - T_{r,s}] \\
kT_m &= \frac{1}{2} [T_m|_{r+1,s} + T_m|_{r,s}] \text{ where} \\
T_m|_{r,s} &\equiv \frac{1}{\Delta \bar{x}_s} \left[k_{s+1} \frac{T_{r,s+1} - T_{r,s}}{\Delta x_{s+1}} - k_s \frac{T_{r,s} - T_{r,s-1}}{\Delta x_s} \right] \\
T_m|_{r+1,s} &\equiv \frac{1}{\Delta \bar{x}_s} \left[k_{s+1} \frac{T_{r+1,s+1} - T_{r+1,s}}{\Delta x_{s+1}} - k_s \frac{T_{r+1,s} - T_{r+1,s-1}}{\Delta x_s} \right] \\
\text{where } \Delta \bar{x}_s &\equiv 1/2 (\Delta x_{s+1} + \Delta x_s)
\end{aligned} \tag{I-9}$$

The equations are rearranged to combine like T 's resulting in the coefficients for Equation I-4:

$$\begin{aligned}
A_s &= \frac{-k_s \Delta t}{2c_s \rho_s \Delta x_s \Delta \bar{x}_s} & C_s &= \frac{-k_{s+1} \Delta t}{2c_s \rho_s \Delta x_{s+1} \Delta \bar{x}_s} \\
B_s &= 1 + \frac{k_s \Delta t}{2c_s \rho_s \Delta x_s \Delta \bar{x}_s} + \frac{k_{s+1} \Delta t}{2c_s \rho_s \Delta x_{s+1} \Delta \bar{x}_s} \\
D_s &= \frac{\dot{q}_{r,s}''' \Delta t}{c_s \rho_s} + \left(\frac{k_s \Delta t}{2c_s \rho_s \Delta x_s \Delta \bar{x}_s} \right) T_{r,s-1} \\
&+ \left[1 - \frac{k_s \Delta t}{2c_s \rho_s \Delta x_s \Delta \bar{x}_s} - \frac{k_{s+1} \Delta t}{2c_s \rho_s \Delta x_{s+1} \Delta \bar{x}_s} \right] T_{r,s} + \left(\frac{k_{s+1} \Delta t}{2c_s \rho_s \Delta x_{s+1} \Delta \bar{x}_s} \right) T_{r,s+1}
\end{aligned} \tag{I-10}$$

This equation can also be simplified with the use of Equation I-8. The heat capacity and density in the above equation are those of the interface. The interface consists of half a node of each phase and the film (if present). The heat capacity used is an average

$$c_s \rho_s = \frac{\Delta x_{s+1} c_\alpha \rho_\alpha + L_{film} c_{film} \rho_{film} + \Delta x_s c_\beta \rho_\beta}{\Delta x_{s+1} + \Delta x_s} \tag{I-11}$$

where α and β are the phases on each side of the interface. The film is assumed to be thermally thin. The film thickness serves only to add heat capacity to the interface by Equation I-11. The thickness of the film is

otherwise considered to be zero by the model. If the film is removed from Equation I-11, the result corresponds to that for secondary/sample interface.

Boundary Nodes

The boundaries are assumed to be isothermal. The excess temperature of the boundaries is zero, i.e., $T_0 = T_n = 0$. The equations at the left and right boundary reduce to

$$\begin{aligned} B_1 T_1 + C_1 T_2 &= D_1, \text{ and} \\ A_n T_{n-2} + B_{n-1} T_{n-1} &= D_{n-1} \end{aligned} \quad \text{[I-12]}$$

The constants, A , B , C , and D , are determined from the interior node equations. The array need only be solved from node 1 to node $n-1$, because nodes 0 and n are fixed.

Heat Input

The heat input term is a volume-specific power, whereas the excitation intensity is an area-specific power. The heat terms are converted with

$$\dot{q}_{r,s}''' = \frac{I_{r,s}}{\Delta \bar{x}_r} \quad \text{[I-13]}$$

This relation applies at the interior nodes and the interfacial node. Square wave modulation of the excitation light is typically used, therefore the excitation intensity is simply turned on and off during the model run. Other modulation types were explored. In this case the intensity of the excitation is varied continuously between off and on.

The Beer-Lambert Law is used to simulate absorption of the excitation light in the electrolyte:

$$\frac{dI}{I} = -\beta dx \quad [I-14]$$

The discretized form of this equation is

$$I_{j+1} = \exp[\ln I_j - \beta(x_{j+1} - x_j)] \quad [I-15]$$

Figure I-3. The intensity of the excitation light is calculated between each spatial node on both the forward and reverse direction.

The intensity of the light is calculated at the half nodes (see Figure I-3). Equation I-15 is used to model the variation of the excitation intensity as it propagates through the electrolyte. When the excitation light reaches the sample surface, a specified fraction is absorbed. Modules were developed which both reflect the

excitation light at the sample surface and scatter it. If the excitation light is reflected, Equation I-15 is used to calculate the decreasing intensity as the excitation light exits the cell. If the excitation light is scattered, the exiting excitation light is ignored.

The excitation light absorbed at each node for use in Equation I-13 is calculated by taking the difference between the intensity of the excitation at the entrance and exit of the node.

$$I_r = (I_{r-1/2} - I_{r+1/2})_{\text{FORWARD}} + (I_{r+1/2} - I_{r-1/2})_{\text{REVERSE}} \quad [I-16]$$

B. Discussion

The model calculates the temperature at a series of time steps. At each time step, the probe deflection is calculated and this value is passed to

the lockin module for processing. The model readily converges using the values in Table I-1.

Table I-1. Typical model parameters

nodes per cycle	200
node spacing in sample phase	2.5 μm
node spacing in primary & secondary phase	1 μm near the sample 4 μm elsewhere
length of primary & secondary phase modelled	1000 μm
nodes along path of probe beam	25
for infinitely thin ray	
nodes across diameter of probe beam	50
for finite beam	

We also checked the model by calculating an energy balance at each time step. The amount of excitation light absorbed by the system is known. From the temperature profile, we calculate the amount of heat absorbed in the system. These numbers always compared very well, typically with a difference of less than 0.1%.

The nodes in the primary and secondary phases are not spaced evenly. Half the spatial nodes are distributed in 20% of the length of the primary and secondary phases, and half are distributed in 80% of the length of the primary and secondary phase. The more closely spaced nodes are near the interfaces. This scheme does not make full use of the variable spacing form of the Crank-Nicolson equations (Equations I-6 and I-7). Only one interior node will have a different spacing on the left and right sides. Because the constants, A , B , C , and D , are evaluated only once at the beginning of the program, there is no computational penalty to using the more-complex equations. A continuously-variable spacing would make better use of these equations. Because the probe beam module interpolates within the

temperature node pattern, there is no restriction on the distribution of the nodes.

The implementation of the model is in Appendix III. The program has a data input module which allows parametric studies to be performed easily. Instead of a typical fixed-format input file, a free-format command file is used. This file consists of a list of commands, e.g., RunName = x1a, Ksecondary = 1.234, NodesCycle = 200, and Solve. The program reads assignment statements until reaching a 'Solve' command. The model is run and results are logged to a data file. The program then returns to read additional lines from the command file. One parameter and the name of the run is changed and another Solve is requested. A sample input file is included that demonstrates this procedure. Some of the figures in this thesis were the results of a batch of 40 runs. Using this free format input method made these large batch runs very easy to execute and error-free. Others should feel free to use this code.

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- A1. Lapidus, L., and Pinder, G.F., *Numerical Solution of Partial Differential Equations in Science and Engineering*, John Wiley, New York, p34, 1982.
- A2. Chapra, S.C., and Canale, R.P., *Numerical Methods for Engineers*, 2nd ed., McGraw-Hill, New York, p533, 1988.

Appendix II:

Numerical Simulation of a Lockin Amplifier

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The thermal model simulates the signal that the PDS system produces. Because this signal was further processed by a lockin amplifier in the real apparatus, the results of the thermal model were not directly comparable to experimental data. To compare the model with experiment, it was necessary to develop a numerical model of the lockin amplifier which could be linked to the thermal model. This appendix considers the lockin from a functional viewpoint. Details of the electronics are not discussed. Further information on lockin amplifiers can be found in References A1, A2 and A3; some lockin manuals also contain good descriptions of the instrument.

To model the lockin required a detailed understanding of its inner workings. Although many scientists and engineers may use this instrument, the "insides" likely remain a mystery. A simple functional description of the lockin follows, which makes the model understandable. The action of the lockin can be considered in either the time domain, or in the frequency domain by using Fourier transforms. We have used both methods each of which has benefits.

A. Real Lockin Amplifier

The lockin is often described as an AC voltmeter. But it does more, because it measures only the component of a complex signal at a specified frequency. The specified frequency is dictated by a separate external reference signal. In our case the external reference signal is generated by a photodiode which senses the excitation light. The type of lockin we will model is a two-phase lockin. This type of instrument determines not only the magnitude of the signal, but also the phase of the signal.

Theoretical Description

As a base case we consider a periodic signal that is free from noise. The signal has the form $S = A \sin(\omega t + \phi)$. The lockin also makes use of an external reference signal at the same frequency, $R = B \sin(\omega t)$. The phase term is dropped because the reference signal defines the zero for phase. The operation of the lockin is represented

Figure II-1. Vector representation of the operation of the lockin in polar coordinates. R is the reference signal, R_A and R_B are the orthogonal internal references, and S is the signal.

by the vector diagram in Figure II-1. From the reference signal, the lockin synthesizes two orthogonal unit references, $\hat{R}_A$ and $\hat{R}_B$ (this is the origin of the name "two-phase"). These references are rotated from the external reference, $\bar{R}$, by an offset set by the user (θ in the figure). The lockin takes the cross product of the signal, $\bar{S}$, with each reference. These two values are the two outputs of the lockin, O_A and O_B . The magnitude of the signal is calculated by the lockin, $|\bar{S}| = \sqrt{O_A^2 + O_B^2}$, and the phase is calculated, $\phi = \theta + \arctan[O_A/O_B]$.

Functional Description

The block diagram of a two-phase lockin in Figure II-2 shows the components which are necessary for the model. The reference section generates two bipolar reference signals which are 90° out of phase from one another. If the lockin uses a square-wave correlation mode, the internal reference signals are bipolar square waves. If the lockin uses sine-wave correlation mode, the internal signals are synthesized sine waves. The internal references have the same frequency as the external reference input. The phase of $\hat{R}_A$ is rotated from the phase of $\bar{R}$ by an offset, θ , which is set by the user. The reference $\hat{R}_B$ is always orthogonal to $\hat{R}_A$. Demodulators simply multiply the signal by one of the internal references. The output of the demodulator is filtered with a low-pass filter, typically a RC filter. These five components can completely model a lockin. The reference section and demodulators are easily simulated. The filters require the majority of the code and computation time. Most of the next section discusses the numerical filters we used.

Figure II-2. The major components of a two-phase lockin: one section to synthesize the internal references, two demodulators, and two filters.

Definition of Phase

The definition of the phase turns out to be tricky. The phase is a time difference between the reference and signal expressed as an angle. The question is: between which points on the two signals do we measure the time difference? Figure II-3 shows a reference and four hypothetical signals.

Table II-1 gives the phase for each of the signals in the figure. This table shows that the lockin calculates the **phase** based on the point where the two signals cross their respective midpoints with a positive slope. The lockin considers all signals to be bipolar, *i.e.* varying between positive and negative. For PDS the signals are monopolar. The excitation light is positive or zero; negative excitation light does not exist. We are interested in the time difference between the moment the excitation light is turned on and the time

the deflection begins to increase; this is called the **delay**. Inspection of the table leads to the relation between the lockin phase and PDS delay

$$\text{delay} = 270^\circ - \text{phase} . \quad [\text{II-1}]$$

Negative values of phase or delay can be shifted by 360° .

Figure II-3. The diagram shows the reference (R) and four signals (A-D) at four different phases.

Table II-1 . The phase of the signal relates to the zero crossing, while the delay is measured from the minimum.

signal	phase	delay
A	0°	270°
B	90°	180°
C	180°	90°
D	270°	0°
	271°	$359^\circ (-1^\circ)$
	315°	$315^\circ (-45^\circ)$
	359°	$271^\circ (-89^\circ)$

B. Time-Domain Numerical Lockin Amplifier

The development of the numerical lockin has several options. Here we discuss aspects which relate to computational efficiency and accuracy of the model. The reference signal is provided by the thermal model, and the demodulators are simple multiplication. For square-wave correlation, the signal is multiplied by a bipolar square wave. For sine-wave correlation, the signal is multiplied by a sine wave. The filtering of the demodulated signals is the most complex operation and is discussed below.

The majority of the lockin calculation is involved in the simulation of the filters. Three filters are discussed below. The obvious starting place is the RC filter which is what is inside a real lockin. This first RC filter was a large computational load on the entire model. A fast algorithm was developed, which is also more precise than the simple RC filter. We also describe an average filter, which responds more quickly than the RC filter.

Filters

RC Filter

An RC filter can be numerically represented by the convolution integral [A1]:

$$O(t) = \int_{\zeta=0}^{\infty} \exp\left[-\frac{\zeta}{t_c}\right] S(t-\zeta) d\zeta \quad [\text{II-2}]$$

where $O(t)$ and $S(t)$ are the output and the input to the filter and t_c is the time constant of the filter. To avoid saving the signal for all previous time, the integral must be truncated to a shorter time. Five time constants yields

sufficient precision for our purposes. Even so, the RC filter represents almost all of the computer time involved in the simulation of the lockin.

Fast RC Filter

An algorithm for the RC filter can be derived which makes use of the calculation at the previous time to greatly reduce the amount of calculation. Consider the filter output at a time, Δt , later than that of Equation II-2

$$O(t + \Delta t) = \int_{\zeta=0}^{\infty} \exp\left[\frac{-\zeta}{t_c}\right] S(t + \Delta t - \zeta) d\zeta . \quad [\text{II-3}]$$

Substitution of $\xi + \Delta t = \zeta$ into Equation II-3 yields

$$O(t + \Delta t) = \int_{\xi=0-\Delta t}^{\infty-\Delta t} \exp\left[\frac{-\Delta t}{t_c}\right] \exp\left[\frac{-\xi}{t_c}\right] S(t - \xi) d\xi . \quad [\text{II-4}]$$

The first exponential is a constant and can be removed from the integral.

The remaining integrand is similar to that in Equation II-2. The limits of integration are different. This integral can be separated into three parts

$$O(t + \Delta t) = \exp\left[\frac{-\Delta t}{t_c}\right] \left\{ \int_{\xi=0-\Delta t}^0 \exp\left[\frac{-\xi}{t_c}\right] S(t - \xi) d\xi + \int_{\xi=0}^{\infty} \exp\left[\frac{-\xi}{t_c}\right] S(t - \xi) d\xi - \int_{\xi=-\Delta t}^{\infty} \exp\left[\frac{-\xi}{t_c}\right] S(t - \xi) d\xi \right\} \quad [\text{II-5}]$$

In Equation II-5 the middle integral is the value at the previous time, $O(t)$ (see Equation II-2). This part is removed. The exponential is returned into the integrands of the two remaining integrals and the dummy variable is returned to its previous value, resulting in

$$\begin{aligned}
 O(t + \Delta t) = \exp\left[\frac{-\Delta t}{t_c}\right] O(t) + \int_{\zeta=0}^{\Delta t} \exp\left[\frac{-\zeta}{t_c}\right] S(t - \zeta) d\zeta \\
 - \int_{\zeta=-\Delta t}^{\bar{\zeta}} \exp\left[\frac{-\zeta}{t_c}\right] S(t - \zeta) d\zeta
 \end{aligned}
 \quad [\text{II-6}]$$

The last integral in this equation can be neglected since $\exp[-\infty]$ approaches zero.

The computational savings becomes evident when we look at the discretized form of Equation II-6. Since Δt is one time step, the integral is very simple. Using trapezoidal integration

$$O_{i+1} = O_i \exp\left[\frac{-\Delta t}{t_c}\right] + \frac{\Delta t}{2} \left[O_{i+1} + O_i \exp\left(\frac{-\Delta t}{t_c}\right) \right]
 \quad [\text{II-7}]$$

where O_{i+1} is the output at the current time step and O_i is the output at the previous time step. This simple formula represents a huge reduction in computation time from Equation II-2 with improved precision. It is more precise because the integration is not truncated at five time constants; in effect, the integral is not truncated at all.

Stable-Average Filter

Any filter can be used after the demodulators. One alternative to the RC filter is to use a simple average. To avoid having to save every previous value comprising the average, we use an algorithm which allows each successive value to be incorporated into the average without knowledge of the previous values. Each sample will be y_i and the average after consideration of the i -th sample will be $\bar{y}_i$. The algorithm is simply derived by inspection

$$\begin{aligned}
 \bar{y}_1 &= y_1 \\
 \bar{y}_2 &= \frac{1}{2}(y_2 + y_1) = \frac{1}{2}y_2 + \frac{1}{2}\bar{y}_1 \\
 \bar{y}_3 &= \frac{1}{3}(y_3 + y_2 + y_1) = \frac{1}{3}(y_3 + 2\bar{y}_2) \\
 \bar{y}_4 &= \frac{1}{4}(y_4 + y_3 + y_2 + y_1) = \frac{1}{4}(y_4 + 3\bar{y}_3) \\
 \bar{y}_n &= \frac{1}{n}[y_n + (n-1)\bar{y}_{n-1}]
 \end{aligned}
 \tag{II-8}$$

This algorithm is often called a stable average, because at every step of its calculation, the average is correct.

The stable average is well suited to steady signals. Figure II-4 demonstrates the response of the average filter and the RC filter to a simple signal, $S(t) = \sin^2(\omega t)$. The stable average achieves the same value as the RC filter, except much sooner. Because our signal reaches steady state quickly and we are only interested in the steady state reading of the lockin, computer time can be saved by reducing the simulation time.

Figure II-4. Comparison of the response of the RC filter and stable average filter to a 5 Hz sine squared signal.

Demonstrations

Figures II-5 and II-6 demonstrate the numerical lockin. The figures show the internal signals from input to output. The input signal is shown in the center of each figure as a unit-amplitude pure sine wave. The internal unit reference signals for the in-phase channel (A) and out-phase channel (B) are shown above and below the signal. The top and bottom pane show the output of the demodulators (solid lines) and the filtered output (dashed lines).

It is difficult to see in Figure II-5, but the lockin does not inherently measure root mean squared voltage. The output of the in-phase demodulator is the solid line in the top pane of Figure II-5. This signal is the absolute value of a sine wave. The average of the absolute value of a sine wave is:

$$\text{average} = 0.6366 = \frac{2}{\pi} = \frac{\int_0^{\pi} \sin t \, dt}{\pi} \quad [\text{II-9}]$$

The dotted line in the top pane of Figure II-5 shows that the output of the RC filter approaches this value. The above factor can be used to convert the value measured by the numerical lockin, O , to rms amplitude, A_{rms} , peak-to-peak amplitude, $A_{\text{p-p}}$, or regular amplitude, A .

$$\begin{aligned} A_{\text{rms}} &= \frac{\pi\sqrt{2}}{4} O \\ A_{\text{p-p}} &= \pi O \\ A &= \frac{\pi}{2} O \end{aligned} \quad [\text{II-10}]$$

Figure II-5. This figure shows the signals in the lockin. The central graph is the signal, in this case a pure sine wave. The top and bottom are the demodulator outputs before and after filtering. The demodulator output is the solid line, and the filtered result is the dashed line.

Figure II-6. Same as Figure II-5 except the signal is at 30 degrees.

Sensitivity to DC

Theoretically, the lockin should not be sensitive to DC, *i.e.*, a constant-value input signal should produce zero on the output channels. The time-domain numerical model was found to be slightly sensitive to DC. When a constant value is input to the demodulators (see Figure II-2 on page 233) it is multiplied by a bipolar square wave. The output of the demodulator will be a bipolar square wave that has an amplitude equal to that of the constant input value. Each filtered output will have an average value of zero. However, the RC filters do not completely eliminate the AC signal at their input; it is only strongly attenuated. A small ripple will remain on the outputs of the in-phase and out-phase channels. When the magnitude is calculated by $|\bar{S}| = \sqrt{O_A^2 + O_B^2}$, the result will not be zero. The phase difference between the two outputs allows a small value to be calculated by the magnitude output. In some tests, the magnitude was found to give a reading of about 1/1000 of the constant input value. This value can be reduced by increasing the time constants of the RC filters.

The real lockin is not sensitive to the DC level at the signal input. AC coupling eliminates the DC baseline before the input signal is fed to the demodulators. We considered improving the time-domain lockin with simulated AC coupling. Instead we developed a frequency-domain lockin. The frequency-domain lockin is more accurate when very small AC signals are imposed on DC baselines.

C. Frequency-Domain Numerical Lockin Amplifier

The time-domain model requires that the thermal model simulate long times. In experimental practice time constants of 1 or 3 s are used. The thermal model would have to run for 4 or 5 time constants for the output of the lockin to stabilize. This is an excessive amount of time to model because the deflection signal approaches a steady state after only a few cycles.

A frequency-domain model requires only 1 cycle of the model to operate. The discrete Fourier transform assumes that the signal being analyzed is repeated for all previous and future times, *i.e.*, the signal is assumed to be at steady state. Thereby the thermal model only has to simulate the few cycles required to approach steady state.

One form of the discrete Fourier transform is [A4]

$$b_s = \frac{1}{\sqrt{n}} \sum_{r=0}^n a_r \exp\left[\frac{2\pi i r s}{n}\right] \quad [\text{II-11}]$$

Here, a_r is the real discrete waveform to be transformed, n is the number of points, and b_s is the complex transform. The magnitude and phase of any frequency component are $2\text{Abs}[b_s]/\sqrt{n}$ and $\text{Arg}[b_s]$. If the temporal spacing of the points a_r is Δt , the frequency spacing of the points b_s is $1/(n \Delta t)$. If a whole number of cycles, N , are evaluated by the transform, the index s that corresponds to the modulation frequency is equal to N .

Sensitivity to Sloping Baselines

The only method for heat to exit the model is at the isothermal boundaries. Because the boundaries are thermally far from the surface, the

model would have to be run for a long time before reaching steady state. To avoid the computation time required to reach steady state, we have used a filter on the lockin to extract the sloping baseline from the AC deflections. This allows an accurate prediction of the steady state value early in the calculations.

A frequency-domain lockin model was constructed using the above equation. Although it allowed short modelling times, it was sensitive to sloping baselines. Problems arise when the signal is not on a flat baseline. Consider the hypothetical PDS signal and its Fourier transform in Figure II-7. The signal is a pure sine wave added to a sloping line.

Figure II-7. A pure sine wave added to a sloping baseline is shown in the left pane. The amplitude of the Fourier transform of this hypothetical signal is shown in the right pane. The phase vs. frequency is not shown, but is similar.

The Fourier spectrum shows a peak at the modulation frequency, but it is superimposed on a background due to the sloping baseline in the signal. If we take the height of this peak as a measure of the amplitude of the AC signal a significant error will result. Most of the value which would be indicated is actually due to the sloping baseline.

When the signal becomes small, reducing the baseline sensitivity becomes necessary. To subtract the baseline, two points on each side of the peak in Figure II-7B were used to interpolate the background value under the peak. A 4-point Lagrange interpolating polynomial was used [A5]:

$$f_4(x) = f(x_0) \frac{(x-x_1)(x-x_2)(x-x_3)}{(x_0-x_1)(x_0-x_2)(x_0-x_3)} + f(x_1) \frac{(x-x_0)(x-x_2)(x-x_3)}{(x_1-x_0)(x_1-x_2)(x_1-x_3)} \\ + f(x_2) \frac{(x-x_0)(x-x_1)(x-x_3)}{(x_2-x_0)(x_2-x_1)(x_2-x_3)} + f(x_3) \frac{(x-x_0)(x-x_1)(x-x_2)}{(x_3-x_0)(x_3-x_1)(x_3-x_2)} \quad \text{[II-12]}$$

to calculate the baseline signal for both the magnitude and phase, (B, β) . The baseline signal is a sine wave that can be subtracted from the peak in Figure II-7B with the trigonometric identity to add two sine or cosine waves of the same frequency¹ (we subtract by adding the baseline with a negative magnitude).

¹ This useful relation could not be found in any reference. It was derived by the author using the complex forms of sine and cosine.

$$C \cos[\omega t + \gamma] = A \cos[\omega t + \alpha] + B \cos[\omega t + \beta], \text{ or}$$

$$C \sin[\omega t + \gamma] = A \sin[\omega t + \alpha] + B \sin[\omega t + \beta]$$

$$\gamma = \arctan \left[\frac{A \sin \alpha + B \sin \beta}{A \cos \alpha + B \cos \beta} \right] \quad [\text{II-13}]$$

$$C^2 = A^2 + B^2 + 2AB \cos(\alpha - \beta)$$

The accuracy of this method was tested by generating small sinusoidal signals superimposed on a linear background and feeding them to the numerical lockin. Since the true magnitude of the signal is known, the error can be calculated. Figure II-8 shows the error for the lockin with and without the filter. The lockin with the filter is more accurate by an order of magnitude than the simple Fourier lockin. The lockin with the filter was used for all the results presented in this thesis.

Figure II-8. The error in the calculated signal magnitude and phase is plotted versus the true magnitude. The test signal is superimposed on a sloping background. The filter increases the accuracy by an order of magnitude. The dips in the curves represent where the error changes from positive to negative.

Conclusion

Each model discussed has unique characteristics. Only the time-domain model with RC filters is able to simulate transient behavior. Its response is closest to the response of the real lockin. A RC filter does not stabilize until 4 to 5 time constants have elapsed. To model a 20 Hz modulation frequency with a 1 s time constant would require running the simulation for 80 to 100 cycles. Because the PDS signal approaches steady state after only a few cycles, using the RC filters imposes a large computational penalty.

The stable average filter responds much more quickly to steady signals. If we only seek a steady state reading, the stable average filter is better than the RC filter. The frequency-domain lockin is the best of all for steady signals. We have used fore-knowledge of the signal characteristics to design a specific filter. The filter allows us to measure very small signals imposed on large, sloping baselines. For all the results presented in this thesis, we have used the frequency-domain lockin with the baseline filter. Because we have been mostly interested in steady state experiments it is considered superior to the RC filter time-domain lockin.

The code for the time-domain lockin using the stable average and the frequency-domain lockin using the baseline filter are provided in Appendix III.

References

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Appendix III:

Code

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The main program is contained in the first section. This module reads the data file and provides the parameters for the model. The remaining modules all attach to the main module. All programs were written in QuickBasic v4.5. The code is available from the author.

The diagram below is a map to aid anyone who may attempt to use this code. Each module (file) is indicated by a box. The functions and subroutines contained by each module are shown in the boxes. The arrows indicate which routines access others. The arrows indicate from the originator of the call to the routine which services the call.

Notes on the Format of the Listings

There are no continuation marks in QuickBasic for lines longer than 80 characters as there are in Fortran. Long lines are maintained inside the IDE as one line up to 255 characters in length. In these listings, long lines are wrapped. You can tell which lines are wrapped by noting the lines which begin in the first column. All code lines are indented, so the continued lines will stand out because they will begin in the first column. The subroutines and functions in each module are printed in alphabetical order. Often the main subroutine is not the first one listed.

A. Base Modules

A.1. PDS Base

PDS model - Main module

written by James David Rudnicki
original version March 1991
last update November 1991
contained in the file PDS.BAS
written in QuickBasic v4.5

Description:

This program models Photothermal Deflection Spectroscopy.
The code is divided into 4 modules. This module
acquires the parameters from the data file. The remaining modules:
i) solve the temperature profile and produce a refractive
index profile
ii) solve the refraction of the probe beam by the above refractive
index profile
iii) solve the lockin amplifier response to the probe beam deflection

There are several options for each of the above. By linking this
Main Module with one of each of the above, a complete program is
produced. There are many possible combinations. Each module is
described below.

The modules attached to this code can be one of each:

i) temperature modules -

PDS51 - thermally thick sample
PDS61 - thermally thin film on thermally thick substrate
Both the above allow the primary phase to be optically
absorbing. Each calculates the probe deflection in the
primary and secondary phase (unless the OnlyPrimary
switch is used.)

modulation modules -

MOD1 - regular square
MOD2
MOD3 - half-wave rectified sine
MOD4

heat modules -

HEAT1 -
HEAT2 -

' ii) probe deflection - calculates probe beam deflection by various means
' (not available) PROBE0 - infinitely thin probe (parallel)

' PROBE1 - infinitely thin probe

' PROBE2 - finite probe thickness (parallel)

' PROBE2A -

' PROBE2AX -

' (not available) PROBE3 - finite probe - nonparallel

' iii) lockin module - simulates a lockin amp

' LOCKIN4 - lockin with RC filters

' LOCKIN5 - lockin with averaging outputs

' LOCKIN6 - frequency domain lockin

' LOCKIN7 - frequency domain lockin w/ filter

' The program must be loaded with the QuickLibrary TRIMAT or
' include the TRIMAT.BAS module. The routines in this library
' solve the tridiagonal matrix problem.

' Program implementation:

' The program requires one input file containing the physical properties

' PDS_IN.DAT.

' The following output files may be generated (can be turned on or off):

' PDS_TAG.x contains parameters,

' PDS_N.x contains the node pattern,

' PDS_T.x contains the temperature profiles,

' PDS_A.x contains the probe beam deflections,

' PDS_D.x contains the signal from the lock-in amplifier, and

' PDS_E.x contains the energy balance.

' Logical Units Usage:

' logical units are allocated dynamically using

' the FREEFILE function

' Revision history -

' 3Nov91 - jdr - input ability added for film parameters - needed

' to support PDS6i

' Consistent Units:

' temperature is in milliKelvin (mK)

' distance is in micrometers (um)

' time is in milliseconds (ms)

' frequency is in kiloHertz (kHz)

' power is in microWatts (uW)

' energy is in nanoJoules (nJ)

' intensity is in uW per square um (uW um-2)

' weight is in milligrams (mg)

' The input data file must define the following variables.

' - any of the separators (space ; , =) will separate a variable
' from its value

- ' - the case of the statements are not important
- ' - many statements can be combined on one line
- ' - strings must be continuous (no spaces are allowed)
- ' - logicals are 0 or 1
- ' - exponentials can be entered as 1.234e-56

physical properties of materials

- ' Materials - name of materials
- ' RunName - run identifier
- ' dndtPrimary - optical properties of liquid
- ' dndtSecondary - optical properties of secondary
- ' Kprimary,CPprimary,DENprimary - physical property data for primary
- ' Ksample,CpSample,DenSample - physical property data for metal
- ' Ksecondary,CPsecondary,DENsecondary - physical property data for secondary
- ' LengthPrimary - length of primary phase
- ' LengthSample - length of metal phase
- ' LengthSecondary - length of secondary phase
- ' BetaSurface - absorption of the surface (0-1)
- ' BetaPrimary - absorption coefficient of the electrolyte

describe the excitation light

- ' PowerExcitation,Power - power of source
- ' DutyCycle,Duty - fraction of time source is on
- ' Frequency,Freq - chopping Frequency in kHz

describe the probe beam

- ' InteractionLength - width of electrode
- ' ProbeAngle,Angle - angle of probe away from electrode
- ' ProbeRadius,Radius - 1/e radius of the probe beam
- ' X0probe,x0 - initial x of probe laser

describe the numerical solution and print out of values

- ' NodesCycle
- ' NodesPrimary
- ' NodesSecondary
- ' NodesSample
- ' ProbeNodes, NodesProbe
- ' PrtIncPrimary - increment at which to print liquid values
- ' PrtIncSample
- ' PrtIncSecondary
- ' PrtIncTime - increment at which to print time steps
- ' StartCycle - start printing this cycle
- ' EndCycle - last cycle to run

logical switches

- ' CalcEnergyBalance - calculate an energy balance ?
- ' LogTemp - print temperature profiles ?
- ' LogNodes - print node pattern ?
- ' VariableSpacing - nodes equal or not ?
- ' OnlyPrimary - calculate only the primary side?
- ' LogModulation - write modulation function?

```

' action statements
' * - comment everything to the end of the line is ignored
' write - causes parameter set to be written to .TAG file
' solve - causes program to run with current parameters
' stop, end, quit, exit - stops the program

'-----

' N.B. make sure the define double a-z line appears in ALL subroutines
' or functions (not just the module level code.) If this is not done,
' the subroutines will create independent SINGLE variables with
' the same names as the variables in the COMMON SHARED blocks.

DEFDBL A-Z
DECLARE SUB Lockin (mode AS INTEGER, Pass AS INTEGER)
DECLARE SUB LoadTriDiagonal (A() AS DOUBLE, b() AS DOUBLE, c() AS DOUBLE, n1 AS
INTEGER, n2 AS INTEGER, ReturnCode AS INTEGER)
DECLARE SUB WriteTag ()
DECLARE SUB SolveTriDiagonal (A() AS DOUBLE, D() AS DOUBLE, u() AS DOUBLE, n1 AS
INTEGER, n2 AS INTEGER, ReturnCode AS INTEGER)
DECLARE SUB EnergyBalance (mode AS INTEGER, HeatInput AS DOUBLE)
DECLARE SUB ProbeDeflection (mode AS INTEGER, ThetaPrimary AS DOUBLE, ThetaSecondary
AS DOUBLE, PrintThisStep AS INTEGER)
DECLARE SUB PrintTemp (mode AS INTEGER, LogTemp AS INTEGER)
DECLARE SUB Solve (i AS INTEGER)
DECLARE SUB ParseLine (text AS STRING, Separator AS STRING, Parts() AS STRING, n AS
INTEGER)

' all arrays will start at index zero and be dynamically allocated

OPTION BASE 0
$DYNAMIC

' include a standard common block file
$INCLUDE: 'pdscmm.bas'

' define constants available globally

CONST TRUE% = -1
CONST FALSE% = NOT TRUE
CONST Separators = " ,="
CONST debug = 0

' local variables

DIM Parts(1 TO 20) AS STRING
DIM TextLine AS STRING
DIM FileIn AS INTEGER, ExitFlag AS INTEGER, Pass AS INTEGER
DIM n AS INTEGER, SyntaxOkay AS INTEGER, Errorcount AS INTEGER

'-----
' start of executable code
'-----

```

```
' collect the names of the various attached modules and combine
' them into VERSION - this will be written to the .TAG file
' to identify the program
' the main subroutine of each module will respond to
' a mode 0 CALL by returning its name in the RetBlock variable
```

```
CALL Solve(0)
Version = RTRIM$(RetBlock.text)
CALL ProbeDeflection(0, dummy, dummy, 0)
Version = Version + RTRIM$(RetBlock.text)
CALL Lockin(0, 0)
Version = Version + RTRIM$(RetBlock.text)
```

```
' read in physical constants and parameters
' The input file is typed on the DOS command line.
' If no file name is given, the default file "pds_in.dat" will
' be used.
```

```
TextLine = COMMANDS
```

```
IF TextLine = "ID" THEN
  PRINT "This executable ID is "; Version
END
END IF
```

```
IF TextLine = "" THEN
  TextLine = "pds_in.dat"
END IF
```

```
FileIn = FREEFILE
OPEN TextLine FOR INPUT AS FileIn
```

```
' get the first line from the data file - if this line
' is "commandfile" then the high level data file input form
' is used (the huge SELECT CASE structure below) - otherwise the
' old hard format is used
' (ParseLine separates the string TextLine into Parts(). Separators
' are all the characters which separate, and n is the number of parts
' found in TextLine.)
```

```
' The input file is first parsed to check its syntax. If any errors
' are found, they are reported immediately. Since the program runs
' for many hours, this lets the user know about errors before wasting
' large amounts of computer time. Once the syntax is found to be okay,
' the file is rewound and execution started.
```

```
LINE INPUT #FileIn, TextLine
CALL ParseLine(TextLine, Separators, Parts(), n)
```

```
IF Parts(1) = "commandfile" THEN
  SyntaxOkay = FALSE
  Errorcount = 0
```

```
FOR Pass = 1 TO 2
```

DO

LINE INPUT #FileIn, TextLine
CALL ParseLine(TextLine, Seperators, Parts(), n)

i = 1

' This monstrosity evaluates each line of the data file

DO

SELECT CASE Parts(i)

' action statements

CASE "write"

IF SyntaxOkay THEN

PRINT "Tagfile written for "; RunName

IF debug < 2 THEN CALL WriteTag

END IF

i = i + 1

CASE "solve"

IF SyntaxOkay THEN

PRINT "Beginning solution of "; RunName

IF debug = 0 THEN CALL Solve(1)

END IF

i = i + 1

CASE "exit", "stop", "quit", "end"

ExitFlag = TRUE

i = n + 1

CASE "*", "rem", "comment"

i = i + n

CASE "commandfile"

i = i + n

' variable definining statments

CASE "runname", "run"

RunName = Parts(i + 1)

i = i + 2

CASE "materials", "mat"

Materials = Parts(i + 1)

i = i + 2

CASE "version"

i = n + 1

CASE "kprimary", "kpri"

Kprimary = VAL(Parts(i + 1))

i = i + 2


```
CASE "cppri", "cppri"  
  CpPrimary = VAL(Parts(i + 1))  
  i = i + 2  
CASE "denpri", "denpri"  
  DenPrimary = VAL(Parts(i + 1))  
  i = i + 2  
  
CASE "ksample", "ksam"  
  Ksample = VAL(Parts(i + 1))  
  i = i + 2  
CASE "cpsam", "cpsam"  
  CpSample = VAL(Parts(i + 1))  
  i = i + 2  
CASE "densam", "densam"  
  DenSample = VAL(Parts(i + 1))  
  i = i + 2  
  
CASE "cpfilm"  
  Cpfilm = VAL(Parts(i + 1))  
  i = i + 2  
CASE "denfilm"  
  Denfilm = VAL(Parts(i + 1))  
  i = i + 2  
  
CASE "ksecondary", "ksec"  
  Ksecondary = VAL(Parts(i + 1))  
  i = i + 2  
CASE "cpsec", "cpsec"  
  CpSecondary = VAL(Parts(i + 1))  
  i = i + 2  
CASE "densec", "densec"  
  DenSecondary = VAL(Parts(i + 1))  
  i = i + 2  
  
CASE "lprimary", "lpri"  
  LengthPrimary = VAL(Parts(i + 1))  
  i = i + 2  
CASE "lsam", "lsam"  
  LengthSample = VAL(Parts(i + 1))  
  i = i + 2  
CASE "lsec", "lsec"  
  LengthSecondary = VAL(Parts(i + 1))  
  i = i + 2  
CASE "lfilm"  
  LengthFilm = VAL(Parts(i + 1))  
  i = i + 2  
  
CASE "nodescycle", "ncyc"  
  NodesCycle = VAL(Parts(i + 1))  
  i = i + 2  
CASE "nodesprimary", "npri"  
  NodesPrimary = VAL(Parts(i + 1))  
  i = i + 2  
CASE "nodessample", "nsam"
```

```

NodesSample = VAL(Parts(i + 1))
i = i + 2
CASE "nodessecondary", "nsec"
NodesSecondary = VAL(Parts(i + 1))
i = i + 2
CASE "probenodes", "nodesprobe"
ProbeNodesX = VAL(Parts(i + 1))
i = i + 2

CASE "prtinctime", "pit"
PrtIncTime = INT(VAL(Parts(i + 1)))
i = i + 2
CASE "prtincprimary", "pipri"
PrtIncPrimary = INT(VAL(Parts(i + 1)))
i = i + 2
CASE "prtincsample", "pisam"
PrtIncSample = INT(VAL(Parts(i + 1)))
i = i + 2
CASE "prtincsecondary", "pise"
PrtIncSecondary = INT(VAL(Parts(i + 1)))
i = i + 2

CASE "powerexcitation", "power"
PowerExcitation = VAL(Parts(i + 1))
i = i + 2

CASE "frequency", "freq"
Frequency = VAL(Parts(i + 1))
i = i + 2
CASE "dutycycle", "duty"
DutyCycle = VAL(Parts(i + 1))
i = i + 2

CASE "startcycle", "start"
StartCycle = VAL(Parts(i + 1))
i = i + 2
CASE "endcycle"
EndCycle = VAL(Parts(i + 1))
i = i + 2

CASE "x0probe", "x0"
X0probe = VAL(Parts(i + 1))
i = i + 2
CASE "probeangle", "angle"
ProbeAngle = VAL(Parts(i + 1))
i = i + 2
CASE "interactionlength"
InteractionLength = VAL(Parts(i + 1))
i = i + 2
CASE "proberadius", "radius"
ProbeRadius = VAL(Parts(i + 1))
i = i + 2

CASE "dndtprimary", "dndtpri"

```

```

dndTprimary = VAL(Parts(i + 1))
i = i + 2
CASE "dndtsecondary", "dndtsec"
  dndTsecondary = VAL(Parts(i + 1))
  i = i + 2

CASE "betasurface"
  BetaSurface = VAL(Parts(i + 1))
  i = i + 2
CASE "betaprimary"
  BetaPrimary = VAL(Parts(i + 1))
  i = i + 2

'switches - logical values control various printouts
'and calculations

CASE "logtemp"
  LogTemp = INT(VAL(Parts(i + 1)))
  i = i + 2
  IF LogTemp = 0 THEN LogTemp = FALSE ELSE LogTemp = TRUE
CASE "lognodes"
  LogNodes = INT(VAL(Parts(i + 1)))
  i = i + 2
  IF LogNodes = 0 THEN LogNodes = FALSE ELSE LogNodes = TRUE
CASE "calcbalance"
  CalcEnergyBalance = INT(VAL(Parts(i + 1)))
  i = i + 2
  IF CalcEnergyBalance = 0 THEN CalcEnergyBalance = FALSE ELSE CalcEnergyBalance =
TRUE
CASE "variablespadding", "vspace"
  VariableSpacing = INT(VAL(Parts(i + 1)))
  i = i + 2
  IF VariableSpacing = 0 THEN VariableSpacing = FALSE ELSE VariableSpacing = TRUE
CASE "onlyprimary"
  OnlyPrimary = INT(VAL(Parts(i + 1)))
  i = i + 2
  IF OnlyPrimary = 0 THEN OnlyPrimary = FALSE ELSE OnlyPrimary = TRUE
CASE "logmodulation"
  LogModulation = INT(VAL(Parts(i + 1)))
  i = i + 2
  IF LogModulation = 0 THEN LogModulation = FALSE ELSE LogModulation = TRUE

CASE "refindex0", "n0"
  RefIndex0 = VAL(Parts(i + 1))
  i = i + 2

CASE ELSE
  PRINT "Unknown command in this line:"
  PRINT TextLine
  Errorcount = Errorcount + 1
  i = n + 1

END SELECT
LOOP WHILE i <= n

```

LOOP UNTIL ExitFlag OR EOF(FileIn)

IF Errorcount = 0 THEN

PRINT "Command file passes syntax check"

SyntaxOkay = TRUE

ExitFlag = FALSE

SEEK FileIn, 1

ELSE

PRINT "Command file does not pass syntax check."

PRINT "Errors must be corrected before continuing."

EXIT FOR

END IF

NEXT Pass

CLOSE FileIn

' This program segment handles the old hard format
' data files. These files have a fixed format for the paramters

ELSE

RunName = Parts(n)

INPUT #FileIn, Materials

INPUT #FileIn, Kprimary, CpPrimary, DenPrimary

INPUT #FileIn, Ksample, CpSample, DenSample

INPUT #FileIn, Ksecondary, CpSecondary, DenSecondary

INPUT #FileIn, LengthPrimary, LengthSample, LengthSecondary

INPUT #FileIn, NodesCycle, NodesPrimary, NodesSample, NodesSecondary

INPUT #FileIn, PowerExcitation

INPUT #FileIn, Frequency, DutyCycle

INPUT #FileIn, EndCycle, StartCycle

INPUT #FileIn, PrtIncTime, PrtIncPrimary, PrtIncSample, PrtIncSecondary

INPUT #FileIn, XProbe, ProbeAngle, InteractionLength, ProbeRadius

INPUT #FileIn, dndTprimary, dndTsecondary

INPUT #FileIn, BetaPrimary, BetaSurface

IF NOT (EOF(FileIn)) THEN INPUT #FileIn, LogTemp, CalcEnergyBalance

IF NOT (EOF(FileIn)) THEN INPUT #FileIn, VariableSpacing

IF NOT (EOF(FileIn)) THEN INPUT #FileIn, OnlyPrimary

IF NOT (EOF(FileIn)) THEN INPUT #FileIn, RefIndex0

CLOSE FileIn

IF LogTemp = 0 THEN LogTemp = FALSE ELSE LogTemp = TRUE

IF CalcEnergyBalance = 0 THEN CalcEnergyBalance = FALSE ELSE CalcEnergyBalance = TRUE

IF VariableSpacing = 0 THEN VariableSpacing = FALSE ELSE VariableSpacing = TRUE

IF OnlyPrimary = 0 THEN OnlyPrimary = FALSE ELSE OnlyPrimary = TRUE

CALL WriteTag

CALL Solve(1)

END IF

END

```

REM $STATIC
DEFSNG A-Z
SUB WriteTag

DEFDBL A-Z
DIM FileTag AS INTEGER

FileTag = FREEFILE
OPEN "pds_tag." + RunName FOR OUTPUT AS FileTag
PRINT #FileTag, "commandfile"
PRINT #FileTag, "RunName= "; RunName
PRINT #FileTag, "Version= "; Version
PRINT #FileTag, "Materials= "; Materials
PRINT #FileTag, "Kprimary= "; Kprimary; "; CpPrimary= "; CpPrimary; "; DenPrimary= "; DenPrimary
PRINT #FileTag, "Ksample= "; Ksample; "; CpSample= "; CpSample; "; DenSample= "; DenSample
PRINT #FileTag, "Ksecondary= "; Ksecondary; "; CpSecondary= "; CpSecondary; "; DenSecondary= ";
DenSecondary
PRINT #FileTag, "LPrimary= "; LengthPrimary; "; LSample= "; LengthSample; "; LSecondary= ";
LengthSecondary
PRINT #FileTag, "NodesCycle= "; NodesCycle; "; NodesPrimary= "; NodesPrimary; "; NodesSample= ";
NodesSample; "; NodesSecondary= "; NodesSecondary
PRINT #FileTag, "ProbeNodes= "; ProbeNodesX
PRINT #FileTag, "PowerExcitation= "; PowerExcitation
PRINT #FileTag, "Frequency= "; Frequency; "; DutyCycle= "; DutyCycle
PRINT #FileTag, "EndCycle= "; EndCycle; "; StartCycle= "; StartCycle
PRINT #FileTag, "PrIncTime= "; PrIncTime; "; PrIncPrimary= "; PrIncPrimary; "; PrIncSample= ";
PrIncSample; "; PrIncSecondary= "; PrIncSecondary
PRINT #FileTag, "X0probe= "; X0probe; "; ProbeAngle= "; ProbeAngle; "; InteractionLength= ";
InteractionLength; "; ProbeRadius= "; ProbeRadius
PRINT #FileTag, "dndTprimary= "; dndTprimary; "; dndTsecondary= "; dndTsecondary
PRINT #FileTag, "BetaPrimary= "; BetaPrimary; "; BetaSurface= "; BetaSurface
PRINT #FileTag, "LogTemp= "; LogTemp; "; CalcBalance= "; CalcEnergyBalance
PRINT #FileTag, "VariableSpacing= "; VariableSpacing; "; OnlyPrimary= "; OnlyPrimary
PRINT #FileTag, "LogNodes= "; LogNodes; "; LogModulation= "; LogModulation
PRINT #FileTag, "RefIndex0= "; RefIndex0
PRINT #FileTag, "write, solve, stop"
CLOSE FileTag

END SUB

```

A.2. Parse

' Parse.bas

' from John Craig, "Microsoft QuickBasic Programmer's Toolbox,"
 ' Microsoft Press, p. 293, 1988.
 ' p

```

DECLARE SUB ParseWord (Text AS STRING, Separator AS STRING, Word AS STRING)
DECLARE SUB ParseLine (Text AS STRING, Separator AS STRING, part() AS STRING, n AS
INTEGER)

```

```

DIM Parts(1 TO 99) AS STRING
DIM LineText AS STRING, Seperator AS STRING
DIM n AS INTEGER

```

```

PRINT
LineText = "This is a test line. A,B = 5.05,C, etc."
Seperator = ",="
PRINT "LineText: "; LineText
PRINT "Seperator: "; Seperator; ":"
CALL ParseLine(LineText, Seperator, Parts(), n)
PRINT "Parts:"
n = 0
DO
    n = n + 1
    PRINT n, Parts(n)
LOOP UNTIL Parts(n + 1) = ""

END

```

```

SUB ParseLine (Text AS STRING, Seperator AS STRING, part() AS STRING, n AS INTEGER)
STATIC

```

```

    t$ = Text
    FOR i = LBOUND(part) TO UBOUND(part)
        ParseWord t$, Seperator, part(i)
        part(i) = LCASE$(part(i))
        IF part(i) = "" THEN
            n = i - 1
            EXIT FOR
        END IF
    NEXT
    t$ = ""

```

```

END SUB

```

```

SUB ParseWord (Text AS STRING, Seperator AS STRING, Word AS STRING) STATIC

```

```

    DIM i AS INTEGER, j AS INTEGER, k AS INTEGER
    DIM LengthText AS INTEGER

```

```

    Word = ""
    LengthText = LEN(Text)

```

```

    IF Text = "" THEN
        EXIT SUB
    END IF
    FOR i = 1 TO LengthText
        IF INSTR(Seperator, MID$(Text, i, 1)) = 0 THEN
            EXIT FOR
        END IF
    NEXT

```

```

    FOR j = i TO LengthText
        IF INSTR(Seperator, MID$(Text, j, 1)) THEN

```

```

EXIT FOR
END IF
NEXT

FOR k = j TO LengthText
  IF INSTR(Seperator, MID$(Text, k, 1)) = 0 THEN
    EXIT FOR
  END IF
NEXT

IF i > LengthText THEN
  Text = ""
  EXIT SUB
END IF

IF j > LengthText THEN
  Word = MID$(Text, i)
  Text = ""
  EXIT SUB
END IF

Word = MID$(Text, i, j - 1)
IF k > LengthText THEN
  Text = ""
ELSE
  Text = MID$(Text, k)
END IF

END SUB

```

A.3. Common Block

```

TYPE block
  code AS INTEGER
  value AS DOUBLE
  text AS STRING * 50
END TYPE

```

```

COMMON SHARED /li1/ CurrentTimeStep AS INTEGER, CycleLength AS DOUBLE, DeltaTime AS
DOUBLE, ThetaPrimary AS DOUBLE, ThetaSecondary AS DOUBLE
COMMON SHARED /li2/ MagnitudePrimary AS DOUBLE, MagnitudeSecondary AS DOUBLE,
PhasePrimary AS DOUBLE, PhaseSecondary AS DOUBLE
COMMON SHARED /solution/ RefIndex() AS DOUBLE, DeltaX() AS DOUBLE, Nint1 AS
INTEGER, Nint2 AS INTEGER, VariableSpacing AS INTEGER
COMMON SHARED /heat/ heat() AS DOUBLE, IntensityOut AS DOUBLE, CpInt1 AS DOUBLE
COMMON SHARED /var/ CurrentTime AS SINGLE, CurrentCycle AS INTEGER
COMMON SHARED /mesh/ xcoord() AS DOUBLE
COMMON SHARED /ret/ RetBlock AS block
COMMON SHARED /IDparam/ Version AS STRING, RunName AS STRING, Materials AS STRING
COMMON SHARED /PhysParam/ Kprimary, CpPrimary, DenPrimary, Ksample, CpSample,
DenSample, Ksecondary, CpSecondary, DenSecondary, Kfilm, Cpfilm, Denfilm, dndTprimary,
dndTsecondary, RefIndex0, BetaPrimary, BetaSurface
COMMON SHARED /GeomParam/ LengthPrimary, LengthSample, LengthSecondary, LengthFilm

```

COMMON SHARED /ExpParam/ PowerExcitation, Frequency, DutyCycle, X0probe, ProbeAngle,
 SectionLength, ProbeRadius

COMMON SHARED /NumParam/ NodesCycle AS INTEGER, NodesPrimary AS INTEGER,
 NodesSample AS INTEGER, NodesSecondary AS INTEGER, NodesTotal AS INTEGER, EndCycle AS
 INTEGER, StartCycle AS INTEGER, ProbeNodesX AS INTEGER

COMMON SHARED /PrtParam/ PrtIncTime AS INTEGER, PrtIncPrimary AS INTEGER, PrtIncSample
 AS INTEGER, PrtIncSecondary AS INTEGER

COMMON SHARED /Switches/ LogTemp AS INTEGER, LogNodes AS INTEGER, OnlyPrimary AS
 INTEGER, CalcEnergyBalance AS INTEGER, LogModulation AS INTEGER

B. Thermal Module

B.1. Main

PDS model version 6

i version - implicit

must be loaded with the Library TRIMAT or
 include the TRIMAT.BAS module

written by James Rudnicki

original version November 1991

last update November 1991

contained in the file PDS6i.BAS

written in QuickBasic v4.5

Description:

This program models Photothermal Deflection Spectroscopy.

Version 6 evaluates the following arrangement:

- a thermally thin film on a thermally thick sample with a semi-infinite
 medium on the back, and a thin layer of fluid on the front side
- an optically absorbing liquid and an opaque sample
- no heat losses in the direction parallel to the sample

The problem was solved in two dimensions, x&t, using implicit finite
 difference equations.

The probe beam deflection and signal processing are simulated
 by attached subroutines.

This code was derived by modifying PDS5ib.BAS. Only the
 primary interfacial node needs to be modified. Because the film
 is assume thin, PDS5 is no longer needed. By setting the length
 of the film to zero, the model will be exactly the same as PDS5.
 No computational penalty is caused by running with LengthFilm=0.

Other modules attached to this code:

' heat module
 ' modulation module
 ' lockin module - simulates a lockin amp
 LOCKIN4 - lockin with RC filters
 LOCKIN5 - lockin with averaging outputs
 LOCKIN6 - frequency domain lockin
 ' probe deflection - calculates probe beam deflection by various means
 (not available) PROBE0 - infinitely thin probe (parallel)
 PROBE1 - infinitely thin probe
 PROBE2 - finite probe thickness (parallel)
 (not available) PROBE3 - finite probe
 ' Program implementation:
 ' The following output files may be generated (can be turned on or off):
 PDS_N.DAT contains the node pattern,
 PDS_T.DAT contains the temperature profiles,
 PDS_A.DAT contains the probe beam deflections,
 PDS_D.DAT contains the signal from the lock-in amplifier
 PDS_E.DAT contains the energy balance.
 PDS_M.DAT contains the modulation waveform
 ' Logical Units Usage:
 ' logical units are allocated dynamically using FREEFILE

Consistent Units:

' temperature is in milliKelvin (mK)
 ' distance is in micrometers (um)
 ' time is in milliseconds (ms)
 ' frequency is in kiloHertz (kHz)
 ' power is in microWatts (uW)
 ' energy is in nanoJoules (nJ)
 ' intensity is in uW per square um (uW um-2)
 ' weight is in milligrams (mg)

Inconsistent units:

' angular deflection is in microradians (urad)
 ' phase is in degrees

Variables:

Vectors

' T(i) - primary medium temperature nodes
 ' TNexT(i) - primary temperature nodes at next time
 ' Heat() - heat absorbed at points in liquid

Scalars

CycleLength - length of cycle in ms
 dndtPrimary - optical properties of liquid
 dndtSecondary - optical properties of secondary
 DeltaTime - time step
 DeltaXprimary - primary phase spatial step
 DeltaXsecondary - secondary medium spatial step
 DutyCycle - fraction of time source is on
 Frequency - chopping Frequency in kHz
 InteractionLength - width of electrode
 Kprimary,CPprimary,DENprimary - physical property data for primary
 Ksample,CpSample,DenSample - physical property data for sample
 Ksecondary,CPsecondary,DENsecondary - physical property data for secondary
 CpFilm,DenFilm - note: the thermal conductivity is irrelevant
 LengthPrimary - length of primary phase
 LengthSample - length of sample phase
 LengthSecondary - length of secondary phase
 LengthFilm - length of film (can be set to zero)
 ModulationFunction - value of modulation function at current time
 Mprimary - liquid phase FDE 'M' parameter
 Msecondary - secondary phase FDE 'M' parameter
 PowerExcitation - power of source
 Qsurf - heat absorbed at surface
 ProbeAngle - angle of probe away from electrode
 ThetaPrimary - probe deflection in primary at each time step
 ThetaSecondary - probe deflection in secondary
 X0probe - initial x of probe laser

Scalars - single

CurrentTime - fractional cycle time

Integers

CurrentCycle - current cycle
 CurrentTimeStep - current time step
 NodesCycle - number of time steps per cycle
 StepMaxPrimary - step of maximum deflection in primary
 StepMaxSecondary - step of maximum deflection in secondary

ITPTS - count of number of time steps printed
 PrIncPrimary - increment at which to print liquid values
 PrIncTime - increment at which to print time steps
 StartCycle - start printing this cycle
 EndCycle - last cycle to run
 NprtCycle - # of time steps to print
 NprtPrimary - # of liquid points to print
 NprtSecondary - # of secondary points to print

Strings

Version - indicates version of program
 Materials - name of materials
 RunName - run identifier

```
' Maskxxx      - assorted format masks
```

```
'           Logicals
```

```
' CalcEnergyBalance - calculate an energy balance ?
```

```
' LogTemp          - print temperature profiles ?
```

```
' VariableSpacing  - nodes equal or not ?
```

```
' PrintThisStep    - controls print for each time step
```

```
' TRUE
```

```
' FALSE
```

```
DEFDBL A-Z
```

```
DECLARE SUB Lockin (mode AS INTEGER, pass AS INTEGER)
```

```
DECLARE SUB LoadTriDiagonal (A() AS DOUBLE, B() AS DOUBLE, C() AS DOUBLE, n1 AS  
INTEGER, n2 AS INTEGER, ReturnCode AS INTEGER)
```

```
DECLARE SUB SolveTriDiagonal (A() AS DOUBLE, D() AS DOUBLE, u() AS DOUBLE, n1 AS  
INTEGER, n2 AS INTEGER, ReturnCode AS INTEGER)
```

```
DECLARE SUB EnergyBalance (mode AS INTEGER, HeatInput AS DOUBLE)
```

```
DECLARE SUB ProbeDeflection (mode AS INTEGER, ThetaPrimary AS DOUBLE,  
ThetaSecondary AS DOUBLE, PrintThisStep AS INTEGER)
```

```
DECLARE SUB PrintTemp (mode AS INTEGER, LogTemp AS INTEGER)
```

```
DECLARE FUNCTION Modulation# (mode AS INTEGER, time AS DOUBLE)
```

```
DECLARE SUB HeatFunction (mode AS INTEGER)
```

```
' all arrays will start at index zero and be dynamically allocated
```

```
OPTION BASE 0
```

```
' $DYNAMIC
```

```
' include a standard common block file
```

```
' $INCLUDE: 'pdscmm.bas'
```

```
' the following variables and constants will be available to all
```

```
' procedures in this module
```

```
COMMON SHARED /temperature/ T() AS DOUBLE
```

```
CONST TRUE% = -1
```

```
CONST FALSE% = NOT TRUE
```

```
CONST Mask1 = "###.#### "
```

```
CONST Mask2 = "#### "
```

```
CONST Mask3 = "### #####.#### ###.## #####.#### ###.##"
```

```
REM $STATIC
```

```
DEFSNG A-Z
```

```
SUB EnergyBalance (mode AS INTEGER, HeatInput AS DOUBLE)
```

```
DEFDBL A-Z
```

```
DIM Qintegral AS DOUBLE
```

```
DIM I AS INTEGER
```

```
STATIC FileQ AS INTEGER
```

```
SELECT CASE mode
```

```

CASE 1
  FileQ = FREEFILE
  OPEN "pds_o." + RunName FOR OUTPUT AS FileQ

CASE 2
  Qintegral = 0
  FOR I = 1 TO Nint2
    Qintegral = Qintegral + .5# * (T(I) + T(I - 1)) * CpSecondary * DenSecondary * DeltaX(I)
  NEXT
  FOR I = Nint2 + 1 TO Nint1
    Qintegral = Qintegral + .5# * (T(I) + T(I - 1)) * CpSample * DenSample * DeltaX(I)
  NEXT
  FOR I = Nint1 + 1 TO Nodestotal
    Qintegral = Qintegral + .5# * (T(I) + T(I - 1)) * CpPrimary * DenPrimary * DeltaX(I)
  NEXT

  PRINT USING "Heat input ##.####^ heat integral ##.####^"; HeatInput; Qintegral
  PRINT #FileQ, USING " ##.####^ , ##.####^"; HeatInput; Qintegral

CASE 3
  CLOSE FileQ

END SELECT

END SUB

DEFSNG A-Z
SUB PrintTemp (mode AS INTEGER, LogTemp AS INTEGER)

DEFDBL A-Z

STATIC itpts AS INTEGER
STATIC FileTemp AS INTEGER

CONST Mask1 = "#### , ##.#### "

SELECT CASE mode

CASE 1
  itpts = 0
  IF LogTemp THEN
    FileTemp = FREEFILE
    OPEN "pds_t." + RunName FOR OUTPUT AS FileTemp
  END IF

CASE 2
  itpts = itpts + 1
  PRINT STRING$(50, ".")
  PRINT USING "Cycle ## of ## for &"; CurrentCycle; EndCycle; RunName
  PRINT USING "Time step ####/#### or ###.###ms / ###.###ms"; CurrentTimeStep; NodesCycle
  - 1; CurrentTimeStep * DeltaTime; (NodesCycle - 1) * DeltaTime
  PRINT

  IF LogTemp THEN PRINT #FileTemp, CHR$(34); itpts; CHR$(34)

```

```

PRINT "Secondary excess temperatures"
FOR I = 0 TO Nint2 - 1
    IF I MOD PrIncSecondary = 0 THEN
        PRINT USING Mask1; INT(I); T(I);
        IF LogTemp THEN PRINT #FileTemp, USING Mask1; INT(I); T(I);
    END IF
NEXT
IF LogTemp THEN PRINT #FileTemp, " "

PRINT "Sample excess temperatures"
FOR I = Nint2 TO Nint1
    IF (I - Nint2) MOD PrIncSample = 0 THEN
        PRINT USING Mask1; INT(I); T(I);
        IF LogTemp THEN PRINT #FileTemp, USING Mask1; INT(I); T(I);
    END IF
NEXT
PRINT
IF LogTemp THEN PRINT #FileTemp, " "

PRINT "Liquid excess temperatures"
FOR I = Nint1 + 1 TO Nodestotal
    IF (I - Nint1) MOD PrIncPrimary = 0 THEN
        PRINT USING Mask1; INT(I); T(I);
        IF LogTemp THEN PRINT #FileTemp, USING Mask1; INT(I); T(I);
    END IF
NEXT
PRINT
IF LogTemp THEN PRINT #FileTemp, " "

CASE 3
    IF LogTemp THEN
        PRINT #FileTemp, " "
        CLOSE FileTemp
    END IF

END SELECT

END SUB

DEFSNG A-Z
SUB Solve (mode AS INTEGER)

DEFDBL A-Z

DIM DeltaXPrimary AS DOUBLE, DeltaXsample AS DOUBLE, DeltaXsecondary AS DOUBLE
DIM AlphaPrimary AS DOUBLE, AlphaSecondary AS DOUBLE, AlphaSample AS DOUBLE
DIM xx1 AS DOUBLE, xx2 AS DOUBLE, xx3 AS DOUBLE, xx4 AS DOUBLE, xx5 AS DOUBLE
DIM HeatIntegral AS DOUBLE, kbar AS DOUBLE, HeatInput AS DOUBLE
DIM AlphaInt1 AS DOUBLE, AlphaInt2 AS DOUBLE, LbarInt1 AS DOUBLE, LbarInt2 AS
DOUBLE
DIM DeltaXPrimaryFine AS DOUBLE, DeltaXprimaryCoarse AS DOUBLE
DIM DeltaXsecondaryFine AS DOUBLE, DeltaXsecondaryCoarse AS DOUBLE

DIM dummy AS DOUBLE

```

```

DIM NprtPrimary AS INTEGER, Nprtsample AS INTEGER, NprtSecondary AS INTEGER
DIM StepMaxPrimary AS INTEGER, StepMaxSecondary AS INTEGER
DIM itpts AS INTEGER
DIM NprtCylce AS INTEGER
DIM I AS INTEGER, j AS INTEGER
DIM ReturnCode AS INTEGER, nn AS INTEGER
DIM PrintThisStep AS INTEGER

DIM z AS STRING

CONST TRUE% = -1
CONST FALSE% = NOT TRUE
CONST Mask1 = "##.#### "
CONST Mask2 = "#### "
CONST Mask3 = "### #####.#### ###.## #####.#### ###.##"

SELECT CASE mode
CASE 0
    z = "pds6i:"
    ModulationFunction = Modulation(0, 0)
    z = z + RTRIMS(RetBlock.text)
    CALL HeatFunction(0)
    z = z + RTRIMS(RetBlock.text)
    RetBlock.text = z
    RetBlock.code = 1

CASE 1

    HeatInput = 0

-----
' START OF THE PROGRAM
' dimension the arrays

    Nodestotal = NodesSecondary + NodesPrimary + NodesSample - 3
    REDIM T(Nodestotal) AS DOUBLE, RefIndex(Nodestotal) AS DOUBLE
    REDIM DeltaX(Nodestotal) AS DOUBLE
    REDIM xcoord(Nodestotal) AS DOUBLE

' arrays only used within this procedure

    REDIM Tnext(Nodestotal) AS DOUBLE
    REDIM A(Nodestotal) AS DOUBLE, B(Nodestotal) AS DOUBLE
    REDIM D(Nodestotal) AS DOUBLE, C(Nodestotal) AS DOUBLE
    REDIM heat(Nodestotal) AS DOUBLE, Lsbar(Nodestotal) AS DOUBLE
    REDIM zza(Nodestotal) AS DOUBLE, zzc(Nodestotal) AS DOUBLE, zzb(Nodestotal) AS
DOUBLE

' calculate various parameters

    CycleLength = 1 / Frequency
    DeltaTime = CycleLength / (NodesCycle - 1)
    DeltaXPrimary = LengthPrimary / (NodesPrimary - 1)

```

```

DeltaXsample = LengthSample / (NodesSample - 1)
DeltaXsecondary = LengthSecondary / (NodesSecondary - 1)
CurrentCycle = 0
CycleToScan = CurrentCycle
itpts = 0
Nint1 = NodesSecondary + NodesSample - 2
Nint2 = NodesSecondary - 1

```

' calculate thermal diffusivities

```

AlphaPrimary = Kprimary / (CpPrimary * DenPrimary)
AlphaSample = Ksample / (CpSample * DenSample)
AlphaSecondary = Ksecondary / (CpSecondary * DenSecondary)

```

' setup the node pattern

' variable spacing puts half of the nodes in the 20% of the
' distance near the surface and the remaining half in 80%

' DeltaX(i) is the distance to the left of the ith node
' the nodes are numbered from zero at the left to the right

' Lsbar(i) is a parameter which arises often in the FD equations
' it is precalculated to reduce computations

' CPint are heat capacities of interfacial nodes

IF VariableSpacing THEN

```

DeltaXsecondaryFine = 2 * .2 * DeltaXsecondary
DeltaXsecondaryCoarse = 2 * .8 * DeltaXsecondary
DeltaXPrimaryFine = 2 * .2 * DeltaXPrimary
DeltaXprimaryCoarse = 2 * .8 * DeltaXPrimary

```

```
FOR I = 1 TO Nint2 / 2
```

```
  DeltaX(I) = DeltaXsecondaryCoarse
```

```
NEXT
```

```
FOR I = Nint2 / 2 + 1 TO Nint2
```

```
  DeltaX(I) = DeltaXsecondaryFine
```

```
NEXT
```

```
FOR I = Nint2 + 1 TO Nint1
```

```
  DeltaX(I) = DeltaXsample
```

```
NEXT
```

```
FOR I = Nint1 + 1 TO (Nint1 + Nodestotal) / 2
```

```
  DeltaX(I) = DeltaXPrimaryFine
```

```
NEXT
```

```
FOR I = 1 + (Nint1 + Nodestotal) / 2 TO Nodestotal
```

```
  DeltaX(I) = DeltaXprimaryCoarse
```

```
NEXT
```

```
CPint2 = (DeltaXsecondaryFine * CpSecondary * DenSecondary + DeltaXsample * CpSample *
DenSample) / (DeltaXsecondaryFine + DeltaXsample)
```

```
CPint1 = (DeltaXPrimaryFine * CpPrimary * DenPrimary + LengthFilm * Cpfilm * Denfilm +
DeltaXsample * CpSample * DenSample) / (DeltaXPrimaryFine + DeltaXsample)
```

```

ELSE
    FOR I = 1 TO Nint2
        DeltaX(I) = DeltaXsecondary
    NEXT
    FOR I = Nint2 + 1 TO Nint1
        DeltaX(I) = DeltaXsample
    NEXT
    FOR I = Nint1 + 1 TO Nodestotal
        DeltaX(I) = DeltaXPrimary
    NEXT

    CPInt2 = (DeltaXsecondary * CpSecondary * DenSecondary + DeltaXsample * CpSample *
DenSample) / (DeltaXsecondary + DeltaXsample)
    CpInt1 = (DeltaXPrimary * CpPrimary * DenPrimary + LengthFilm * Cpfilm * Denfilm +
DeltaXsample * CpSample * DenSample) / (DeltaXPrimary + DeltaXsample)

END IF

FOR I = 0 TO Nodestotal - 1
    Lsbar(I) = (DeltaX(I) + DeltaX(I + 1)) / 2#
NEXT

' place the node information in a file
' the file contains a list of the node number and x coordinate

xcoord(0) = 0
FOR I = 1 TO Nodestotal
    xcoord(I) = xcoord(I - 1) + DeltaX(I)
NEXT
IF LogNodes THEN
    FileN = FREEFILE
    OPEN "pds_n." + RunName FOR OUTPUT AS FileN
    PRINT #FileN, "0, 0"
    FOR I = 1 TO Nodestotal
        PRINT #FileN, USING "#### , #####.##"; I; xcoord(I)
    NEXT
    CLOSE FileN
END IF

' setup temperature array to initial condition

FOR I = 0 TO Nodestotal
    T(I) = 0#
NEXT
' initialize subprograms

CALL HeatFunction(1)
dummy = Modulation(1, 0)
CALL PrintTemp(1, LogTemp)
IF CalcEnergyBalance THEN CALL EnergyBalance(1, dummy)
CALL ProbeDeflection(1, dummy, dummy, OnlyPrimary)
nn = 1 + (EndCycle - StartCycle + 1) * (NodesCycle - 1)

```



```

CALL Lockin(1, nn)

'-----
' setup tridiagonal array

' the first equation is the end of the secondary phase

B(1) = 1 + (1 / DeltaX(1) + 1 / DeltaX(2)) * DeltaTime * AlphaSecondary / (2 * Lsbar(1))
C(1) = -DeltaTime * AlphaSecondary / (2 * DeltaX(1 + 1) * Lsbar(1))
zza(1) = DeltaTime * AlphaSecondary / (2 * DeltaX(1) * Lsbar(1))
zzb(1) = B(1) - 2
zzc(1) = -C(1)

' these nodes are the secondary phase equations

FOR I = 2 TO Nint2 - 1
  A(I) = -DeltaTime * AlphaSecondary / (2 * DeltaX(I) * Lsbar(I))
  B(I) = 1 + ((1 / DeltaX(I)) + (1 / DeltaX(I + 1))) * DeltaTime * AlphaSecondary / (2 * Lsbar(I))
  C(I) = -DeltaTime * AlphaSecondary / (2 * DeltaX(I + 1) * Lsbar(I))
  zza(I) = -A(I)
  zzb(I) = B(I) - 2
  zzc(I) = -C(I)
NEXT

' the secondary/sample interface

A(Nint2) = -DeltaTime * Ksecondary / (2# * CPlnt2 * DeltaX(Nint2) * Lsbar(Nint2))
B(Nint2) = 1 + (DeltaTime / (2# * CPlnt2 * Lsbar(Nint2))) * (Ksecondary / DeltaX(Nint2) +
Ksample / DeltaX(Nint2 + 1))
C(Nint2) = -DeltaTime * Ksample / (2# * CPlnt2 * DeltaX(Nint2 + 1) * Lsbar(Nint2))
zza(Nint2) = -A(Nint2)
zzb(Nint2) = B(Nint2) - 2
zzc(Nint2) = -C(Nint2)

' the sample interior nodes

FOR I = Nint2 + 1 TO Nint1 - 1
  A(I) = -DeltaTime * AlphaSample / (2 * DeltaX(I) * Lsbar(I))
  B(I) = 1 + ((1 / DeltaX(I)) + (1 / DeltaX(I + 1))) * DeltaTime * AlphaSample / (2 * Lsbar(I))
  C(I) = -DeltaTime * AlphaSample / (2 * DeltaX(I + 1) * Lsbar(I))
  zza(I) = -A(I)
  zzb(I) = B(I) - 2
  zzc(I) = -C(I)
NEXT

' the primary/sample interface

A(Nint1) = -DeltaTime * Ksample / (2# * CPlnt1 * DeltaX(Nint1) * Lsbar(Nint1))
B(Nint1) = 1 + (DeltaTime / (2# * CPlnt1 * Lsbar(Nint1))) * (Ksample / DeltaX(Nint1) + Kprimary /
DeltaX(Nint1 + 1))
C(Nint1) = -DeltaTime * Kprimary / (2# * CPlnt1 * DeltaX(Nint1 + 1) * Lsbar(Nint1))
zza(Nint1) = -A(Nint1)
zzb(Nint1) = B(Nint1) - 2
zzc(Nint1) = -C(Nint1)

```

' the primary phase interior nodes

```

FOR I = Nint1 + 1 TO Nodestotal - 2
  A(I) = -DeltaTime * AlphaPrimary / (2 * DeltaX(I) * Lsbar(I))
  B(I) = 1 + (1 / DeltaX(I) + 1 / DeltaX(I + 1)) * DeltaTime * AlphaPrimary / (2 * Lsbar(I))
  C(I) = -DeltaTime * AlphaPrimary / (2 * DeltaX(I + 1) * Lsbar(I))
  zza(I) = -A(I)
  zzb(I) = B(I) - 2
  zzc(I) = -C(I)
NEXT

```

' the edge node for the primary phase

```

  A(Nodestotal - 1) = -DeltaTime * AlphaPrimary / (2 * DeltaX(Nodestotal - 1) *
Lsbar(Nodestotal - 1))
  B(Nodestotal - 1) = 1 + (1 / DeltaX(Nodestotal - 1) + 1 / DeltaX(Nodestotal - 1 + 1)) *
DeltaTime * AlphaPrimary / (2 * Lsbar(Nodestotal - 1))
  zza(Nodestotal - 1) = -A(Nodestotal - 1)
  zzb(Nodestotal - 1) = B(Nodestotal - 1) - 2
  zzc(Nodestotal - 1) = DeltaTime * AlphaPrimary / (2 * DeltaX(Nodestotal - 1 + 1) *
Lsbar(Nodestotal - 1))

```

```

CALL LoadTriDiagonal(A(), B(), C(), 1, Nodestotal - 1, ReturnCode)

```

' MAIN LOOP

' repeat the loop for the requested number of cycles

```

FOR CurrentCycle = 0 TO EndCycle

```

```

  FOR CurrentTimeStep = 0 TO NodesCycle - 2

```

' determine the current time and the ModulationFunction

' The modulation function determines whether the excitation light
' is on.

```

    CurrentTime = CurrentCycle + CurrentTimeStep / (NodesCycle - 1)

```

```

    ModulationFunction = Modulation(2, CurrentTimeStep * DeltaTime)

```

' establish d matrix

' the secondary end node

```

    D(1) = 2 * zza(1) * T(1 - 1) + zzc(1) * T(1 + 1) - zzb(1) * T(1)

```

' the secondary interior nodes

```

    FOR I = 2 TO Nint2 - 1
      D(I) = zza(I) * T(I - 1) + zzc(I) * T(I + 1) - zzb(I) * T(I)
    NEXT

```

' the sample/secondary interface

```
D(Nint2) = zza(Nint2) * T(Nint2 - 1) + zzc(Nint2) * T(Nint2 + 1) - zzb(Nint2) * T(Nint2)
```

```
' the sample interior nodes
```

```
FOR I = Nint2 + 1 TO Nint1 - 1
  D(I) = zza(I) * T(I - 1) + zzc(I) * T(I + 1) - zzb(I) * T(I)
NEXT
```

```
' the sample/primary interface and adjacent nodes
```

```
D(Nint1) = ModulationFunction * heat(Nint1) + zza(Nint1) * T(Nint1 - 1) + zzc(Nint1) * T(Nint1 + 1) - zzb(Nint1) * T(Nint1)
```

```
' the primary interior nodes
```

```
FOR I = Nint1 + 1 TO Nodestotal - 2
  D(I) = ModulationFunction * heat(I) + zza(I) * T(I - 1) + zzc(I) * T(I + 1) - zzb(I) * T(I)
NEXT
```

```
' the primary edge node
```

```
D(Nodestotal - 1) = ModulationFunction * heat(Nodestotal - 1) + zza(Nodestotal - 1) * T(Nodestotal - 1 - 1) + 2 * zzc(Nodestotal - 1) * T(Nodestotal - 1 + 1) - zzb(Nodestotal - 1) * T(Nodestotal - 1)
```

```
-----
' Solve for the next time step
```

```
CALL SolveTriDiagonal(A(), D(), Tnext(), 1, Nodestotal - 1, ReturnCode)
Tnext(0) = 0
Tnext(Nodestotal) = 0
```

```
-----
' Make calculations based on the temperature profile
```

- ' i) calculate the energy balance if requested
- ' ii) calculate the refractive index profile
- ' ii) solve the beam deflection
- ' iii) process the beam deflection through the lockin amp

```
IF (CurrentCycle >= StartCycle) AND (CurrentTimeStep MOD PrtInctime = 0) THEN
  PrintThisStep = TRUE
  CALL PrintTemp(2, LogTemp)
  IF CalcEnergyBalance THEN
    CALL EnergyBalance(2, HeatInput)
  END IF
ELSE
  PrintThisStep = FALSE
END IF
```

```
FOR I = 0 TO Nint2
  RefIndex(I) = T(I) * dndTsecondary
NEXT
FOR I = Nint1 TO Nodestotal
```

```

    RefIndex(I) = T(I) * dndTprimary
NEXT
CALL ProbeDeflection(2, ThetaPrimary, ThetaSecondary, PrintThisStep)
IF (CurrentCycle >= StartCycle) THEN
    CALL Lockin(2, PrintThisStep)
END IF

```

```

' roll back the time data

```

```

    HeatInput = HeatInput + ModulationFunction * (PowerExcitation - IntensityOut) * DeltaTime

```

```

FOR I = 0 TO Nodestotal
    T(I) = Tnext(I)
NEXT

```

```

NEXT
NEXT

```

```

' done - finish up

```

```

CurrentTimeStep = 0
CALL PrintTemp(3, LogTemp)
IF CalcEnergyBalance THEN CALL EnergyBalance(3, dummy)
CALL ProbeDeflection(3, ThetaPrimary, ThetaSecondary, TRUE)
CALL Lockin(3, OnlyPrimary)
dummy = Modulation(3, dummy)

```

```

CASE ELSE
    RetBlock.code = 0
    RetBlock.text = "no such mode"

```

```

END SELECT

```

```

END SUB

```

Heat

```

' HEAT1.BAS

```

```

' written by James D. Rudnicki
' June 1991
' last update August 1991

```

```

' Description:

```

```

' Beer's law is used to model electrolyte absorption. The light
' is considered to specularly reflect from the electrode. Therefore,
' absorption in the electrolyte is considered on both the inbound and
' outbound path.

```

```
' variables
```

```
' IntensityForward(i) - light intensity during forward direction of
                        propagation of PowerExcitation light
' IntensityReverse(i) - light intensity during reverse direction of
                        propagation of PowerExcitation light
                        (after reflection)
```

```
DEFDBL A-Z
```

```
' include a standard common block file
'$INCLUDE: 'pdscmm.bas'
```

```
DEFSNG A-Z
```

```
SUB HeatFunction (mode AS INTEGER)
```

```
DEFDBL A-Z
```

```
DIM IntensityForwardSurf AS DOUBLE, IntensityReverseSurf AS DOUBLE
DIM IntensityForward(Nodestotal) AS DOUBLE, IntensityReverse(Nodestotal) AS DOUBLE
```

```
SELECT CASE mode
```

```
  CASE 0
```

```
    RetBlock.code = 1
    RetBlock.text = "h1:"
```

```
  CASE 1
```

```
' solve for the light intensities
```

```
' The light is absorbed according to Beer's law. It is
' assumed to be partially reflected by the surface
' and also absorbed on the exit path.
```

```
IntensityForward(Nodestotal - 1) = EXP(LOG(PowerExcitation) - BetaPrimary * .5# *
DeltaX(Nodestotal))
```

```
FOR i = Nodestotal - 2 TO Nint1 STEP -1
```

```
  IntensityForward(i) = EXP(LOG(IntensityForward(i + 1)) - BetaPrimary * .5# * (DeltaX(i + 1) +
DeltaX(i + 2)))
```

```
NEXT
```

```
IntensityForwardSurf = EXP(LOG(IntensityForward(Nint1)) - BetaPrimary * .5# * DeltaX(Nint1 + 1))
IntensityReverseSurf = (1 - BetaSurface) * IntensityForwardSurf
```

```
IF IntensityReverseSurf > 0 THEN
```

```
  IntensityReverse(Nint1 + 1) = EXP(LOG(IntensityReverseSurf) - BetaPrimary * .5# * DeltaX(Nint1 +
1))
```

```
FOR i = Nint1 + 2 TO Nodestotal
```

```
  IntensityReverse(i) = EXP(LOG(IntensityReverse(i - 1)) - BetaPrimary * .5# * (DeltaX(i) + DeltaX(i
- 1)))
```

NEXT

IntensityOut = EXP(LOG(IntensityReverse(Nodestotal)) - BetaPrimary * .5# * DeltaX(Nodestotal))

END IF

' determine the heat term at each node

' it is assumed that all light absorbed at a node is converted to heat

heat(Nint1) = DeltaTime * (IntensityForwardSurf - IntensityReverseSurf) / (.5# * (DeltaX(Nint1 + 1) + DeltaX(Nint1))) * CpInt1

FOR i = Nint1 + 1 TO Nodestotal - 1

heat(i) = (IntensityForward(i) - IntensityForward(i - 1) + IntensityReverse(i) - IntensityReverse(i + 1)) * DeltaTime / (CpDenPrimary * .5# * (DeltaX(i) + DeltaX(i + 1)))

NEXT

END SELECT

END SUB

Modulation

' MOD1.BAS

' written by James Rudnicki

' May 1991

' for use with PDS models.

' This Function is square wave modulation. The wave shape has

' straight sides. The duty cycle does not have to be 50%.

DEFDBL A-Z

DECLARE FUNCTION Modulation# (mode AS INTEGER, time AS DOUBLE)

' include a standard common block file

' \$INCLUDE: 'pdscmm.bas'

FUNCTION Modulation (mode AS INTEGER, time AS DOUBLE)

STATIC FileM AS INTEGER

STATIC Ton AS DOUBLE

DIM wave AS DOUBLE

SELECT CASE mode

CASE 0

RetBlock.code = 1

RetBlock.text = "m1:"

CASE 1

IF LogModulation THEN

FileM = FREEFILE

OPEN "pds_m." + RunName FOR OUTPUT AS FileM

```

END IF
Ton = DutyCycle / Frequency

CASE 2
IF time < Ton THEN
    wave = 1#
ELSE
    wave = 0#
END IF
IF LogModulation THEN
    PRINT #FileM, USING "##.##### ##.#####"; CurrentTime, wave
END IF
Modulation = wave

CASE 3
IF LogModulation THEN
    CLOSE FileM
END IF

END SELECT

END FUNCTION

```

B.2. Tridiagonal Matrix Inverter

' Tridiagonal Matrix Inversion Routines

' written by James Rudnicki
 ' November 1989
 ' contained in file TRIMAT.BAS
 ' compiled in library TRIMAT.QLB
 ' written in QuickBasic v4.5

' Description:

' The two functions contained here are used to invert
 ' the tridiagonal matrix and solve the matrix equation typical
 ' in implicit FDE models:

$$[T] [f] = [d]$$

' where [T] is the tridiagonal matrix composed of elements
 ' a(), b(), and c(), [f] is a vector matrix of the values at the
 ' next time step to be determined, and [d] is a vector matrix of
 ' constants from the current time step. The matrix [T] is inverted
 ' and multiplied by [d] to determine the next time step [f].

' The solution is broken into two steps. In many cases [T] contains
 ' only constants. The calculations can thereby be greatly reduced.
 ' LoadTriDiagonal is called once at the beginning of the model to partially
 ' process the matrix problem. At each time step, SolveTriDiagonal is
 ' called to yield the next time step.

' Algorithm:

' The algorithm is from Lapidus, L. and Pinder, G.F.,
 ' "Numerical solution of Partial Differential Equations in Science
 ' and Engineering," John Wiley, New York, p.217 (1982).

' There is an error in equation (4.7.8a) which was corrected
 ' to read: $f[i] = (d[i] - a[i] * f[i-1]) / \alpha[i]$.

' Local variables available to the two subroutines

DIM SHARED Alpha(2000) AS DOUBLE, Beta(2000) AS DOUBLE

SUB LoadTriDiagonal (a() AS DOUBLE, b() AS DOUBLE, c() AS DOUBLE, n1 AS INTEGER, n2
 AS INTEGER, ReturnCode AS INTEGER)

' a(), b(), and c() are the diagonals of the matrix
 ' n1 is the first element of the matrix and n2 is the last
 ' Using two parameters allows the arrays to be processed for a variety
 ' of boundary conditions.
 ' There is no error checking to speed things up.

DIM i AS INTEGER

ReturnCode = 1

' determine alpha and beta

Alpha(n1) = b(n1)
 Beta(n1) = c(n1) / Alpha(n1)

FOR i = n1 + 1 TO n2 - 1
 Alpha(i) = b(i) - a(i) * Beta(i - 1)
 Beta(i) = c(i) / Alpha(i)
 NEXT

Alpha(n2) = b(n2) - a(n2) * Beta(n2 - 1)

END SUB

SUB SolveTriDiagonal (a() AS DOUBLE, d() AS DOUBLE, u() AS DOUBLE, n1 AS INTEGER, n2
 AS INTEGER, ReturnCode AS INTEGER)

' a() is the same diagonal passed to the LoadTriDiagonal subroutine
 ' d() is the vector matrix of knowns
 ' u() is the values at the next time step to be determined
 ' n1 and n2 are the limits of the matrix - again allowing for a variety
 ' of boundary conditions to be used
 ' f() holds an intermediate calculation

DIM i AS INTEGER
 DIM f(2000) AS DOUBLE

RetCode = 1

' determine f

f(n1) = d(n1) / Alpha(n1)


```

FOR i = n1 + 1 TO n2
  f(i) = (d(i) - a(i) * f(i - 1)) / Alpha(i)
NEXT

' determine u

u(n2) = f(n2)

FOR i = n2 - 1 TO n1 STEP -1
  u(i) = f(i) - Beta(i) * u(i + 1)
NEXT

END SUB

```

C. Probe Modules

C.1. Probe 1

```

' Probe beam deflection
' variant 1a
'
' for use with the PDS5i program and PDSCX program
'
' written by James D. Rudnicki
' last updated April 1991
'
' this module requires the function in DFDXB.BAS
'
' this module calculates the deflection of the probe beam
' assuming:
' - the beam is an infinitely thin ray,
' - the probe deflection is small, and
' - the probe is NOT parallel to the sample.
'
' This variant considers the refractive index on each side of the beam
' and calculates the gradient
'
' The answer is returned in microradians.
'
' 23 April 1991 - variant a
' - Correction for refraction at the cell exit is made. It is assumed that
' air is the surrounding medium. The displacement of the beam
' through the cell windows is NOT considered. This should be negligible.
' This is made by deleting RefIndex0 from the denominator of the deflection
' equation.
' - Correction is made for negative probe beam angles. This will allow
' the beam to travel towards the sample. The user must assure
' that the beam does not hit the sample!

```

```

DEFDBL A-Z
' $INCLUDE: 'pdscmm.bas'

DIM ProbexPrimary(50) AS DOUBLE, ProbeIndexPrimary(50) AS INTEGER
DIM ProbexSecondary(50) AS DOUBLE, ProbeIndexSecondary(50) AS INTEGER

DECLARE FUNCTION dfdx# (x AS DOUBLE, fa AS DOUBLE, fb AS DOUBLE, fc AS DOUBLE, xa
AS DOUBLE, xb AS DOUBLE, xc AS DOUBLE)

DEFSNG A-Z
SUB ProbeDeflection (Mode AS INTEGER, ThetaPrimary AS DOUBLE, ThetaSecondary AS
DOUBLE, PrintThisStep AS INTEGER)

DEFDBL A-Z

' This subroutine calculates the probe deflection
' The Mode parameter controls the action taken by the routine
' Mode=0 - identify thyself
' Mode=1 - initialize the routine
'   PrintThisStep=False - calc both primary and secondary
'   =True - calc only primary gradient
' Mode=2 - calculate the deflection
' Mode=3 - close up

DIM dx AS DOUBLE, dndx AS DOUBLE
DIM i AS INTEGER, j AS INTEGER

STATIC dy AS DOUBLE
STATIC NodesY AS INTEGER
STATIC BothSides AS INTEGER
STATIC FileN AS INTEGER

SHARED ProbexPrimary() AS DOUBLE, ProbeIndexPrimary() AS INTEGER
SHARED ProbexSecondary() AS DOUBLE, ProbeIndexSecondary() AS INTEGER

CONST Mask1 = "##.### #####.####.####.####"
CONST TRUE% = -1
CONST FALSE% = NOT TRUE

SELECT CASE Mode

CASE 0
  RetBlock.code = 1
  RetBlock.text = "p1a:"

' calculate the path of the unperturbed probe beam
' then setup an index table to locate node numbers quickly - the index table
' ProbeIndexPrimary contains the number of the node adjacent to and farther
' from the electrode.

CASE 1
  IF NOT (PrintThisStep) THEN
    BothSides = TRUE
  ELSE

```

```

BothSides = FALSE
END IF

NodesY = 50
dy = InteractionLength / NodesY
dx = dy * TAN(ProbeAngle)

FOR i = 0 TO NodesY
  ProbexPrimary(i) = xcoord(Nint1) + X0probe + i * dx
  j = Nint1
  DO WHILE xcoord(j) < ProbexPrimary(i)
    j = j + 1
  LOOP
  ProbeIndexPrimary(i) = j
NEXT

IF BothSides THEN
  FOR i = 0 TO NodesY
    ProbexSecondary(i) = xcoord(Nint2) - X0probe - i * dx
    j = Nint2
    DO WHILE xcoord(j) < ProbexSecondary(i)
      j = j - 1
    LOOP
    ProbeIndexSecondary(i) = j
  NEXT
END IF

FileN = FREEFILE
OPEN "pds_a." + RunName FOR OUTPUT AS #FileN

CASE 2
  ThetaPrimary = 0
  ThetaSecondary = 0
  FOR i = 1 TO NodesY
    j = ProbeIndexPrimary(i)
    dndx = dfdx(ProbexPrimary(i), RefIndex(j - 1), RefIndex(j), RefIndex(j + 1), xcoord(j - 1), xcoord(j),
xcoord(j + 1))
    ThetaPrimary = ThetaPrimary + dndx
    IF BothSides THEN
      j = ProbeIndexSecondary(i)
      dndx = dfdx(ProbexSecondary(i), RefIndex(j - 1), RefIndex(j), RefIndex(j + 1), xcoord(j - 1),
xcoord(j), xcoord(j + 1))
      ThetaSecondary = ThetaSecondary + dndx
    END IF
  NEXT
  ThetaPrimary = ThetaPrimary * dy * 1000000#
  IF BothSides THEN
    ThetaSecondary = ThetaSecondary * dy * 1000000#
  END IF

  IF PrintThisStep THEN
    IF BothSides THEN
      PRINT USING "Primary deflection ####.#### " + CHR$(230) + "rad"; ThetaPrimary
      PRINT USING "Secondary deflection ####.#### " + CHR$(230) + "rad"; ThetaSecondary
    END IF
  END IF

```

```

    PRINT #FileN, USING Mask1; CurrentTime; ThetaPrimary; ThetaSecondary
  ELSE
    PRINT USING "Primary deflection ####.#### " + CHR$(230) + "rad"; ThetaPrimary
    PRINT #FileN, USING Mask1; CurrentTime; ThetaPrimary
  END IF
END IF

CASE 3
  CLOSE FileN

END SELECT

END SUB

```

C.2. Probe 2

```

' PROBE2AX.BAS - Probe beam deflection
' type 2
' variant a - responds to mode 0 calls
' variant x - nodes changeable from input data file
'
' written by James D. Rudnicki
' last updated July 1991
'
' Required external routines:
'   requires the subroutine DFDX be attached - this is contained
'   in DFDXB.BAS
'
' Description:
'   for use with the PDS6i program and PDSCX program
'
'   this module calculates the deflection of the probe beam
'   assuming:
'   - the beam is a Gaussian beam of finite diameter,
'   - the probe deflection is small, and
'   - the probe is parallel to the sample.
'   a correction is made for refraction at the exit of the cell - it
'   is assumed that air is the surrounding medium - the properties of
'   the cell windows are not relevant
'
'   The sub divides the probe beam into small elements. The grid is
'   independent of the refractive index grid. Trapezoidal integration is
'   used to calculate the intensity weighted integral. The refractive index
'   gradient is calculated with a 3rd order interpolating polynomial.
'   Since the two grids do not match, an interpolating numerical derivative
'   is required.
'
'   The integral solves easily. Few nodes are required--50 are used but as
'   few as 10 often gave reasonable precision. Trapezoidal integration was
'   a moderate, but not large improvement to rectangular integration.
'
' 29 July 90
' This sub was checked against three gradients for which an analytic

```

```
' solution could be derived. They were linear, 2nd, and 3rd order
' refractive index profiles:  $n=n_0 + c * x^m$ 
' The agreement with the analytic solutions was good. The linear and
' quadratic agreed to 6 significant figures. The cubic varied from
' the analytic solution by < 0.1%.
```

```
' 6 May 91
```

```
' NOTE - This module does not allow the probe beam to extend beyond
' the region of calculation. If a large beam is used, it is quite possible
' that the beam will extend beyond the typical 1000um region calculated
' this will cause the program to bomb. Since array limits are not checked
' in compiled programs, this error may go undetected during debugging.
```

```
DEFDBL A-Z
```

```
' $INCLUDE: 'pdscmm.bas'
```

```
DECLARE FUNCTION dfdx# (X AS DOUBLE, fim1 AS DOUBLE, fi AS DOUBLE, fip1 AS
DOUBLE, xim1 AS DOUBLE, xi AS DOUBLE, xip1 AS DOUBLE)
```

```
  DIM ProbexPrimary(0 TO 200) AS DOUBLE, ProbeIndexPrimary(0 TO 200) AS INTEGER,
  WeightPrimary(0 TO 200) AS DOUBLE
```

```
  DIM ProbexSecondary(0 TO 200) AS DOUBLE, ProbeIndexSecondary(0 TO 200) AS INTEGER,
  WeightSecondary(0 TO 200) AS DOUBLE
```

```
DEFSNG A-Z
```

```
  SUB ProbeDeflection (Mode AS INTEGER, ThetaPrimary AS DOUBLE, ThetaSecondary AS
DOUBLE, PrintThisStep AS INTEGER)
```

```
DEFDBL A-Z
```

```
  DIM i AS INTEGER
```

```
  DIM xim1 AS DOUBLE, xi AS DOUBLE, xip1 AS DOUBLE
```

```
  DIM dndx AS DOUBLE
```

```
  STATIC dx AS DOUBLE, WeightPrimaryTotal AS DOUBLE, WeightSecondaryTotal AS DOUBLE
```

```
  STATIC BothSides AS INTEGER
```

```
  STATIC NFirstPrimary AS INTEGER, NFirstSecondary AS INTEGER
```

```
  STATIC FileN AS INTEGER
```

```
  SHARED ProbexPrimary() AS DOUBLE, ProbeIndexPrimary() AS INTEGER, WeightPrimary() AS
DOUBLE
```

```
  SHARED ProbexSecondary() AS DOUBLE, ProbeIndexSecondary() AS INTEGER, WeightSecondary()
AS DOUBLE
```

```
  CONST Mask1 = "###.### , #####.##### , #####.#####"
```

```
  CONST Mask2 = "###.### , #####.##### "
```

```
  CONST SqrtPi = 1.772453851#
```

```
' The Mode parameter controls the action taken by the routine
```

```
' If Mode=1 - initialize the routine
```

```
'   PrintThisStep=False - calc both primary and secondary
'   =True - calc only primary gradient
```

```
' Mode=2 - calculate the probe deflections
```

```
' Mode=3 - print file tail & close files
```

SELECT CASE Mode

CASE 0

RetBlock.code = 1

RetBlock.text = "p2ax:"

CASE 1

' Initialization routine

' The probe beam is modelled from +/- 2.5r where r is the 1/e radius.

' The probe beam is discretized into ProbeNodesX+1 elements. The elements

' are numbered starting at 0 which is the side of the probe beam closest to

' the electrode. For each element, ProbexPrimary or ProbexSecondary contains

' the distance of that element from the electrode surface (in um). The center

' of the probe beam is allowed to be closer than 2.5r to the electrode surface.

' Elements which result in negative ProbexPrimary/Secondary's will be ignored.

' An index table is setup to speed calculations. For each element, the table

' contains the node number (from the temperature distribution) which is

' immediately adjacent to the probe beam element and on the side farther

' from the sample.

' An intensity weight is calculated for each probe beam element. These need

' only to be calculated once. The probe beam elements which hit the edge of

' the electrode are ignored by assigning the element a weight of zero

BothSides = NOT (PrintThisStep)

dx = 5 * ProbeRadius / ProbeNodesX

j = Nint1

XcoordInt1 = xcoord(Nint1)

NFirstPrimary = 0

FOR i = 0 TO ProbeNodesX

ProbexPrimary(i) = XcoordInt1 + X0probe - 2.5 * ProbeRadius + i * dx

IF ProbexPrimary(i) > XcoordInt1 THEN

DO WHILE xcoord(j) < ProbexPrimary(i)

j = j + 1

LOOP

ProbeIndexPrimary(i) = j

WeightPrimary(i) = EXP((- (ProbexPrimary(i) - (X0probe + XcoordInt1)) ^ 2) / (ProbeRadius ^ 2))

ELSE

NFirstPrimary = i

ProbeIndexPrimary(i) = Nint1 + 1

WeightPrimary(i) = 0

END IF

NEXT

WeightPrimaryTotal = WeightPrimary(0)

FOR i = 1 TO ProbeNodesX - 1

WeightPrimaryTotal = WeightPrimaryTotal + 2 * WeightPrimary(i)

NEXT

WeightPrimaryTotal = WeightPrimaryTotal + WeightPrimary(ProbeNodesX)

WeightPrimaryTotal = dx * WeightPrimaryTotal / 2

IF BothSides THEN

j = Nint2

```

XcoordInt2 = xcoord(Nint2)
NFirstSecondary = 0
FOR i = 0 TO ProbeNodesX
  ProbexSecondary(i) = XcoordInt2 - X0probe + 2.5 * ProbeRadius - i * dx
  IF ProbexSecondary(i) < XcoordInt2 THEN
    DO WHILE xcoord(j) > ProbexSecondary(i)
      j = j - 1
    LOOP
    ProbeIndexSecondary(i) = j
    WeightSecondary(i) = EXP((- (ProbexSecondary(i) - (XcoordInt2 - X0probe)) ^ 2) / (ProbeRadius ^
2))
  ELSE
    NFirstSecondary = i
    ProbeIndexSecondary(i) = Nint2
    WeightSecondary(i) = 0
  END IF
NEXT

WeightSecondaryTotal = WeightSecondary(0)
FOR i = 1 TO ProbeNodesX - 1
  WeightSecondaryTotal = WeightSecondaryTotal + 2 * WeightSecondary(i)
NEXT
WeightSecondaryTotal = WeightSecondaryTotal + WeightSecondary(ProbeNodesX)
WeightSecondaryTotal = dx * WeightSecondaryTotal / 2

END IF

FileN = FREEFILE
OPEN "pds_a." + RunName FOR OUTPUT AS #FileN

CASE 2
' calculate the deflection of the beam
' this is simply an intensity weighted average of the probe beam
' element deflections - correction is made for the refraction at the
' exit of the cell - this is done by eliminating RefIndex0 from the
' denominator of the final equation

i = NFirstPrimary
j = ProbeIndexPrimary(i)
xi = xcoord(j)
xim1 = xcoord(j - 1)
xip1 = xcoord(j + 1)
dndx = dfdx(ProbexPrimary(i), RefIndex(j - 1), RefIndex(j), RefIndex(j + 1), xim1, xi, xip1)
ThetaPrimary = WeightPrimary(i) * dndx
ThetaSecondary = 0

FOR i = NFirstPrimary + 1 TO ProbeNodesX - 1
  j = ProbeIndexPrimary(i)
  xi = xcoord(j)
  xim1 = xcoord(j - 1)
  xip1 = xcoord(j + 1)
  dndx = dfdx(ProbexPrimary(i), RefIndex(j - 1), RefIndex(j), RefIndex(j + 1), xim1, xi, xip1)
  ThetaPrimary = ThetaPrimary + 2 * WeightPrimary(i) * dndx
NEXT

```

```

i = ProbeNodesX
xi = xcoord(j)
xim1 = xcoord(j - 1)
xip1 = xcoord(j + 1)
dndx = dfdx(ProbexPrimary(i), RefIndex(j - 1), RefIndex(j), RefIndex(j + 1), xim1, xi, xip1)
ThetaPrimary = ThetaPrimary + WeightPrimary(i) * dndx

ThetaPrimary = dx * ThetaPrimary * InteractionLength * 1000000# / (WeightPrimaryTotal * 2)

IF BothSides THEN
  i = NFirstSecondary
  j = ProbeIndexSecondary(i)
  xi = xcoord(j)
  xim1 = xcoord(j - 1)
  xip1 = xcoord(j + 1)
  dndx = dfdx(ProbexSecondary(i), RefIndex(j - 1), RefIndex(j), RefIndex(j + 1), xim1, xi, xip1)
  ThetaSecondary = WeightSecondary(i) * dndx

  FOR i = NFirstSecondary + 1 TO ProbeNodesX - 1
    j = ProbeIndexSecondary(i)
    xi = xcoord(j)
    xim1 = xcoord(j - 1)
    xip1 = xcoord(j + 1)
    dndx = dfdx(ProbexSecondary(i), RefIndex(j - 1), RefIndex(j), RefIndex(j + 1), xim1, xi, xip1)
    ThetaSecondary = ThetaSecondary + 2 * WeightSecondary(i) * dndx
  NEXT

  i = ProbeNodesX
  xi = xcoord(j)
  xim1 = xcoord(j - 1)
  xip1 = xcoord(j + 1)
  dndx = dfdx(ProbexSecondary(i), RefIndex(j - 1), RefIndex(j), RefIndex(j + 1), xim1, xi, xip1)
  ThetaSecondary = ThetaSecondary + WeightSecondary(i) * dndx

  ThetaSecondary = dx * ThetaSecondary * InteractionLength * 1000000# / (WeightSecondaryTotal *
2)

END IF

IF PrintThisStep THEN
  IF BothSides THEN
    PRINT USING "Primary deflection ####.##### " + CHR$(230) + "rad"; ThetaPrimary
    PRINT USING "Secondary deflection ####.##### " + CHR$(230) + "rad"; ThetaSecondary
    PRINT #FileN, USING Mask1; CurrentTime; ThetaPrimary; ThetaSecondary
  ELSE
    PRINT USING "Primary deflection ####.##### " + CHR$(230) + "rad"; ThetaPrimary
    PRINT #FileN, USING Mask2; CurrentTime; ThetaPrimary
  END IF
END IF

CASE 3
' close up shop

```



```

CLOSE FileN
END SELECT
END SUB

```

C.3. Interpolating Derivative

```

'DFDXB.BAS - Interpolating Numerical Derivative
'
' written by James D. Rudnicki
' last updated July 1991
'
' This function estimates a first order derivative
' The calling routine supplies three (x,f(x)) points and
' the x value at which the derivative is to be calculated
'
' A second-order Lagrange polynomial is fit to the points, and
' the derivative is calculated with the expression
' from Steven C. Chapra, and Raymond P. Canale, "Numerical Methods for
' Engineers, 2nd ed.," McGraw-Hill, p532-3, 1988.

DECLARE FUNCTION dfdx# (x AS DOUBLE, fa AS DOUBLE, fb AS DOUBLE, fc AS DOUBLE, xa
AS DOUBLE, xb AS DOUBLE, xc AS DOUBLE)

FUNCTION dfdx# (x AS DOUBLE, fa AS DOUBLE, fb AS DOUBLE, fc AS DOUBLE, xa AS
DOUBLE, xb AS DOUBLE, xc AS DOUBLE)

    dfdx = fa * (2 * x - xb - xc) / ((xa - xb) * (xa - xc)) + fb * (2 * x - xa - xc) / ((xb - xa) * (xb - xc)) + fc *
    (2 * x - xa - xb) / ((xc - xa) * (xc - xb))

END FUNCTION

```

D. Lockin Modules

D.1. Time Domain

```

' Lockin Simulator Program - Averaging outputs
'
' written by James Rudnicki
' last updated September 89
' written in QuickBasic v4.5

DEFDBL A-Z

DECLARE SUB Average4 (X AS DOUBLE, y AS DOUBLE, mode AS INTEGER)
DECLARE SUB Average3 (X AS DOUBLE, y AS DOUBLE, mode AS INTEGER)
DECLARE SUB Average2 (X AS DOUBLE, y AS DOUBLE, mode AS INTEGER)

```

```

DECLARE SUB Average1 (X AS DOUBLE, y AS DOUBLE, mode AS INTEGER)
DECLARE FUNCTION ArcTan4# (x1 AS DOUBLE, y1 AS DOUBLE)

```

```

' Lockin Simulator
' for use with the PDS5i program

```

```

' written by James D. Rudnicki
' last updated October 1989

```

```

' this lockin uses averaging outputs for speed of computation
' it is feasible that the rolling averages could overflow

```

```

' $INCLUDE: 'pds5icmm.bas'

```

```

DEFSNG A-Z
FUNCTION ArcTan4# (X AS DOUBLE, y AS DOUBLE)

```

```

    DIM z AS DOUBLE
    CONST Pi = 3.141592654#

```

```

    IF X = 0 THEN
        z = Pi / 2
    ELSE
        z = ATN(ABS(y / X))
    END IF

```

```

    IF X >= 0 THEN
        IF y >= 0 THEN
            z = z
        ELSE
            z = -z
        END IF
    ELSE
        IF y > 0 THEN
            z = Pi - z
        ELSE
            z = -Pi + z
        END IF
    END IF

```

```

    ArcTan4# = 180 * z / Pi

```

```

END FUNCTION

```

```

SUB Average1 (add AS DOUBLE, average AS DOUBLE, mode AS INTEGER) STATIC

```

```

' if mode=1 then initialize the average
' if mode=2 then add a value and compute average

```

```

    DIM SampleCount AS INTEGER

```

```

    SELECT CASE mode

```

```
CASE 1
  SampleCount = 0
  average = 0#

CASE 2
  SampleCount = SampleCount + 1
  IF SampleCount = 1 THEN
    average = add
  ELSE
    average = ((SampleCount - 1) * average + add) / SampleCount
  END IF

END SELECT

END SUB

SUB Average2 (add AS DOUBLE, average AS DOUBLE, mode AS INTEGER) STATIC
' if mode=1 then initialize the average
' if mode=2 then add a value and compute average

DIM SampleCount AS INTEGER

SELECT CASE mode

CASE 1
  SampleCount = 0
  average = 0#

CASE 2
  SampleCount = SampleCount + 1
  IF SampleCount = 1 THEN
    average = add
  ELSE
    average = ((SampleCount - 1) * average + add) / SampleCount
  END IF

END SELECT

END SUB

SUB Average3 (add AS DOUBLE, average AS DOUBLE, mode AS INTEGER) STATIC
' if mode=1 then initialize the average
' if mode=2 then add a value and compute average

DIM SampleCount AS INTEGER

SELECT CASE mode

CASE 1
  SampleCount = 0
  average = 0#
```

```

CASE 2
  SampleCount = SampleCount + 1
  IF SampleCount = 1 THEN
    average = add
  ELSE
    average = ((SampleCount - 1) * average + add) / SampleCount
  END IF
END SELECT

END SUB

SUB Average4 (add AS DOUBLE, average AS DOUBLE, mode AS INTEGER) STATIC
' if mode=1 then initialize the average
' if mode=2 then add a value and compute average

DIM SampleCount AS INTEGER

SELECT CASE mode

CASE 1
  SampleCount = 0
  average = 0#

CASE 2
  SampleCount = SampleCount + 1
  IF SampleCount = 1 THEN
    average = add
  ELSE
    average = ((SampleCount - 1) * average + add) / SampleCount
  END IF
END SELECT

END SUB

SUB Lockin (mode AS INTEGER, PrintThisStep AS INTEGER)

  SHARED DeltaTime AS DOUBLE, CurrentTimeStep AS INTEGER
  SHARED CycleLength AS DOUBLE
  SHARED ThetaPrimary AS DOUBLE, ThetaSecondary AS DOUBLE
  SHARED PhasePrimary AS DOUBLE, MagnitudePrimary AS DOUBLE
  SHARED PhaseSecondary AS DOUBLE, MagnitudeSecondary AS DOUBLE
  SHARED OutA AS DOUBLE, OutB AS DOUBLE, OutC AS DOUBLE, OutD AS DOUBLE

  DIM Time AS DOUBLE, dummy AS DOUBLE
  CONST Pi = 3.141592654#
  CONST Mask1 = "##.## #####.##### ####.## #####.##### ####.##"

  SELECT CASE mode
    CASE 1
      CALL Average1(dummy, dummy, 1)
      CALL Average2(dummy, dummy, 1)

```

```

CALL Average3(dummy, dummy, 1)
CALL Average4(dummy, dummy, 1)

OPEN "pds5i_d.dat" FOR OUTPUT AS #3
PRINT #3, RunName; "-"; Version
PRINT #3, "cyc  pri def  phase  sec def  phase"

CASE 2

' synchronous demodulation and filtration
Time = CurrentTimeStep * DeltaTime
DemodA = SGN(SIN(2# * Pi * (Time / CycleLength + Offset)))
DemodB = SGN(SIN(2# * Pi * (Time / CycleLength + Offset + .25)))
CALL Average1(DemodA * ThetaPrimary, OutA, 2)
CALL Average2(DemodB * ThetaPrimary, OutB, 2)
CALL Average3(DemodA * ThetaSecondary, OutC, 2)
CALL Average4(DemodB * ThetaSecondary, OutD, 2)

' calculate magnitude and phase

MagnitudePrimary = SQR(OutA ^ 2 + OutB ^ 2)
PhasePrimary = ArcTan4(OutA, OutB)
MagnitudeSecondary = SQR(OutC ^ 2 + OutD ^ 2)
PhaseSecondary = ArcTan4(OutC, OutD)

IF PrintThisStep THEN
PRINT USING Mask1; CurrentTime; MagnitudePrimary; PhasePrimary; MagnitudeSecondary;
PhaseSecondary
PRINT #3, USING Mask1; CurrentTime; MagnitudePrimary; PhasePrimary; MagnitudeSecondary;
PhaseSecondary
END IF

CASE 3
CLOSE 3

END SELECT

END SUB

```

D.2. Frequency Domain

```

' Lockin Amplifier Simulator Program
' LOCKIN7
' frequency domain model - background subtraction

' written by James Rudnicki
' February 91
' last updated March 91
' written in QuickBasic v4.5

' Description

' This module simulates a lockin amplifier in the frequency

```

' domain.

' Lockin 7 incorporates a background subtraction filter. It is designed to subtract a linear sloping background. Precision is good up to very small Signal-to-Background ratios (SBR). The SBR is defined in the frequency domain. At SBR's of less than 0.5, errors in magnitude are less than 1% and phase errors less than 5 degrees. This is a significant improvement over Lockin 6 and the time domain lockin models.

' Description of Algorithm

' A Fourier transform is used to convert the signal train (a series of signal data points) into a frequency spectrum. A cosine series is calculated. The spectrum is calculated only at 5 frequencies, the modulation frequency and 2 frequencies above and below. The routine which produces the signal passes the signal to the lockin one point at a time.

' When all the points have been passed, the lockin will calculate the result. The 2 points on each side of the modulation frequency are used to calculate a baseline value. A 4 point interpolation routine is used. The baseline is subtracted from the raw signal, and the filtered result is returned.

' Notes on usage

' The SUB Lockin is called in the same manner as the time-domain lockin modules. The output during the calculation is not produced. This is because the Fourier calculation is only accurate after all the data points have been passed to the subroutine. The calculation is accumulated--the entire signal need not be stored.

' 4 June 91 - JDR -

' SBR calculation was corrected by reversing the sign. The negation of the baseline vector before being passed to SumSine, resulted in previous SBR's to be reported as negative when they were actually positive.

```
DECLARE SUB Lagrange4 (arry() AS ANY, interp AS ANY)
DECLARE SUB SumSine (a AS ANY, B AS ANY, C AS ANY)
DECLARE FUNCTION ArcTan4# (x1 AS DOUBLE, y1 AS DOUBLE)
```

' The following user-defined variable types are used:

- ' Complex - complex variable
 - ' .re is real part
 - ' .im is imaginary part
- ' PolarVector - used to represent sine waves
 - ' .mag is magnitude
 - ' .ph is phase

' For those not familiar with user-defined types:

' User-defined types are collections of regular variables. The complex type is a good example. A complex variable has a real and imaginary component. The user-defined type Complex, combines

' these into one variable. To access the individual parts of a Complex
' type variable, .re or .im are appended onto the base name.

```
TYPE Complex
  re AS DOUBLE
  im AS DOUBLE
END TYPE
```

```
TYPE Polarvector
  mag AS DOUBLE
  ph AS DOUBLE
END TYPE
```

' attach the standard common blocks
DEFDBL A-Z
' \$INCLUDE: 'pdscmm.bas'

```
DEFSNG A-Z
  FUNCTION ArcTan4# (y AS DOUBLE, X AS DOUBLE)
```

' This routine returns the 4 quadrant Arc tangent
' in degrees. The angle returned is between -Pi/2 to +Pi/2.

```
DIM z AS DOUBLE
CONST Pi = 3.141592654#
```

```
IF X = 0 THEN
  z = Pi / 2
ELSE
  z = ATN(ABS(y / X))
END IF
```

```
IF X >= 0 THEN
  IF y >= 0 THEN
    z = z
  ELSE
    z = -z
  END IF
ELSE
  IF y > 0 THEN
    z = Pi - z
  ELSE
    z = -Pi + z
  END IF
END IF
```

```
ArcTan4# = z
```

```
END FUNCTION
```

```
SUB Lagrange4 (arry() AS Polarvector, interp AS Polarvector)
```

' 4 point Lagrange Interpolation
' A third order polynomial is fit to the 4 points. From this

' interpolations are made.

' This routine accepts PolarVector arguments -- presumably from
' a Fourier transform -- which are of the form (X.mag,Y.ph).

' This routine takes the values in array and interpolates a new value
' The values in array are assumed to be equally spaced on either side
' of the point to be interpolated:

' array(-2) array(-1) interp array(1) array(2)

interp.mag = -array(-2).mag / 6 + 2 * array(-1).mag / 3 + 2 * array(1).mag / 3 - array(2).mag / 6
interp.ph = -array(-2).ph / 6 + 2 * array(-1).ph / 3 + 2 * array(1).ph / 3 - array(2).ph / 6

END SUB

SUB Lockin (mode AS INTEGER, Pass AS INTEGER) STATIC

DEFDBL A-Z

' Mode controls the operation of the sub:

- ' 1 - opens files and initializes
- ' Pass contains the number of data points - this must be known
' up front
- ' 2 - add a value to the accumulators
- ' if Pass is TRUE then calc only the primary signal
- ' 3 - calculate the answer and close up
- ' if Pass is TRUE then print only the primary signal

DIM Primary(-2 TO 2) AS Complex
DIM Secondary(-2 TO 2) AS Complex
DIM raw(-2 TO 2) AS Polarvector

DIM Back AS Polarvector
DIM Corrected AS Polarvector
DIM baseline AS Polarvector

DIM SBRprimary AS SINGLE, SBRsecondary AS SINGLE
DIM n AS LONG, r AS LONG, s AS LONG
DIM FileLockin AS INTEGER

CONST Pi = 3.141592654#
CONST TwoPi = 2 * Pi
CONST mask1 = "#####.##### ####.### ####.#####"
CONST mask2 = "#####.##### ####.### ####.##### ####.### ####.##### ####.#####"

SELECT CASE mode

CASE 0

RetBlock.code = 1
RetBlock.text = "I7"

CASE 1


```
' establish a file and initialize paramters
' n is the number of data points
' r is the data point number
' s is the number of cycles in the signal
```

```
FileLockin = FREEFILE
OPEN "pds_d." + RunName FOR OUTPUT AS FileLockin
n = Pass
r = 0
s = EndCycle - StartCycle + 1
ERASE Primary
ERASE Secondary
```

CASE 2

```
' accumulate the transforms - if Pass is TRUE then calculate
' only the primary signal
```

```
FOR i = -2 TO 2
  Primary(i).re = Primary(i).re + ThetaPrimary * COS(TwoPi * r * (s + i) / n)
  Primary(i).im = Primary(i).im + ThetaPrimary * SIN(TwoPi * r * (s + i) / n)
NEXT
IF NOT (Pass) THEN
  FOR i = -2 TO 2
    Secondary(i).re = Secondary(i).re + ThetaSecondary * COS(TwoPi * r * (s + i) / n)
    Secondary(i).im = Secondary(i).im + ThetaSecondary * SIN(TwoPi * r * (s + i) / n)
  NEXT
END IF

r = r + 1
```

CASE 3

```
' convert transform to vector form
```

```
FOR i = -2 TO 2
  raw(i).mag = SQR(Primary(i).re ^ 2 + Primary(i).im ^ 2)
  raw(i).ph = ArcTan4#(Primary(i).re, Primary(i).im)
NEXT
```

```
' calculate the baseline by interpolation
```

```
CALL Lagrange4(raw(), baseline)
```

```
' negate the magnitude of the baseline and add to the raw signal
```

```
baseline.mag = -baseline.mag
CALL SumSine(raw(0), baseline, Corrected)
```

```
' adjust to actual units
```

```
MagnitudePrimary = 2 * Corrected.mag / n
PhasePrimary = Corrected.ph * 180 / Pi
SBRprimary = -MagnitudePrimary * n / (baseline.mag * 2)
```

' if Both sides are to be calculated repeat the above

```

IF NOT (Pass) THEN
  FOR i = -2 TO 2
    raw(i).mag = SQR(Secondary(i).re ^ 2 + Secondary(i).im ^ 2)
    raw(i).ph = ArcTan4#(Secondary(i).re, Secondary(i).im)
  NEXT
  CALL Lagrange4(raw(), baseline)
  baseline.mag = -baseline.mag
  CALL SumSine(raw(0), baseline, Corrected)
  MagnitudeSecondary = 2 * Corrected.mag / n
  PhaseSecondary = Corrected.ph * 180 / Pi
  SBRsecondary = -MagnitudeSecondary * n / (baseline.mag * 2)
END IF

```

' print out the results to screen and file

```

IF Pass THEN
  PRINT USING mask1; MagnitudePrimary; PhasePrimary; SBRprimary
  PRINT #FileLockin, USING mask1; MagnitudePrimary; PhasePrimary; SBRprimary
ELSE
  PRINT USING mask2; MagnitudePrimary; PhasePrimary; MagnitudeSecondary; PhaseSecondary;
  SBRprimary; SBRsecondary
  PRINT #FileLockin, USING mask2; MagnitudePrimary; PhasePrimary; MagnitudeSecondary;
  PhaseSecondary; SBRprimary; SBRsecondary
END IF

```

CLOSE FileLockin

END SELECT

END SUB

DEFSNG A-Z

SUB SumSine (a AS Polarvector, B AS Polarvector, C AS Polarvector)

' This routine sums two sine waves which have the same frequency

```

  C.ph = ArcTan4((a.mag * SIN(a.ph) + B.mag * SIN(B.ph)), (a.mag * COS(a.ph) + B.mag *
  COS(B.ph)))
  C.mag = a.mag * COS(a.ph) / COS(C.ph) + B.mag * COS(B.ph) / COS(C.ph)

```

END SUB

E. Sample Input File

The input to the program is through a easily constructed input file.

The format is not strict as in typical programs, but instead is free format.

Variables are set with "*variablename* = 1234.5" statements. The possible variable names are described in the PDS Base code. Multiple set statements can be combined on one line if separated by a space or semicolon. Once all variables are set (there are NO default values) the instruction *solve* cause the model to run with the given paramaters. After that a parameter can be changed and *solve* issued again. Any number of runs can be combined into one input file. This makes large parametric studies very easy. The sample input file below demonstrates the flexibility of this input method.

commandfile

```
*
* Logical switches are entered 0=No anything else=Yes
* Text strings must not have spaces.
* Values can be entered in decimal or scientific notation.
* Anything after the '*' is ignored
* Case is unimportant.
* Statements are separated by any of the following:
* (comma,semicolon,equal,space)
*
* These are the baseline settings.
*
Materials= water(0%a):Pt(125um):PFA
Kprimary= .000606 ;CpPrimary= 4181 ;DenPrimary= .000000001
Ksample= .0716 ;CpSample= 133 ;DenSample= .00000002145
Ksecondary= 1.95d-4 ;CpSecondary= 1172# ;DenSecondary= 2.15d-9
LPrimary= 1000 ;LSample= 125 ;LSecondary= 1000
NodesCycle= 201 ;NodesPrimary= 401 ;NodesSample= 51 ;NodesSecondary= 401
PowerExcitation= .0001389
Frequency= .01 ;DutyCycle= .5
EndCycle= 10 ;StartCycle= 7
PrIncTime= 10 ;PrIncPrimary= 40 ;PrIncSample= 10 ;PrIncSecondary= 40
X0probe= 100 ;ProbeAngle= 0 ;InteractionLength= 9000 ;ProbeRadius= 132
dndTprimary= -.0000000788 ;dndTsecondary= 0
BetaPrimary= 0 ;BetaSurface= .2
LogNodes=0 ; LogModulation=0
LogTemp= 0 ;CalcBalance= 0
VariableSpacing= -1
OnlyPrimary= -1
RefIndex0= 0
*
* This study will vary the modulation frequency at several probe
* offsets. There are 5 frequencies at 8 offsets. The forty runs
* took 24 hours on a 286/287-10MHz PC.
* Each run is stored in a separate series of files with the extension
* given by the 'run' variable.
*
```

```
x0probe=80
run=sa1, frequency=.005, write solve
run=sa2, frequency=.01, write solve
run=sa3, frequency=.02, write solve
run=sa4, frequency=.03, write solve
run=sa5, frequency=.04, write solve
x0probe=100
run=sb1, frequency=.005, write solve
run=sb2, frequency=.01, write solve
run=sb3, frequency=.02, write solve
run=sb4, frequency=.03, write solve
run=sb5, frequency=.04, write solve
x0probe=120
run=sc1, frequency=.005, write solve
run=sc2, frequency=.01, write solve
run=sc3, frequency=.02, write solve
run=sc4, frequency=.03, write solve
run=sc5, frequency=.04, write solve
x0probe=140
run=sd1, frequency=.005, write solve
run=sd2, frequency=.01, write solve
run=sd3, frequency=.02, write solve
run=sd4, frequency=.03, write solve
run=sd5, frequency=.04, write solve
x0probe=160
run=se1, frequency=.005, write solve
run=se2, frequency=.01, write solve
run=se3, frequency=.02, write solve
run=se4, frequency=.03, write solve
run=se5, frequency=.04, write solve
x0probe=180
run=sf1, frequency=.005, write solve
run=sf2, frequency=.01, write solve
run=sf3, frequency=.02, write solve
run=sf4, frequency=.03, write solve
run=sf5, frequency=.04, write solve
x0probe=200
run=sg1, frequency=.005, write solve
run=sg2, frequency=.01, write solve
run=sg3, frequency=.02, write solve
run=sg4, frequency=.03, write solve
run=sg5, frequency=.04, write solve
x0probe=220
run=sh1, frequency=.005, write solve
run=sh2, frequency=.01, write solve
run=sh3, frequency=.02, write solve
run=sh4, frequency=.03, write solve
run=sh5, frequency=.04, write solve
stop
```

Appendix IV: System Specifications

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This appendix contains the specifications of the equipment used in the PDS system.

A. Excitation Subsystem

Sources

- Xenon arc lamp, 1000 W, parahaloid mirror, 50 mm diameter, focused with 175 mm focal length glass lens, from ILC (Sunnyvale, California)
- 45° hot mirror, model 03MHG009, from Mells Griot (Irvine, California)
Placed before entrance slit of the monochromator to remove near infrared light, which totals about 125 W.
- Infrared glowbar, 50 W, 1900 K, p/n 28649, from Beckman

Monochromator

- Monochromator, Ebert type, $f/3.5$, 0.25 m, from Aries/Jarrel-Ash (Concord, Massachusetts)
- Gratings: 1180 g/mm 550 nm blaze, 590 g/mm 1.0 μm blaze, 295 g/mm 2.1 μm blaze
- Monochromator controller, model MC20, from Spectradata through Aries/Jarrel-Ash (Concord, Massachusetts)
- Variable Frequency Optical Chopper, model Benthon 218F, from Ithaco (Ithaca, New York)

Excitation Optics

- CaF_2 plano-convex lenses: 150 mm focal length, 50.8 mm diameter, model 34-4945, and 100 mm focal length, 50.8 mm diameter, model 34-3558, from Ealing (Holliston, Massachusetts)
- Glass lenses: 175 mm focal length, 50.8 mm diameter, and 69 mm focal length, 50.8 mm diameter, AR.2 anti-reflection coating, Newport, Inc. (Fountain Valley, California)
- Infrared mirrors: first surface aluminum, 50.8 mm diameter, ER.2 broadband coating, Newport, Inc. (Fountain Valley, California)
- Visible mirrors: first surface aluminum, 50.8 mm diameter

Light Measurement

- Silicon photodiode, model PIN 10DP4205, from United Detector Technology (UDT, Culver City, California)
- Silicon photodiode, model SD-290-11-11-041, from Silicon Detector Corporation (Camarillo, California)
- Current to voltage amplifier, model 101A, United Detector Technology (UDT, Culver City, California)
- Pyroelectric detector, model P1-43CC, s/n 6009, from Molelectron Detector, Inc. (Campbell, California)

- Correction carbon Spezialschwarz 4, from Degussa Corp.(Teterborro, New Jersey)

B. Probe Beam Subsystem

Lasers

- Helium-Neon laser model 1103P, 2 mW, 632.8 nm, 0.630 mm beam diameter ($1/e^2$), 1.3 mrad divergence, angular drift <0.01 mrad, from Uniphase, Inc. (San Jose, California)
- Helium-Neon laser model 1122P, 2 mW, 632.8 nm, 0.630 mm beam diameter ($1/e^2$), 1.3 mrad divergence, angular drift <0.01 mrad, from Uniphase, Inc. (San Jose, California)

Probe Beam Optics

- Plano-convex lens, 150 mm focal length, 22.4 mm diameter, model 01LPX237/123, from Mells Griot (Irvine, California)
- Achromat lens, 160 mm focal length, 30 mm diameter, model 01LAO149/123, from Mells Griot (Irvine, California)

Position Detectors

- Linear position detector, 5.3 x 2.1 mm, model LSC/5D, from United Detector Technology (Hawthorne, California)
- Bicell position detector, 2.7 x 2.7 mm with 0.13 mm divider, model SPOT 2DG, from United Detector Technology (Hawthorne, California)
- Bicell position detector, 2.5 x 2.5 mm with 0.10 mm divider, model SD-113-24-21-021, Silicon Detector Corporation (Camarillo, California)
- Bicell position detector, 1.19 x 1.19 mm with 0.02 mm divider, model SD-066-24-21-011, Silicon Detector Corporation (Camarillo, California)
- Position monitor, model 301DV, from United Detector Technology (Hawthorne, California)

Beam Profilometer

Our beam profilometer costs about 10 k\$ less than the competitors' computer-controlled photodiode array systems. Its performance is similar. It is made with a precision 5 μm diameter pinhole (model 29-7028, from Ealing) and one of the photodiodes above. The face of the photodiode is covered with the pinhole. The photodiode and pinhole assembly is mounted on translation stages that allow vertical and horizontal adjustment. A constant-speed motor is attached to the horizontal translation stage. The motor turns at 2 rpm, thereby causing a 100 μm per minute translation of the pinhole. While the pinhole is scanning across the diameter of the probe beam, the voltage from the photodiode is recorded on chart paper. The resulting chart represents the intensity profile at one cross section. These profiles allow the diameter to be calculated, and indicate the quality of the focus achieved.

C. Electronics Subsystem

- Low Noise Preamplifiers, model 1201, from Ithaco (Ithaca, New York)
- Otholoc lockin amplifier, model SC 9505, from Ortec-Brookdeal (Berkshire, England)
- Programmable Function Generator, model 42, from Nicolet (Madison, Wisconsin)
- Condenser Microphone Cartridge, model 4144, s/n 563431, 2 Hz - 6 kHz frequency response, and Microphone Power Supply, Type 2801, from Bruel & Kjaer (Marlborough, Massachusetts)
- Potentiostat, model 273, from EG&G Princeton Applied Research (Princeton, New Jersey)

Appendix V: Physical Data

Thermophysical Data

Table V-1. Thermophysical data for materials used in the PDS model.

	k (W m ⁻¹ K ⁻¹)	C _p (J kg ⁻¹ K ⁻¹)	ρ (kg m ⁻³)
water ¹	0.606	4181	1000
Pt ²	71.6	133	21450
Cu ²	401	385	8933
PFA ³	0.195	1172	2150
acrylic ⁴	0.1883	1464	1190
quartz ¹	1.381	753	2200

¹ source: R.C. Weast, ed., *CRC Handbook of Chemistry and Physics*, 68th ed., CRC Press, Boca Raton, 1987.

² source: Incropera, F.P., and DeWitt, D.P., *Fundamentals of Heat Transfer*, John Wiley & Sons, New York, 1981.

³ source: Dupont, "PFA Properties Bulletin", 1990.

⁴ source: Romm&Haas product literature, 1985.

Thermal Diffusion Lengths

Table V-2. A sampling of thermal diffusion lengths.

	α (m ² s ⁻¹)	μ (f=10 Hz)	μ (f=30 Hz)	μ (f=50 Hz)
water	$1.449 \cdot 10^{-7}$	68 μm	39 μm	30 μm
Pt	$1.166 \cdot 10^{-4}$	894 μm	516 μm	400 μm
Cu	$1.166 \cdot 10^{-4}$	1927 μm	1112 μm	862 μm
acrylic	$1.081 \cdot 10^{-7}$	59 μm	34 μm	26 μm
quartz	$8.336 \cdot 10^{-7}$	163 μm	94 μm	73 μm

The thermal diffusion length is defined as $\mu = \sqrt{\frac{\alpha}{f\pi}}$.

Refractive Index Data

Table V-3. Refractive index and thermal refractivities for deflection medium.

	n	$\partial n / \partial T$ (K ⁻¹)
water ¹	1.33	$-7.3 \cdot 10^{-5}$
acrylic ²	1.49	$-8.5 \cdot 10^{-5}$
quartz ¹	1.455	$-6.6 \cdot 10^{-7}$

¹ source: R.C. Weast, ed., *CRC Handbook of Chemistry and Physics*, 68th ed., CRC Press, Boca Raton, 1987.

² Estimated from published thermal expansion coefficients, using the assumption that the main factor effecting the refractive index is the density. This approximation is described by Spear, J.D., and Russo, R.E., in "Transverse Photothermal Beam Deflection Within a Solid," *J. Appl. Phys.*, 70(2), 580 (1991).

Concentrative Refractivities

Table V-4. Concentrative refractivities for electrolytes at 25 °C .

	n	$\partial n / \partial c$ (M ⁻¹)
sulfuric acid(0-0.2 M) ¹	1.3342 (0.102 M)	1.226×10^{-2}
perchloric acid (0-0.1 M) ²	1.3347 (0.1 M)	7.7×10^{-3}
water in sulfuric acid ^{1 *}		$-0.52 \times 1.226 \times 10^{-2}$
water in perchloric acid ^{2 *}		$-0.33 \times 7.7 \times 10^{-3}$
K ₃ Fe(CN) ₆ in water ³		5.2×10^{-2}
K ₄ Fe(CN) ₆ in water ³		7.2×10^{-2}

¹ Weast, R.C., and Lide, D.R., (eds.), *CRC Handbook of Chemistry and Physics*, 70th ed., CRC Press, Boca Raton, p. D-265, 1989.

² derived with density data from: Lobo, V.M.M., *Handbook of Electrolyte Solutions*, Elsevier, Oxford, p. 581, 1989.

³ Royce, B.S.H., Voss, D., and Bocarsly, A., "Mirage Effect Studies of Electrochemical Processes," *J. de Phys.*, 44(10), c6-325 (1983).

* The derivation of these values is described in the following text.

The model uses an excess water concentration and needs values for how the refractive index changes with water concentration. In a binary electrolyte, the concentration of solvent and solute are not independent. Therefore we can derive one concentrative refractivity from the other.

$$\frac{\partial n}{\partial c_w} = \frac{\partial c_E}{\partial c_w} \cdot \frac{\partial n}{\partial c_E}$$

In this equation W is the solvent (water) and E is the electrolyte (solute).

The total density of the solution is

$$\rho = c_E M_E + c_w M_w$$

This equation is solved for the electrolyte concentration, and then differentiated with respect to the solvent concentration to yield

$$\frac{\partial c_E}{\partial c_W} = \frac{1}{M_E} \cdot \frac{\partial \rho}{\partial c_W} - \frac{M_W}{M_E}$$

The change in density can be determined from tabulated data. The data are not typically reported with respect to solvent concentration. The derivative can be exchanged using the chain rule to yield

$$\frac{\partial c_E}{\partial c_W} = \frac{-\frac{M_W}{M_E}}{1 - \frac{1}{M_E} \cdot \frac{\partial \rho}{\partial c_E}}$$

Diffusion Coefficients

Table V-5. Diffusion coefficients, transference numbers, and charge numbers.

	D (cm ² s ⁻¹) @25 °C	t ₊	z ₊	z ₋
water in water ¹	2.44 x 10 ⁻⁵			
water in water ²	2.299 x 10 ⁻⁵			
K ₃ Fe(CN) ₆ (dilute) ³	0.896 x 10 ⁻⁵			
K ₄ Fe(CN) ₆ (dilute) ³	0.739 x 10 ⁻⁵			
sulfuric acid ^{3,4}	2.600 x 10 ⁻⁵	0.8138	+1	-2
perchloric acid ³	3.006 x 10 ⁻⁵	0.8386	+1	-1
sodium hydroxide ³	2.128 x 10 ⁻⁵	t ₊ =0.7976	+1	-1

¹ Sherwood, T., Pigford, R.L., and Wilke, C.R., *Mass Transfer*, McGraw-Hill, San Francisco, p.26, 1975.

² Mills, R., and Lobo, V.M.M., *Self-diffusion in Electrolyte Solutions*, Elsevier, New York, 1989.

³ calculated from diffusivities in Newman, J.S., *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, p. 232, 1970.

⁴ the acid is assumed to be completely dissociated

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