POLARIZED AND DEPOLARIZED LIGHT-SCATTERING STUDIES
ON BROWNIAN DIFFUSIONAL AND CRITICAL FLUID SYSTEMS:

THEORY AND EXPERIMENT

by

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This Thesis for the Doctor of Philosophy Degree by

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Department of

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Brownian Diffusional and Critical Fluid Systems:
Theory and Experiment.
Thesis directed by Professor Richard C. Mockler and
William J. O'Sullivan.

This thesis represents an effort to expand light-scattering autocorrelation techniques to Brownian diffusional and critical fluid systems in which multiple-scattering effects are important, and to understand the observed similarity of the Rayleigh linewidth of light scattered from these two seemingly different systems. Thus, there are two distinguishable, yet interrelated, classes of contributions that we report here. First, we formulate a solution for the correlation function of the light field multiple scattered from systems of Brownian diffusing particles and critical fluid systems. Second, we present a theory, the Dynamic Droplet Model, to interpret the Rayleigh linewidth of light scattered from critical fluid systems, based on an analogy with Brownian diffusional systems. We present extensive experimental evidence to support these two areas of theoretical work.

In particular, we develop a formalism to find the light field multiple scattered from a suspension of Brownian diffusing particles. We find that for the

field double scattered from a system of noninteracting Brownian particles, the intensity and correlation time are much less dependent on the scattering angle than for the single-scattered component. The correlation time is equal to or slightly larger than the single-scattered correlation time at a scattering angle of 180° . We extend our results to multiple scattering, wherein we develop a method to determine the average number of scattering events from depolarization ratio measurements, and predict the polarized and depolarized light-scattering correlation times as a function of this parameter.

We measure the polarized and depolarized correlation times of light scattered from Brownian particle systems. We find good agreement between our theory and experiment and explain the results of experiments of other workers on highly scattering systems of suspended particles.

We extend our double-scattering formalism to light scattered from critical fluid systems. We show that in the region $k\xi > 5$ the double and single-scattered correlation times are nearly equal. This result explains why previous Rayleigh linewidth measurements have been successful despite the effects of multiple scattering having been ignored near the critical point.

We describe our attempts to model critical fluid light-scattering behavior with a Brownian diffusional system and present the results of light-scattering correlation measurements on emulsions and other polydisperse suspensions which simulate this behavior. With the concept of polydispersity, we develop the dynamic droplet model of critical phenomena. The model gives the proper, experimentally verified, forms for the intensity and linewidth of light scattered from a critical fluid.

In an effort to test the dynamic droplet model and the mode theories Rayleigh linewidth predictions, we perform light-scattering measurements on the critical fluid system methanol and cyclohexane. Using new methods of temperature control we measure the polarized linewidth to $k\xi \approx 80$, a value larger than any previously reported measurement. The data agree with both the dynamic droplet and decoupled mode theory predictions. We measure, for the first time, the depolarized scattered spectra from a critical fluid and find qualitative agreement with our double-scattering theory. Depolarization ratio measurements indicate multiple scattering becomes significant in the region $k\xi > 1$. Thus we can not use our Rayleigh linewidth data in this region as a critical test of the critical fluid theories.

We indicate how our knowledge of the effects of multiple scattering should make possible a definitive experiment for the Rayleigh linewidth of light scattered from a critical fluid system in the large $k\xi$ region. We discuss the implications and relationship of the dynamic droplet model to other theories of critical phenomena.

This abstract is approved as to form and content. I recommend its publication.

Signed

Richard C. Mockler

William J. O'Sullivan

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CHAPTER I

INTRODUCTION

1.1 Purpose.

This thesis concerns itself with the properties of light scattered by a binary fluid system near its thermodynamic critical point. While such a study has interest strictly in terms of developing our understanding of the light-scattering process, it holds a deeper relation to the methods of science as a whole. That is, the light acts as an observational probe of the workings of the critical system, it allows us to infer the molecular mechanics of motion which make such a system so interesting. Once our observational phenomenon has been understood, we may extend this understanding to explain other related phenomena. In the case of a critical fluid system, a knowledge of the molecular mechanics of motion gleaned from light-scattering experiments will lead us to develop theories to explain the unusual macroscopic properties of such a system near a critical point. In this work, our purpose is to contribute to the development of light scattering as a probe of fluid systems near the critical point, and then to use this probe to gain insight

into understanding of the molecular mechanics of such systems which in turn will lead us to new theories of critical phenomena in general.

Specifically, we wish to contribute in two areas. First, we make a critical examination of the analogy between diffusional systems and critical systems implied by the light-scattered Rayleigh linewidth obtained from these systems (see Eqs. (1.15) and (1.16)). This analogy leads us to simulate light scattering critical fluid behavior with a normal fluid diffusional system (Sorensen, Mockler and O'Sullivan, 1976c). Based on what we learn from this simulation and other light-scattering experiments on diffusing microspheres suspended in a normal fluid, we propose a new model of a critical fluid, the Dynamic Droplet Model.

While the mode theories of critical phenomena developed in the late 1960's and early 1970's (Kawasaki, 1966, 1970a and 1970b, Kadanoff and Swift, 1968 and Perl and Ferrell, 1972a and 1972b) have proved quite successful in describing a diversity of phenomena near the critical point, the physics of these theories was not intuitively obvious. On the other hand, the droplet model is based on simple physical reasoning, and it leads to a clear picture of a critical system on a microscopic level. Thus far the droplet model has been applied to understanding light scattering from critical

fluids (Ackerson et al., 1975, O'Sullivan et al., 1975, and Sorensen et al., 1976), critical shear viscosity (Oxtoby and Metiu, 1976) and sound absorption in critical fluids (Sorensen, 1976).

Second, we concern ourselves with the effects of multiple scattering on the intensity and spectrum of the scattered light. Very near the critical point the fluid system may become highly opalescent and so the probability for multiple scattering becomes large. Thus, the usual assumption of single scattering loses validity. Heretofore, most experimenters have treated this problem either in a cursory manner or have completely ignored any possible effects of multiple scattering. Obviously, one may not justify such a procedure until a complete theoretical and experimental program has been carried out on the intensity and spectrum of multiply scattered light. In this work we develop a method for predicting the double-scattered intensity and spectrum; the double-scattered light being the lowest-order contribution to the multiple-scattered light. These results may be applied as corrections to the light-scattering spectrum and an improved Rayleigh linewidth obtained.

To solve this double-scattering problem, we consider light scattered from a system of Brownian diffusing particles. We find theoretical expressions

for the intensity and intensity correlation function of the double-scattered light. We then perform light-scattering experiments on suspensions of Brownian particles. We find that the depolarized scattered correlation function, which is due to double scattering, agrees with our theoretical prediction (Sorensen, Mockler and O'Sullivan, 1976a). We also consider the effects of scattering of higher order than double.

We next apply our double-scattering formalism to scattering from critical fluids. In particular, we find by interpreting our depolarization measurements on a critical fluid with our double-scattering formalism that multiple-scattering is a much larger fraction of the total light scattering than previously thought. For our fluid system (methanol and cyclohexane), which has a fairly typical light-scattering cross section, higher-order scattering becomes important for $k\xi > 2$. Yet it is precisely in this nonhydrodynamic region ($k\xi > 1$) where the most interest in light-scattering experiments has been placed and the effects of multiple scattering have been ignored. We go on to show, theoretically and experimentally, the very remarkable result that the linewidths of the single and double-scattered light are nearly equal in this region (Sorensen, Mockler and O'Sullivan, 1976b). Thus, while double scattering is much more intense than had been

thought, its effects went unnoticed by others because of the similarity in the single and double-scattered linewidths.

We shall present data in support of the above theoretical work. We have performed light-scattering experiments on emulsions and polydisperse suspensions of Brownian diffusing particles which yield a k -dependent diffusion constant qualitatively similar to that found in light-scattering experiments on critical fluids. Insight afforded by these experiments led us to propose the dynamic droplet model.

We have achieved temperature control for our critical fluid mixture good to $30\mu^{\circ}\text{C}$ with no detectable thermal gradients. This represents the best temperature control reported to date for a light-scattering experiment. We have measured for the first time the effects of the incident laser beam heating of the critical fluids, and find the heating effects to be dangerously large. With these techniques we have succeeded in performing light-scattering experiments deep into the critical region to values of $k\xi \approx 80$.

Our final set of experimental data will cover light-scattering measurements from a critical fluid system. The system we used was the binary system methanol and cyclohexane which has a critical, or consolute, point at approximately $T_c = 45.13^{\circ}\text{C}$. We have

performed extensive spectral light-scattering measurements of both the single-scattered Rayleigh line component from temperatures of $T - T_c = 6^\circ\text{C}$ to $0.2\text{m}^\circ\text{C}$.

In summary, this work represents a careful and comprehensive study of light scattering from fluids near the critical point. Our theory for the attendant phenomena is novel and physically appealing and will undoubtedly lead to further application. Our work on multiple scattering clears up problems at least ten years old. It indicates the extent to which the results of other workers who have neglected the effects of multiple scattering, have been fortuitous. We present the first measurement of the depolarized spectra of light scattered from a Brownian diffusion system of particles and a critical fluid and explain these spectra in terms of our double-scattering formalism. We also consider the effects of scattering of higher order than double. We obtain superior temperature control and measure, for the first time, the heating effects of the incident laser beam. Lastly, we measure the Rayleigh linewidth for our binary fluid mixture up to the value $k\xi \approx 80$.

1.2 Review of Critical Phenomena

We know from chemistry and thermodynamics that all gases have a critical temperature such that if the gas is held at or above that temperature it can not be

liquified at any pressure. Since the state of a gas is given uniquely by the three thermodynamic parameters temperature, pressure and density, we can define the critical pressure and density as those values at which the gas begins to condense when held at the critical temperature. The point on the phase diagram of the gas defined by these three parameters is a unique point, called the critical point; the phenomena which occur in the region of that point are called critical phenomena.

We may also define (see, for example, Stanley (1971)) an n^{th} -order phase transition as one for which the n^{th} -order derivative of the free energy with respect to temperature is discontinuous, while all lower-order derivatives are continuous. It may be shown that the transition from a liquid to a gaseous phase is a first-order phase transition while at the critical point we have a second-order phase transition. We may consider a critical point as that point on the phase diagram of a substance at which a second-order phase transition takes place.

Interesting effects take place near the critical point of a fluid system. One observes that the fluid begins to get quite cloudy. This is the phenomenon of critical opalescence first observed by Andrews in 1869. It is due to the fact that near the critical point the molecules, which are normally correlated with each other

over a distance of a few Angstroms, begin to correlate over much larger distances, comparable to the wavelength of light. Such large scale correlations scatter light effectively, giving rise to the critical opalescence. Thus, we might say that the correlation length, characterizing local spatial order in the fluid, grows anomalously large near the critical point.

In an effort to add detail to our understanding of the critical region, we might also measure certain thermodynamic derivatives and transport coefficients such as specific heat or the thermal conductivity. These quantities characterize the equilibrium and nonequilibrium response of the fluid. We would find that these quantities increase anomalously near the critical point. One may write this increase in these measured properties as the power law

$$A = A_0 t^{-x}. \quad (1.1)$$

Here A is the physical parameter, t is the reduced temperature $t = (T - T_C)/T_C$, and x is the critical exponent, usually positive. Equation (1.1) is a common form seen in the literature of critical phenomena, and most of the modern work on critical phenomena has been concerned with determining the values of the critical exponents, and in justifying relations of the form Eq. (1.1). In particular, it can be shown with scaling theory (Widom,

1965, and Kadanoff et al., 1967) that all the critical exponents for the various transport coefficients etc. can be expressed in terms of just two parameters, the scaling exponents.

One of the most remarkable features of critical phenomena is that a wide range of otherwise disparate systems display critical behavior. Besides the liquid-gas system, critical phenomena are observed in binary fluid systems, the ^4He superfluid transition, ferro and antiferromagnetic systems, superconductivity, structural phase transitions, and in laser transitions. In all these systems, relations of the form of Eq.(1.1) are found to hold, and most amazingly the critical exponents for analogous parameters of various systems are found experimentally to be nearly equal. As an example of analogous variables, we may consider a liquid-gas system and a ferromagnetic system. For the liquid-gas system the density difference, $\rho_L - \rho_G$, between the liquid and gaseous phases is the analogue of the magnetization M of the magnet. Both of these parameters are found to go to zero near the critical point as shown in Eq.(1.1) with nearly the same critical exponent called β where $\beta \approx 1/3$. This similarity for systems of different type and composition is called the universality of critical phenomena.

It has been shown (Wilson, 1971a and 1971b and

Wilson and Fisher, 1972) that the universality of the scaling exponents, and thus the universality of all the exponents, is determined by the universality class of the particular system. The universality class is defined by the spatial dimensionality d and the order parameter dimensionality n . As examples, the liquid-gas and binary systems are in the same universality class where $(d,n)=(3,1)$. The ^4He superfluid transition is in the class $(d,n)=(3,2)$. Heisenberg ferromagnets are in the class $(d,n)=(3,3)$. In general, the exponents for different systems of the same spatial dimensionality have nearly the same exponents. Thus, for liquid systems it is found that $\beta \approx 0.32$ whereas for ferromagnetic systems $\beta \approx 0.35$. Thus, it appears that for three dimensional systems at least, the overall universality of the critical exponents holds to an approximate degree; while for systems of the same universality class, universality appears to hold rigorously.

Why do we observe this universality between seemingly different physical systems? Why even universality for different systems of the same universality class, such as the liquid-gas system of xenon, and the binary fluid system of methanol-cyclohexane? Surely the interaction between xenon atoms is different than those between cyclohexane and methanol molecules. Even more striking are the differences between

the interparticle interactions in such systems and those between atoms in an antiferromagnetic insulator, for example. Some underlying characteristic common to all systems must be responsible for this universality. It can be shown (Stanley, 1971) that near a second-order phase transition all systems exhibit extended short range order regardless of the particular types of interactions between molecules of the system. It is this extended order, these large scale fluctuations, that are the underlying common characteristic of all systems near the critical point. These fluctuations give rise to the macroscopic effects of critical phenomena and the observed universality must be linked in some intimate way to them. Thus, it would seem that a reasonable way to study critical phenomena would be to study these fluctuations.

The above sentence is a leading statement. The fact is that light scattering is an ideal probe of the properties of a system with fluctuations when these fluctuations couple to the index of refraction. Indeed, if one considers light scattering from a system of uniform density with no fluctuations, there will be no light scattered at finite angles. Fluctuations are essential to the scattering process. The intensity and spectral characteristics of the scattered light yield information concerning the static and dynamic

properties of the fluctuations, respectively. It is for this reason that light scattering makes such an excellent experimental tool in the study of critical phenomena.

We shall now consider some specific areas of critical phenomena and light scattering which will be of use later in the development of this work. An excellent review of light scattering and critical phenomena by Cummins (1971) may be referred to.

We start by considering the Ornstein-Zernike (1914) theory for fluctuations in a fluid near the critical point. If we write the density at a point $\vec{r}$ as $\rho(\vec{r})$, then a measure of the correlation in density is given by

$$g(\vec{r}_1, \vec{r}_2) = \frac{\langle \rho(\vec{r}_1) \rho(\vec{r}_2) \rangle}{\langle \rho^2 \rangle} - 1. \quad (1.2)$$

Here the angular brackets $\langle . . . \rangle$ imply the usual ensemble average. If we consider an isotropic fluid, invariance under a spatial transformation exists and we may set $g(\vec{r}_1, \vec{r}_2) = g(\vec{r})$ where $\vec{r} = \vec{r}_1 - \vec{r}_2$. Furthermore, if we write the local density as the sum of the average density and fluctuations about that density, $\rho(\vec{r}) = \langle \rho \rangle + \delta\rho(\vec{r})$, Eq. (1.2) becomes

$$g(\vec{r}) = \langle \delta\rho(\vec{r}) \delta\rho(0) \rangle / \langle \rho^2 \rangle. \quad (1.3)$$

$g(\vec{r})$ is called the density correlation function.

Physically, we see that if there are no fluctuations in density, $g(\vec{r})=0$. For finite sized fluctuations, $g(\vec{r})$ is nonzero only for distances over which the density fluctuations are correlated, i.e. nonrandom. The average distance over which the density fluctuations are correlated is called the correlation length.

The Ornstein-Zernike theory predicts a particular form for the density correlation function

$$g(r) \propto \frac{e^{-r/\xi}}{r}. \quad (1.4)$$

The parameter ξ is usually called the Ornstein-Zernike correlation length and, as mentioned above, represents the average distance over which the density is correlated.

From light-scattering theory (see Cummins, 1971), one can show that the scattering amplitude for light is the Fourier transform of the density correlation function. Thus to find how much light will be scattered from a fluid obeying the Ornstein-Zernike scattering law, we Fourier transform Eq.(1.4) to find

$$S(\vec{k}) \propto \frac{1}{(k^2 + \xi^{-2})} \quad (1.5)$$

$S(\vec{k})$ is the structure factor and is proportional to the amount of scattered light scattered at a given scattering

angle. The vector $\vec{k}$ is the scattering wave vector and is equal to $k = (4\pi n/\lambda) \sin (\theta/2)$, where n is the index of refraction of the medium, λ is the wavelength of the incident light and θ is the experimental scattering angle.

Experimentally, one may plot the inverse of the measured scattered intensity versus k^2 . If the Ornstein-Zernike theory is valid, straight lines will result. Such is the case found experimentally (see Stanley (1971) for examples), and the theory is considered to hold in general. From such measurements, ξ can be determined. It diverges in a form similar to Eq. (1.1)

$$\xi = \xi_0 t^{-\nu} \quad (1.6)$$

where $\nu \approx .64$ and ξ_0 may vary from one to four Angstroms for typical fluid systems.

Fisher (1964) has suggested that Eq. (1.5) may have the more general form

$$S(\vec{k}) \propto (k^2 + \xi^{-2})^{-(1-\eta/2)} \quad (1.7)$$

Here η is another critical exponent expected to be quite small (Wilson (1972) predicts $\eta \approx 0.037$) and thus hard to measure.

Equation (1.7) gives us information concerning the statics of the fluctuations. The scattered light will also have a spectrum associated with it which is

determined by the dynamics, motion and decay, of the fluctuations. This spectrum is found to be Lorentzian in shape and the width at half height is called the Rayleigh linewidth. In terms of correlation spectroscopy, the intensity correlation function which is the Fourier transform of the lineshape would be exponential with a decay time equal to the reciprocal of the Rayleigh linewidth. In this work, we will often use the term "Rayleigh linewidth" for both situations.

Following the development of Swinney and Henry (1973), we write the linewidth, Γ , as the sum of a background part and a critical part

$$\Gamma = \Gamma_B(1+k^2\xi^2) + \Gamma_C. \quad (1.8)$$

The background part of the linewidth, Γ_B , can be evaluated from hydrodynamics as was shown by Mountain and Duetch (1969) and Foch (1972). These workers found that the background linewidth seen from a normal fluid goes as

$$\Gamma_B = \frac{\Lambda}{\rho C_p} k^2 \quad (1.9)$$

where Λ is the thermal conductivity, ρ is the density and C_p is the specific heat at constant pressure of the fluid. This result was experimentally verified by Lastovka and Benedek (1966).

For a binary fluid one finds theoretically

$$\Gamma_B = \frac{\alpha}{\left(\frac{\partial c}{\partial \Delta}\right)_{T, \rho}} k^2. \quad (1.10)$$

Here α is the concentration conductivity, c is the concentration and $\Delta = \mu_1 - \mu_2$ where μ_i is the chemical potential of the i^{th} component.

Near the critical point the second term in Eq. (1.8) becomes large relative to the background term especially in the case of a binary mixture. It is this critical linewidth which has been the object of so much interest in the past several years.

Recently, the so called mode coupling theories have been developed which enable the divergent part of the transport coefficients to be calculated. In particular the mode-mode theory of Kawasaki (1970a) predicts a form

$$\Gamma_C = \frac{k_B T}{6\pi\eta_s \xi^3} K_O(k\xi) H(k\xi) \quad (1.11)$$

where k_B is Boltzman's constant, T is the temperature, η_s is the shear viscosity,

$$K_O(x) = 3/4 [1+x^2+(x^3-x^{-1})] \tan^{-1}(x) \quad (1.12)$$

and

$$H(x) = R(x) V(x) C(x). \quad (1.13)$$

$R(x)$ represents viscosity corrections (Kawasaki and Lo, 1972), $V(x)$ is the vertex correction (Lo and Kawasaki, 1973) and $C(x)$ is a correction for nonzero η (Swinney and Saleh, 1973).

This expression is rather complex and many of the terms can only be evaluated numerically. Therefore, we concern ourselves only with the predictions of the mode-mode theory and plot the results in Fig. 1 as curve (a).

The other mode theory is the decoupled mode theory of Ferrell (1970) and Perl and Ferrell (1972). They find a form very similar to that given by the mode-mode theory,

$$\Gamma_C = \frac{k_B T}{6\pi\eta_{\text{eff}}\xi^3} K_O(k\xi). \quad (1.14)$$

Here $K_O(x)$ has the same form as Eq. (1.12) and η_{eff} is a complex function of the viscosity and $k\xi$ (see Swinney and Henry, 1973). Again for simplicity, we plot the decoupled mode theory results in Fig. 1 as curve (b).

Empirically, Perl and Ferrell (1972) pointed out that the critical linewidth data are well fit by the simple expression

$$\Gamma_C = \frac{k_B T}{6\pi\eta_s \xi} k^2 (1+k^2 \xi^2)^{\frac{1}{2}} \quad (1.15)$$

where the viscosity is now a variable used to obtain a

Figure 1. Scaled linewidth versus $k\xi$ for the mode-mode theory, curve (a); the decoupled mode theory, curve (b); and the empirical (and dynamic droplet model) result, curve (c).

best fit. We plot Eq. (1.15) as curve (c) in Fig.1 where η_s has been adjusted so as to have Eq.(1.15) agree with the other curves in the $k\xi \ll 1$ region.

We point out that Eqs. (1.11), (1.14) and (1.15) all have the common factor $k_B T / 6\pi\eta_s \xi$. It has long been known, however, (Clark, Lunacek and Benedek, 1970) that the light-scattered linewidth obtained from a system of Brownian diffusing particles is (the spectrum is Lorentzian)

$$\Gamma = Dk^2 = \frac{k_B T}{6\pi\eta_s \ell} k^2 \quad (1.16)$$

where $D = k_B T / 6\pi\eta_s \ell$ is the Stokes-Einstein relation for the diffusion constant of particles of radius ℓ diffusing in a medium of viscosity η_s . This remarkable similarity in the light-scattering Rayleigh linewidth of critical fluid systems and Brownian motion systems implies, as was first noted by Arcovito et al. (1969), that the correlations in density of size ξ may be undergoing some sort of diffusion. We shall make more of this point later (see Chapter II).

In Fig. 1 to normalize out the various fluid dependent parameters such as viscosity and temperature, we plot the scaled Rayleigh linewidth of Swinney and Henry (1973) defined as

$$\Gamma^* = \frac{6\pi\eta_s}{k_B T} \frac{1}{k^3} \Gamma_C. \quad (1.17)$$

Using this form data from different fluids should all lie on the same curve as was shown by Swinney and Henry.

The mode theories have been successful in predicting the behavior of dynamical aspects of critical phenomena other than the Rayleigh linewidth mentioned above. The anomalies in the transport coefficients and the sound absorption have been reasonably successfully explained by these theories. The mode theories are based on the physical reasoning first put forward by Fixman (1962) that different transport modes of the system couple together near the critical point. Thus, the critical Rayleigh linewidth is viewed as arising from a coupling between a thermal mode and a viscous mode of the system.

The Rayleigh linewidth prediction of the mode theories fits the data well except for a region around $k\xi \approx 1$ where the linewidth prediction is perhaps 20% too low (Swinney and Henry, 1973). Also there may be problems for the mode-mode theory in the region $k\xi > 10$ where the predicted linewidth may be too large (see Theil et al. (1975) but also Lai and Chen (1972)). This region is difficult to obtain experimentally due to the extremely precise temperature control necessary (better than $\pm 0.2\text{m}^\circ\text{C}$, see section 5.5) and also because it is in this region where multiple-scattering effects should become important.

Other, less exacting, objections to the mode theories might be made. The theories are very mathematical and the physical reasoning is often obscured by the mechanics of the formalism. The similarity between the calculated linewidth and that one would obtain for Brownian diffusional system is unexplained. While these criticisms seem petty in the light of the successes of the mode theories, we must also remember that one of the joys of science is an understanding of complex phenomena in a simple light. Thus, it seems to us, that a simple physical picture of these phenomena would have its own rewards.

CHAPTER II

THE DYNAMIC DROPLET MODEL OF CRITICAL PHENOMENA

2.1 General considerations concerning the similarity of the Rayleigh linewidth of critical and diffusional systems.

As was first pointed out by Arcovito et al. (1969), and undoubtedly noticed by other workers in the field, the similarity of the Rayleigh linewidth of critical fluids and Brownian diffusional systems might be explained by assuming that in a critical fluid there are fluctuations of size ξ executing Brownian motion. This is a reasonable idea, for we know from the Ornstein-Zernike theory that the fluid molecules are correlated with one another over a range ξ . Thus, if we assume these correlated regions act as globs or droplets of radius ξ diffusing in the normal fluid viscosity η_s , we would measure a linewidth of

$$\Gamma = \frac{k_B T}{6\pi\eta_s \xi} k^2 \quad (2.1)$$

in a light-scattering experiment on a critical fluid. From Eq. (1.15) we see that this is exactly the linewidth one obtains from a critical fluid far from the critical point where $k\xi \ll 1$.

Equation (2.1) will hold for a monodisperse diffusional system regardless of the size of $k\xi$; whereas, for the values of $k\xi$ approaching unity or greater, Eq. (1.15) will no longer be in agreement with Eq. (2.1). So, the diffusing droplet picture is no longer adequate in the critical, or nonhydrodynamic, region where $k\xi \geq 1$.

Several ways of fixing the diffusional picture of Eq. (2.1) to agree with the critical linewidth data come to mind. One way is to use the concepts of dynamic scaling (Ferrell et al., 1968, Halperin and Hohenberg, 1969 and Hankey and Stanley, 1972). The scaling argument is that one may assume certain variables of the system, such as the free energy or linewidth decay time, are homogeneous functions of k and ξ^{-1} . Thus the decay time may be written as

$$\Gamma = f(k, \xi^{-1}) = k^z f(1/k\xi) \quad (2.2)$$

where z is the degree of homogeneity of f . From the known form of Γ for $k\xi \ll 1$ it can be shown (Hankey and Stanley 1972) that $z=3$. In the region $k\xi \gg 1$, $f(1/k\xi) \rightarrow B$, a constant, thus for $k\xi \gg 1$

$$\Gamma = Bk^3 \quad (2.3)$$

which is of the same form as Eqs. (1.11), (1.14) and (1.15) for $k\xi \gg 1$.

There are problems with this approach. This scaling argument is not based on rigorous theoretical grounds. The coefficient B is not predicted by the scaling argument. We find ourselves still looking for an explanation for the critical diffusional system similarity.

We considered the possibility that while the fluctuations of a critical system were diffusing, they might also be interacting with each other. Their interactions may become large near the critical point where we expect many large fluctuations, and may be responsible for the extra k-dependence (the $(1+k^2\xi^2)^{\frac{1}{2}}$ term in Eq. (1.15)). At that time there had been no work published on interacting Brownian systems and so there were no data or theoretical predictions which we could apply to the droplet model. The idea seemed reasonable, however, and we felt it would be worthwhile to pursue it.

We also considered the work of Lyons, Mockler and O'Sullivan (1973) done in our laboratory. They found that Brownian particles diffusing in a binary fluid mixture near the critical point exhibited a k-dependent diffusion constant similar to that observed in the Rayleigh linewidth (again the $(1+\xi^2k^2)^{\frac{1}{2}}$ term in Eq. (1.15)). Was it possible to treat the diffusing fluctuations in terms of their result?

These were some of the ideas on our minds at the time we decided to approach this problem. At length, however, we decided to pursue the diffusional analogy by trying to model a critical fluid with a diffusional system. By scattering light and measuring its linewidth from various model systems, perhaps we could reproduce some of the qualities of the critical fluid linewidth, in particular the extra k -dependent term in Eq. (1.15). If so, our model systems could tell us what else is needed besides the diffusional degree of freedom implied by the $(k_B T / 6\pi\eta_s \xi) k^2$ term.

2.2 The simulation of a critical fluid system.

We recall the Ornstein-Zernike theory for fluctuations near the critical point discussed in our introduction, section 1.2. This theory gives us the physical picture of a fluid with regions of lower or higher density (or relative concentration in the case of a binary fluid) which have an average size ξ . Also, because of the large amount of critical opalescence for small fluctuations ($\xi \approx 1\mu\text{m}$), we expect many fluctuations per unit volume. The point was made above that these regions are solely responsible for scattering light and their dynamics should be responsible for the spectral characteristics of the scattered light. From the diffusional analogy discussed above, we shall take the

dynamics of the fluctuations near the critical point to be governed by simple Brownian diffusion.

We are now ready to model a critical fluid system on these ideas. We make a dense suspension of particles in a fluid. The average size of the particles should be equal to ξ in the critical region. This would be $\xi \approx 0.1\mu\text{m}$ to $1.0\mu\text{m}$.

The first problem that had to be overcome to use such a model was the extreme turbidity of a suspension of particles at the required density. For particles of diameter of a few tenths micron, a suspension of one part particles to a hundred of liquid medium, a reasonable estimate of the density of the critical fluctuations, is very turbid. A laser beam incident on such a sample was found to be well attenuated in less than a centimeter. Such a system would be too complicated for simple evaluation of our model system because of multiple-scattering effects and attenuation of the incident beam.

One can reduce the amount of scattering by obtaining a close index of refraction match between the suspended particles and the suspending medium; the cross section for scattering being proportional to the index mismatch. The most convenient suspending medium is water of index $n=1.33$. However, nearly all solid particles that could be used have indices of refraction

of 1.45 or greater. Thus a simple aqueous suspension did not appear feasible for our purpose.

Liquids of higher index of refraction might be used. Transferring the particles from their usual water suspensions to the new suspending medium might prove difficult if not impossible when the water and the new medium are immiscible, which is usually the situation for high index liquids. Also, it is the highly polar nature of water which allows stable suspensions to form due to the solvation process, otherwise coagulation and precipitation result. Thus many fluids are unsuitable due to their inability to solvate.

Water's index of refraction may be increased by adding a solute. Ionic solutes would be unsuitable, however, because they cause coagulation of suspensions, like polystyrene and ludox, which depend on electrostatic repulsion of the individual particles for stability. An ionic reagent screens this repulsion and coagulation results. One might use nonionic reagents, but it is still very hard to increase the index of refraction of the medium to the values required. Also, even if this could be done, the viscosity of the medium would become so high that linewidths of less than 10 Hertz would result which are difficult to measure with our apparatus.

We either considered or experimentally tried all

of the above procedures with a lack of success. With experimentation it seemed that a compromise between increasing the water's index of refraction and lowering the suspended particle index would be the best procedure. This compromise led to our use of emulsions.

We found that we could make reasonably stable emulsions of an alkane such as octane and water using a wetting agent. Octane has an index of refraction of $n=1.3974$ at 20°C . Other than its low index of refraction, octane was a rather arbitrary choice. To raise the index of refraction of the water, we dissolved sucrose into the water. Sucrose was used because it is nonionic, common, and tables of index of refraction and viscosity versus concentration are available (Handbook of Chemistry and Physics Vol. 54, 1973-1974). A 38.72% by weight solution of sucrose in water at 20°C has an index of refraction of $n=1.3974$ and viscosity of 5.61 cp. Thus, we are able to make an emulsion of near perfect index of refraction match with a reasonably small suspending medium viscosity.

Our recipe was quite simple. Approximately three parts to one of sucrose solution to octane were added to a small vial. A few milligrams of wetting agent were then added. This mixture was shaken well by hand and then the whole vial was placed in an ultrasonic cleaner for approximately five minutes. The ultrasound served to disperse and emulsify the two components.

The difference in physical appearances of an octane-water and an octane-water/sucrose emulsion at a concentration of, say, 1:15 octane is startling. The former emulsion is completely opaque, visually similar to rich cream. The latter emulsion, if carefully made, is quite clear with a fine graininess and a tinge of yellow. A laser beam easily passes through it with no hint of a "Tyndall cone."

Our emulsions once made were allowed to set for three or four hours to allow for an initial "creaming" period. This common process is due to the very large globules of the dispersed phase, in this case octane, separating out and floating to the top. After this initial creaming period, it was found from our light-scattering data that the emulsion was relatively stable for a period of approximately a day. Periods longer than this usually showed the slow trend to nearly complete separation of the components. Therefore, our light-scattering data to be reported pertains to this intermediate time region.

Our first group of emulsions ranged about $8 \pm 1\%$ by volume concentration of octane and $(2.5 \pm 1.0) \times 10^{-2}\%$ by weight of wetting agent. From our light-scattering data we obtained the diffusion constant and thus via the Stokes-Einstein relation found the average diameter of the octane globules to be $d \approx 0.6 \pm 0.1 \mu\text{m}$. Data from

three separate runs on three different emulsions prepared in the same way are given in Fig. 2.

Figure 2 is a plot of the diffusion constant inferred from our linewidth measurements (see Eq. (1.16)). The error bars are large because of the long correlation times (correlation time = reciprocal of linewidth), of order 10 msec, which are hard to measure with our apparatus, and because of the large degree of nonexponentiality of the scattered-light correlation function. Also, the emulsions tended to be somewhat unstable though serviceable. For a normal monodisperse (one size) suspension of Brownian particles the diffusion constant does not depend upon the wave vector $\vec{k}$. However, as seen in Fig. 2, the emulsions exhibited a large irregular k -dependence outside the error bars. Thus, we had succeeded in creating a system with a k -dependent diffusion constant.

The k -dependence of the inferred diffusion constant of the emulsions is different than that of the critical fluids. In a critical fluid the diffusion constant varies monotonically with k , whereas that for the emulsions doesn't. Also, the critical fluid diffusion constant develops from a $k^0 = \text{constant}$ dependence when $k\xi \ll 1$ to a k^1 dependence when $k\xi \gg 1$. Our emulsion data have some sort of k^{-x} behavior where $x > 0$; again, qualitatively unsuitable to model the critical fluid.

Figure 2. Diffusion constant versus k inferred from light-scattering measurements on an emulsion.

The data presented in Fig. 2 are probably too complicated to ever be analyzed sensibly. The octane globules are very likely polydisperse in size. As we were to discover, this leads to a k -dependence. Also, the globules are quite close together; at 8% by volume there is an average center to center distance of 4.6 globule radii. We know from the theory of emulsion stability (Verwey and Overbeek, 1948) that there are large surface and counter ion charge layers in such a system. Globules at the above average distance are probably interacting and thus, no longer executing random Brownian motion. Because of these strong interactions we might well explain the oscillatory behavior of the data in Fig. 2 as some sort of structure factor similar to that observed in a liquid in X-ray scattering measurements. Indeed, such effects were subsequently observed by Shaeffer and Ackerson (1975) in polystyrene systems. Future work in this area might prove of interest.

Up to this point, our attempts to understand the k -dependent diffusion constant of the critical Rayleigh linewidth had been well conceived and coherently pursued. However, as often happens in research, at least in the short experiences of this worker, such orderly designs are not always fulfilled. It was at this point that apparent experimental difficulties led us to new

results which eventually gave us a new understanding of light scattering and the k -dependence.

In the course of our experimentation, we found that a variety of Brownian particle type systems gave a k -dependence similar to that of a critical fluid. By "similar" we mean D increased monotonically with some power of k . Usually the more careless we were in preparing the suspension, the more likely we were to observe a k -dependence. However, at first, we only observed the k -dependence in sucrose or ethylene glycol solutions; not in pure water. This led us to believe that these solutions might be slightly non-Newtonian and the Brownian motion in such a fluid might exhibit a k -dependence. After some work we found that pure water suspensions also exhibited a k -dependence and our original non- k -dependent measurements in water had been erroneous and highly misleading. After much difficult and unrewarding work, we at last came to a reasonable theory for this k -dependence.

We found that if care was taken to insure that the suspended particles were monodisperse—all one size—no k -dependence of the diffusion constant was observed. However, in dirty or uncarefully prepared systems a k -dependence was usually seen. Such a dirty system may not be monodisperse but rather polydisperse, i.e. a finite size distribution. Can it be that the

k-dependence is solely a result of this polydispersity? As we shall shortly see, it can; but first we shall proceed with our modeling of a critical fluid system with emulsions.

Having found that emulsions may have liquid-like structure which may be exhibited in the k-dependent diffusion constant measured in light-scattering experiments, we decided to make a less concentrated emulsion in which the globules should be farther apart and so less strongly interacting. We made another octane-water/sucrose emulsion by the recipe described above only with $(3.5 \pm 1) \times 10^{-2}$ concentration by weight wetting agent and less octane. An emulsion of about 5% by volume dispersed octane resulted. Since there is less octane per unit wetting agent, we expect the octane globules to be smaller than in the first set of emulsions (Verwey and Overbeek, 1948). An emulsion of average globule radius of $\bar{R} = 0.088 \mu\text{m}$ resulted as determined from using Eq. (1.16) and a background viscosity of $\eta_s = 5.6 \text{ lcp}$ for the 38.72% sucrose solution (from p.D-229, Handbook of Chemistry and Physics Vol. 54, 1973-1974).

To compare our linewidth measurements to those of a critical fluid, we then use Eq. (1.17) to determine the reduced Rayleigh linewidth and plot this against the experimentally varied values of k ($k = 4\pi n \lambda^{-1} \sin(\theta/2)$) times $\bar{R}$. In this case, $k\bar{R}$ corresponds to $k\xi$ for a

critical fluid. For details of this work see Sorensen, Mockler and O'Sullivan (1976c).

The results are plotted in Fig. 3. Also shown in Fig. 3 is the empirical critical fluid behavior given in Eq. (1.15). We see a remarkable agreement. In Fig. 4 we have plotted the correlation time of the scattered field ($1/\Gamma$) versus k on a log-log plot. Here we see that the $\Gamma \propto k^2$ dependence characteristic of Brownian diffusion is giving over to the $\Gamma \propto k^3$ dependence observed in the nonhydrodynamic ($k\xi \gg 1$) region of a critical fluid. Thus, it seems we have succeeded in simulating critical fluid Rayleigh linewidth behavior using a diffusional system. The properties of this emulsion should add to the physical picture of a critical fluid.

Indeed, we expect the k -dependence in the emulsion to be due to the same polydispersity effects seen in dirty samples. We can not expect all the globules in the emulsion to have the same size. This finite size distribution seen in emulsions and our dirty systems may be the key factor missing in interpreting the critical Rayleigh linewidth in terms of a diffusional system.

Figure 3. The experimental scaled linewidth of light scattered from an emulsion. The solid line represents the empirical critical fluid behavior, Eq. (1.15).

Figure 4. The correlation time of light scattered from an emulsion showing a nearly $\sin^3(\theta/2)$ dependence.

2.3 The k-dependent diffusion constant inferred from polydisperse systems.

In this section, we shall show how light-scattering measurements on a polydisperse system of Brownian particles will lead us to infer a k-dependent diffusion constant. We will develop a simple theory to predict this k-dependence and compare this theory to systems of known polydispersity. We shall find that in general polydispersity leads to a k-dependence qualitatively similar to that observed in critical phenomena.

To understand the origin of the k-dependence, one must examine the Mie scattering function for a dielectric sphere. The key to this understanding is to plot the relative light-scattering intensity against the particle size, using the scattering angle as the curve parameter as in Fig. 5. The Mie functions were obtained from standard tables (Denham, Heller and Pangonis, 1966). In this way, it is easy to see how the relative light-scattering intensities for different sized particles change with scattering angle. For example, the ratio of the relative light-scattering intensity of a $0.20\mu\text{m}$ particle to a $0.15\mu\text{m}$ particle is 4.8:1 at a scattering angle of 45° , whereas at 135° this ratio is only 1.6:1. Thus for a system consisting of an equal number concentration of each size, one would expect the larger balls to dominate the spectrum at small scattering angles, but as we go to larger angles the smaller

Figure 5. Plot of the relative Mie scattering intensity versus particle diameter parameterized by the scattering angle, for microspheres with $m=1.20$ and $\lambda=5145\text{\AA}$.

balls would begin to contribute more and more to the spectrum. The measured diffusion constant is some average, dependent on the relative Mie scattering intensities.

We performed light-scattering measurements on known polydisperse systems of polystyrene microspheres suspended in water to test our ideas above (Sorensen et al., 1976). The experiment involved scattering from two systems of polystyrene microspheres. System I was made up of microspheres $0.109\mu\text{m}$ and $0.234\mu\text{m}$ in diameter; system II was made up of microspheres $0.234\mu\text{m}$ and $0.500\mu\text{m}$ in diameter. The microspheres were obtained from Dow Chemical Company and come in lots that are very monodisperse in size ($\sigma(\text{dia.}) \sim 1\%$). Their index of refraction in air is 1.59. They were suspended in distilled water which had been filtered through a $0.05\mu\text{m}$ millipore filter. Three monodisperse suspensions were made, one for each microsphere size, each at a concentration of $1:10^5$ microspheres by weight. The polydisperse systems were made by mixing various proportions of the monodisperse suspensions. The results of our measurements are given in Fig. 6 where we plot the diffusion constant inferred from our light-scattering measurements versus the scattering angle ($k \propto \sin(\theta/2)$).

Also plotted in Fig. 6 are our theoretical curves. To derive these curves we put the ideas discussed above

Figure 6. Plot the diffusion constant inferred from light-scattering measurements on polydisperse systems. Each set of data and theory is labeled with the concentration by weight of the smaller microsphere relative to the larger.

into a more precise mathematical form. The field correlation function of the light scattered from a system of Brownian diffusing particles of radius ℓ and diffusion constant $D(\ell)$ is

$$\langle \vec{E}^*(t) \cdot \vec{E}(0) \rangle = I_m(\ell) e^{-D(\ell)k^2 t}, \quad (2.4)$$

where E is the scattered electric field, and E^* is the complex conjugate of E . We write the intensity of the scattered light from particles of radius ℓ as the Mie scattering intensity, $I_m(\ell)$, times the probability density $N(\ell)$ for that particle size, $I(\ell) = N(\ell)I_m(\ell)$. The average field correlation function is then given by

$$\langle \langle \vec{E}^*(t) \cdot \vec{E}(0) \rangle \rangle = \int d\ell N(\ell) I_m(\ell) e^{-D(\ell)k^2 t}. \quad (2.5)$$

Here the second set of angular brackets indicates an average over ℓ . We make the usual assumption of Gaussian scattering statistics (Cummins and Swinney, 1970) and find the intensity-intensity autocorrelation function of the scattered light to be

$$\langle \langle I(t)I(0) \rangle \rangle = \langle \langle |E|^2 \rangle \rangle^2 + A \langle \langle \vec{E}^*(t) \cdot \vec{E}(0) \rangle \rangle^2, \quad (2.6)$$

where A is a constant independent of the radius.

To compare theory and experiment, we use Eq. (2.6) to generate an average correlation function for the different experimental values of concentration and microsphere size. Because Eq. (2.6) predicts a

nonexponential correlation function, we account for both the first and second cumulants in the experimental data and the simulated data from Eq. (2.6) by fitting to the form $\exp(-at+bt^2)$ using a least-squares routine. The details of this fitting scheme are given elsewhere (Lyons, 1973 and section 5.2). This form fits the data and Eq. (2.6) quite well, and we find that both the experimental and theoretical autocorrelation functions are nearly exponential. That is, the ratio b/a^2 is ≤ 0.04 . We plot our results in Fig. 6.

The agreement between experiment and theory is good for all the suspensions studied. In particular, the k -dependence of D for system I, which consists of microspheres whose diameters are slightly smaller than λ , is qualitatively similar to the behavior shown by the diffusion constant for critical fluids in the nonhydrodynamic regime. That is, D increases with increasing k (increasing scattering angle). The k -dependence for system II is more complicated due to interference effects from the larger ($0.5\mu\text{m}$) microspheres (see Fig. 5). While this is consistent with theory, such effects are not observed in critical fluids. However, these strong interference effects can be shown to be markedly reduced for a microsphere whose index of refraction does not change discontinuously at its boundary.

We conclude that a polydisperse suspension of dielectric microspheres of size comparable to the incident light wavelength will produce a k -dependent diffusion constant when investigated by light-scattering techniques. This diffusion constant increases with increasing wave number just as does the diffusion constant for a critical fluid when $k\xi \gg 1$.

We may summarize by describing the origin of this wave-number dependence and its relation to particle size and polydispersity in the following way. When the particle radius ℓ does not satisfy the condition $\ell \ll \lambda$, the scattered-light intensity becomes a very sensitive function of ℓ (see Fig. 5). When light is scattered from a polydisperse suspension of particles, the diffusion constant inferred from the intensity autocorrelation of the light scattered by the particles represents an average over the diffusion rates of all the particles weighted by the particle-size-dependent light intensity, and the particle-size distribution. For small scattering angles (small k) the larger particles in the dispersion provide the dominant contribution to the scattered light. Since the diffusion constant for a specific particle size varies inversely with the particle diameter through the Einstein-Stokes relation, the D extracted for small k is small. As the scattering angle is increased, inspection of Fig. 5 confirms that

the relative contribution of the smaller particles to the scattered intensity increases, leading to an average D which increases as k increases.

2.4 The Dynamic Droplet Model.

We have described in our last sections how our attempts to model a critical fluid system with a diffusional system led us to the concept of a k -dependent diffusion constant due to polydispersity. We have seen that nearly any size distribution of particles gave a k -dependent diffusion constant qualitatively similar to that observed in light-scattering experiments on critical phenomena. In particular, emulsion systems could be made that exhibited spectra very similar to that of a critical fluid in equivalent regions of $k\xi$. In this section, we will use these ideas to develop the dynamic droplet model of critical phenomena.

We first emphasize the point made earlier, that if there were no fluctuations of density or concentration in a critical fluid (which lead to fluctuations in the index of refraction), there would be no light scattered. Thus, as surely as the static properties, such as number density and relative index of refraction, of the fluctuations determine the static properties of the scattered light, the intensity, the dynamic properties, such as the lifetime and motion, of the fluctuations determine the dynamic properties of the scattered light, i.e. the spectrum.

Far from its critical region, the spectrum of light Rayleigh scattered by a fluid is described by the temporal decay of the fluctuations. This was shown by Mountain and Deutch (1968). This linewidth represents the lifetime of the fluctuations. Near the critical point, the linewidth becomes dominated by what is called the critical part as shown in Eq. (1.8). It is this critical linewidth which we shall ascribe to the motion, in particular Brownian diffusional motion, of the fluctuations in the dynamic droplet model.

Let us summarize what we have to this point. We have that the dynamics of the fluctuations in a field determine the spectral properties of the scattered light. The temporal decay of the fluctuations is described by the background transport coefficients given far from the critical region by Eqs. (1.9) or (1.10). We shall take the diffusion of the fluctuations as determining the critical part of the Rayleigh linewidth. A poly-disperse system of diffusing particles will exhibit a k -dependent diffusion constant inferred from light-scattering techniques very similar to that obtained from critical fluids. Large particles of radius $\ell \gg \lambda$ yield interference effects in a k -dependent diffusion constant which might be removed by a continuous change in the index of refraction between the background fluid

and the particle. With these concepts, we are ready to propose the dynamic droplet model of critical phenomena.

We assume that the critical fluid fluctuations may be thought of as clusters of molecules diffusing like Brownian particles in a host fluid characterized by a normal background viscosity. As yet we will not consider the effects of possible interactions between the diffusing clusters or droplets. We would expect an interaction to appear as some sort of critical viscosity influencing the diffusion.

We assume these clusters have a spherically symmetric density or concentration distribution which we take as Gaussian. By the Lorentz-Lorenz relation (Born and Wolf, 1975), this implies that the index of refraction profile will also correspond to a Gaussian. This assumption is quite reasonable for we expect the individual molecules of a cluster to be undergoing self diffusion, and thus a region of higher or lower density would with time have a Gaussian distribution in the density of the molecules. It is this assumption that frees us from the possibility of interference effects in the k -dependence that were seen in system II above.

We will also assume that the droplets do not grow or decay significantly during time periods of the order of the correlation time of the scattered light in the critical region. This will allow us to use a much

simpler formalism. Such an assumption may well be false. We have seen, however, that the temporal decay appears as the background term of the critical Rayleigh linewidth and is much slower than the critical term in the critical region (see Swinney and Henry (1973)). This temporal decay may still have important effects, particularly on the shape of the scattered-light correlation function.

Finally, we assume that these droplets are polydisperse in size. This is reasonable because from the statistical nature of the fluid we do not expect all the fluctuations to be of the same size. As we have seen above, this assumption was the key to the application of the diffusing droplet model because it gives us a k -dependent diffusion constant. We furthermore point out that any reasonable size distribution was found to give a qualitatively correct k -dependence, but we shall pick a particular size distribution which will best fit the data.

The particle-size distribution we use is given by

$$N(\ell) = B \exp\{-\ell^2/2\xi^2\} / \ell^{5+\eta}, \quad (2.7)$$

where B is an approximately temperature-independent factor related to the density of the fluid, ξ is a parameter which will be seen to be identical to the

Ornstein-Zernike correlation length, and η is a variable exponent to be identified later and not to be confused with the symbol for shear viscosity. While we have picked Eq. (2.7) to suit our needs in fitting the intensity and linewidth data, the general form of this distribution is as we shall see similar to that used for static droplet models of critical phenomena (Fisher, 1967 and Kiang and Stauffer, 1970).

For the Gaussian index of refraction profile of the diffuse spherical clusters we take

$$m^2(r, \ell) - 1 \approx 2(m(r, \ell) - 1) = A \exp(-r^2/\ell^2), \quad (2.8)$$

where $m(r, \ell)$ is the relative index of refraction of the cluster to the average background index of refraction, A is a measure of the deviation of the index of refraction and is the same for all cluster sizes, and r is the distance from the center of the cluster.

To calculate the scattered intensity, the Rayleigh-Debye theory (see Kerker, 1969) is employed. This theory has a simple analytic form and is a good approximation to the Mie theory when

$$2k_0 \ell (m-1) \ll 1. \quad (2.9)$$

Since we expect the fluctuations in the density or concentration to be small compared to the mean, m should be near unity and Eq. (2.9) will hold in general.

The Rayleigh-Debye theory gives the scattered intensity from a single cluster of index of refraction profile $m(r, \ell)$ at a scattering wave vector k to be

$$I(\ell, k) = (k_0^4 / 32\pi^2 R^2) \left| \int d^3r (m^2(r, \ell) - 1) e^{ikr} \right|^2 \quad (2.10)$$

for incident light polarized perpendicular to the plane of incidence, where the incident intensity is unity, and R is the distance from the scatterer to the point of observation. Here $k_0 = 2\pi n / \lambda$. For our choice of $m(r, \ell)$, Eq. (2.8), the scattered intensity from a cluster of size ℓ becomes

$$I(\ell, k) = (A^2 k_0^4 \ell^6 \pi / 32R^2) \exp(-k^2 \ell^2 / 2). \quad (2.11)$$

Assuming single scattering from clusters, the total light intensity scattered by our dispersion is found by using Eqs. (2.7) and (2.11) to be

$$I(k) = \int N(\ell) I(\ell, k) d\ell = (A^2 B k_0^4 \pi / 32R^2) \cdot (k^2 + \xi^{-2})^{-1+\eta/2} \Gamma(2-\eta) D_{-2+\eta}(0), \quad (2.12)$$

where Γ is the gamma function and $D_{-2+\eta}$ is the parabolic cylinder function of order $2-\eta$. For small η , $\Gamma(2-\eta) D_{-2+\eta}(0) \approx 1$. Thus we write

$$I(k) = A^2 B k_0^4 \pi / 32R^2 (k^2 + \xi^{-2})^{1-\eta/2}. \quad (2.13)$$

This is the Fisher corrected Ornstein-Zernike form for the scattered light intensity as given in

Eq. (1.7). The critical exponent η comes in through our size distribution, Eq. (2.7). If the cluster-size distribution is cut off at atomic sizes, the value of B can be shown to be essentially constant as T_c is approached. So far, the model correctly predicts the experimentally verified form for the light-scattered intensity.

Having picked reasonable expressions for the index of refraction profile and size distribution which yield the proper scattered-light intensity form, we now allow the clusters to diffuse and use the formalism of Eq. (2.5) to calculate the correlation function of the scattered field. From (2.8) we write the normalized field correlation function as

$$\frac{\langle \vec{E}^*(t) \cdot \vec{E}(0) \rangle}{\langle |\vec{E}|^2 \rangle} = \frac{\int_0^\infty d\ell N(\ell) I(\ell, k) \exp(-k_B T k^2 t / 6\pi\eta_b \ell)}{\int_0^\infty d\ell N(\ell) I(\ell, k)} \quad (2.14)$$

$k_B T / 6\pi\eta_b$ is the diffusion constant for a particle of size ℓ moving through a background composed mostly of small or atomic-sized particles as indicated by the form of $N(\ell)$, with a background viscosity η_b .

Since the average correlation function is a sum of exponentials, it is not in general an exponential. However, our work on polydisperse systems of polystyrene particles discussed above showed that spectra from polydisperse systems may be well described by a single

exponential. To analyse Eq. (2.14), we evaluate its first cumulant (see Koppel, 1972) which is identical to the Rayleigh linewidth for a perfectly exponential correlation function. The first cumulant is given by

$$K_1 = -\lim_{t \rightarrow 0} \frac{d}{dt} \frac{\langle \vec{E}^*(t) \cdot \vec{E}(0) \rangle}{\langle |\vec{E}|^2 \rangle}.$$

Applying this to Eq. (2.14) we have

$$\Gamma = K_1 = \frac{k_B T}{6\pi\eta_b} k^2 \frac{\int_0^\infty d\ell N(\ell) I(k, \ell) \ell^{-1}}{\int_0^\infty d\ell N(\ell) I(\ell, k)}. \quad (2.16)$$

From Eqs. (2.7) and (2.11) we have

$$\Gamma = \frac{k_B T}{6\pi\eta_b \xi} k^2 (1+k^2 \xi^2)^{\frac{1}{2}} \frac{\Gamma(1-\eta) D_{-1+\eta}(0)}{\Gamma(2-\eta) D_{-2+\eta}(0)}. \quad (2.17)$$

Evaluating the coefficients near $\eta=0$,

$$\Gamma = \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \frac{k_B T}{6\pi\eta_b \xi} k^2 (1+k^2 \xi^2)^{\frac{1}{2}}. \quad (2.18)$$

Except for a numerical factor of order unity, this is identical to the experimentally fitted result of Eq. (1.15).

This is our dynamic droplet model of light scattering from fluids near the critical point. Both the intensity and spectral characteristics of the scattered light follow from our reasonable assumptions concerning the density profile, Eq. (2.7), and size distribution of the droplets.

2.5 Discussion and criticism.

The droplet model as presented above is quite successful in explaining the light-scattering phenomena with a simple physical picture. However, its major drawback is that it predicts a non-Lorentzian line shape or, equivalently, a nonexponential correlation function. This is because Eq. (2.14) represents a sum of exponentials, the sum itself being nonexponential. Data reported up to the time we first proposed the droplet model indicated that the spectra were exponential. Recently Wonica, Swinney and Cummins (1976) have reported correlation function measurements on xenon 18m°C from the critical point which indicate the correlation function is quite exponential. As we shall see later, our own measurements on a binary mixture indicate a high degree of exponentiality too.

In Fig. 7 we plot the results of computer evaluation of the droplet model correlation function in Eq. (2.14) versus time on a semilog plot. An exponential on such a plot would be a straight line. Also plotted in Fig. 7 is the line corresponding to the first cumulant in Eq. (2.18). While the first cumulant does adequately describe the correlation function, the correlation function is noticeably nonexponential. As a measure of the nonexponentiality, we may evaluate the second cumulant (Koppel, 1972) of the droplet correlation

Figure 7. Scattered light correlation function predicted by the dynamic droplet model, Eq. (2.14).

function. The second cumulant is defined as

$$K_2 = \lim_{t \rightarrow 0} \frac{1}{2} \frac{d^2}{dt^2} \ln \langle \vec{E}^*(t) \cdot \vec{E}(0) \rangle. \quad (2.19)$$

If $K_2=0$, the correlation function is exponential. A second cumulant of $K_2/K_1^2=0.15$ is found for the droplet model as compared to the data of Wonica et al. and our own data both of which indicate $K_2/K_1^2 \leq 0.03$. We conclude that the droplet model incorrectly predicts a nonexponential scattered-light correlation function.

As yet we have not removed this problem from our theory. One possible approach to this problem may be to consider the temporal decay of the droplets. As emphasized above, the droplet model assumes the individual droplets only diffuse; they do not grow and decay with time. This assumption is certainly wrong to a degree and its effects on the lineshape have yet to be determined. We have worked along these lines but as yet have had no success.

Another approach would be to consider possible interactions between the diffusing droplets. The droplets might be quite close and so their motion nonrandom. We have observed that the correlation function shape of interacting Brownian systems changes with the interaction strength. Thus, it is conceivable that if the droplets are interacting, the correlation function shape might change.

The possibility of interactions between the diffusing droplets brings up another area of possible improvement of the model. We assume the droplets are diffusing in a background shear viscosity η_b . Near the critical point it is known that the viscosity exhibits an anomalous increase (see our data in section 5.7). This increase in viscosity can be explained in terms of the droplets behaving as a suspension, and a suspension has a higher viscosity than the background fluid (Oxtoby and Metiu, 1976). Since the critical increase in the viscosity is due to the droplets, if the droplets experienced a larger viscosity than η_b they would be experiencing each others presence, i.e. interacting. At this point, we can not predict the extent of this interaction or the effective viscosity to be used in place of η_b .

To explore these possibilities experimentally, we can fit the data to Eq. (2.18) and adjust η_b for a best fit. Then we compare this η_b to the actual measured value.

Certainly one of the more pleasant surprises of the droplet model was the similarity between our droplet model size distribution, Eq. (2.7), and that proposed by Fisher (1967) in his static droplet model of condensation.

Fisher assumes that the size distribution will

be determined by a Boltzman type weighting function where

$$P(n) = e^{-G(n)/k_B T} \quad (2.20)$$

is the probability of having a cluster of n molecules. $G(n)$ is the Gibbs free energy of the n -cluster. Fisher then shows that $P(n)$ can be expressed as

$$P(n) = g_0 x^{n^\sigma} y^{n/\tau} \quad (2.21)$$

where g_0 is a constant and σ determines the variation of the surface area with the number of molecules. For a spherical particle $\sigma = (d-1)/d$ where d is the dimensionality. Also

$$x = \exp(-a_0 (E_s - S_s T)/k_B T)$$

$$y = z \exp((E_B - TS_B)/k_B T). \quad (2.22)$$

Here E_s and S_s are the surface energy and entropy, E_B and S_B are the bulk energy and entropy, z is the fugacity, a_0 is a constant and $\tau \approx 2.2$.

Near the critical point, and especially on the coexistence curve, the chemical potentials of the two phases become equal. Thus, the relative bulk free energy becomes zero and so $y=1$. The surface tension of a critical fluid system has been found to behave as (Widom, 1965 and Warren and Webb, 1969)

$$\sigma_T = c_0 \frac{k_B T}{\xi^2} \quad (2.23)$$

where the constant of proportionality c_0 is near unity. The surface energy is given by $E_s = k_B T \xi^{-2} n^\sigma$; thus, Eq. (2.21) becomes

$$P(n) = g_0 \frac{e^{-n^\sigma/\xi^2}}{n^\tau} \quad (2.24)$$

For nearly spherical clusters when $d=3$, $n \propto \ell^3$ and (2.24) will have the form

$$N(\ell) = g_0 \frac{e^{-\ell^2/\xi^2}}{\ell^{6.6}}, \quad (2.25)$$

Which is quite similar to Eq. (2.7).

Fisher's form and ours are, of course, not exactly the same. However, we must remember that Fisher's work applies below the critical point in the two phase region whereas ours should apply to both the regions above and below the critical temperature. Also, our size distribution stands on its own merits by predicting the experimentally observed light-scattering spectrum.

Recently Oxtoby and Metiu (1976) have proposed a slightly different form for Eqs. (2.7) and (2.8). Based on obtaining the proper scaling form for the free energy of the system they generalize Eqs. (2.7) and (2.8) to the form

$$N(\ell) = B \frac{e^{-\ell^2/2\xi^2}}{\ell^Y} \quad (2.26)$$

and

$$m(r, \ell) - 1 = \frac{Ae^{-r^2/\ell^2}}{\ell^X} \quad (2.27)$$

The proper scaling form for the free energy gives for x and y

$$\begin{aligned} y &= d+1 \\ x &= \frac{1}{2}(d-2+\eta) \end{aligned} \quad (2.28)$$

where d is the spatial dimensionality. For $d=3$, $y=4$ and $x=\frac{1}{2}(1+\eta)$; whereas, our values in Eqs. (2.7) and (2.8) are $y=5+\eta$ and $x=0$. The light-scattering results are equivalent if $y+2x$ (see Eqs. (2.10) and (2.14)) is the same in each case, which they are. Thus, for our purposes in light scattering, either our form or that of Oxtoby and Metiu properly describes the phenomena.

Finally, we point out the difference between the droplet model linewidth prediction and the mode theory predictions at large $k\xi$. As seen in Fig. 1, the droplet model result curve (c) stays flat in the region $k\xi > 10$, whereas the mode-mode theory increases significantly. Obviously, it would be very interesting to explore the large $k\xi$ region experimentally; as yet measurements at $k\xi > 20$ have not been achieved. One measurement by Lai and Chen (1972) has gone deeper into the

critical region than $k\xi=20$ and their results support the mode-mode theory prediction. However, as we shall see, their results may well be erroneous.

2.6 The droplet model in relation to other critical phenomena theories.

We have seen that the droplet model offers us an alternate view of the dynamics of critical point fluctuations from that given by the mode theories. In this section, we discuss some of the basic conceptual differences between the droplet model and mode theory pictures of the decay rate of the density fluctuations.

We have stressed the important role of the extended short-range order, or fluctuations, as an underlying factor in determining the behavior of macroscopic properties near the critical point. One could say, that it is this extended order in all types of critical systems that is the most prominent microscopic feature of these systems. This order is a consequence of the thermodynamics of the system in the critical region. While the location of the critical point itself on the phase diagram is a function of the particular molecular interactions of the system, the critical fluctuations are predominantly only a function of how close the system is to the critical point, and only weakly dependent on the particulars of the system.

Thus, we have that thermodynamics, which is universal to all macroscopic systems, predicts the same sort of fluctuations or extended order for all critical systems. Near the critical point, where the fluctuations are the dominant influence on the macroscopic properties, we expect this universal characteristic to be manifested in universal behavior of the macroscopic phenomena. This is indeed observed as discussed in section 1.2.

Having established the important role of the fluctuations, we now ask what significance the value of the decay rate has for the dynamical properties of the fluctuations? In the mode theories, it is reasoned that since the decay rate far from the critical point is given by $\Gamma = (\Lambda/\rho C_p)k^2$, the same expression applies in the critical region where Λ and C_p now take on their critical values. A, perhaps naive, interpretation of the mode theory physical description is that the divergent critical properties cause the decay rate for the critical fluctuations to slow down.

The underlying description we advance differs from the above point of view. To help us delineate these physical descriptions, we consider the Sengers-Keyes ansatz (Sengers and Keyes, 1971). Sengers and Keyes proposed that to obtain the true critically divergent part of a macroscopic property, one must

subtract off the proper nondivergent background of that property. This background is found by evaluating the property far from the critical point and then extrapolating into the critical region using known microscopic laws for that property. In this way, Sengers and Keyes found that the critical part of the thermal conductivity of various fluids determined by this method displayed universality. We take this ansatz to imply that even in the critical region, the microscopic laws that govern fluid behavior far from the critical point are still at work; the critical behavior being due to new phenomena-the fluctuations as discussed above. (See also the discussion on microscopic and macroscopic diffusion by Lyons, 1973).

Thus, we propose the picture that the critical part of the macroscopic properties in the critical region are determined by the influence of many fluctuations universal to all critical systems. On a microscopic level, as implied by the Sengers-Keyes ansatz, the properties are still given by the same interactions, peculiar to each particular system, which operate far from the critical point. Thus, in particular, the decay rate of an individual fluctuation is still given by the same microscopic laws that determined it far from the critical point. The macroscopic expression of these laws is $\Gamma = (\Lambda / \rho C_p) k^2$ where Λ and C_p are the background

properties of the fluid. The mode theories tell us nothing about the properties of an individual fluctuation, only about the properties of a region containing many fluctuations.

We did not, therefore, describe the Rayleigh linewidth in the critical region in terms of the critical parts of Λ and C_p or as the decay rate of the fluctuations. Rather we made use of the diffusional properties of the fluctuations based on the diffusional analogy. The droplet model allows for both sorts of dynamics, temporal decay and diffusion. In the mode theories, the Rayleigh linewidth is described solely as a temporal decay.

We may rectify the two points of view discussed above. We consider the diffusional mechanism of the dynamic droplet model. If we look at a system containing a large number of these fluctuations, we may consider it as a gas of fluctuations. Because the individual fluctuations are diffusing, this gas will have fluctuations of its own in density; fluctuations in the density of the fluctuations. These "superfluctuations" will decay in time and the decay rate is determined by the spatial diffusional properties of the constituent fluctuations. It is easy to show that the decay time of a superfluctuation is given by $\Gamma = (k_B T / 6\pi\eta_s \xi) k^2$ where ξ is the size of the constituent fluctuations.

We have now gone from the droplet model picture to what might be called the mode theory picture. Considering many fluctuations, all dynamics become temporal decay. We may also identify this decay rate with the thermal diffusivity of the gas of fluctuations, D_T , where

$$D_T = \frac{k_B T}{6\pi\eta_s \xi} = \frac{\Lambda'}{\rho C_p'} . \quad (2.29)$$

Here Λ' and C_p' are the thermal conductivity and specific heat of this gas of fluctuations. Their values, however, are identical to the critical parts of the corresponding properties in the real system. With this reasoning we have the new and satisfying picture of a critical fluid as a gas of fluctuations which has its own transport properties and thermodynamic derivatives which dominate the fluid properties in the critical region. These properties of the fluctuation gas are the critical properties of the real system.

This gas of fluctuations has been identified before. Kadanoff (1966) has presented a similar idea in his cell model of critical phenomena. He proposed that as the correlation length, ξ , became larger in the critical region, one may consider the system as composed of cells of size ξ . As we approach the critical point and ξ increases, the microscopic mechanics of

the system becomes less and less important relative to the mechanics of the system of cells. The cell system hamiltonian describes the macroscopic properties of the system, the critical properties. These are the same ideas discussed above for our fluctuation gas. The cell model has been a concept of major importance in critical phenomena leading to the scaling relations for the critical exponents and the renormalization group (Fisher, 1974).

CHAPTER III

MULTIPLE SCATTERING

3.1 Introduction.

In this chapter we develop a formalism which has been successfully applied to the understanding of the intensity and spectrum of light multiply scattered, in particular doubly scattered, from dense optical systems. This formalism has been applied to both systems of suspended Brownian particles (Sorensen, Mockler and O'Sullivan, 1976a) and critical fluid systems (Sorensen, Mockler and O'Sullivan, 1976b).

We decided to investigate the phenomenon of multiple-scattering for two reasons. First our interest had been raised to develop a theoretical explanation of the multiple-scattering data of Colby et al. (1975) on Brownian motion systems. Brownian motion systems have long been of interest in light-scattering work, but since the problem of multiple-scattering was not understood, concentrated systems which are more likely to multiple-scatter were often avoided. Recent work on such concentrated systems to study interacting Brownian motion had also raised the problem of what effect the multiple-scattering had on the light-scattering spectrum.

Second, because of the large amount of critical opalescence, the measurement of the Rayleigh line near the critical point of a critical fluid often involved the problem of multiple-scattering. Work by Oxtoby and Gelbart (1974a) and (1974b) and Bray and Chang (1975) had indicated the importance of multiple-scattering effects on intensity measurements near the critical point. They found that multiple-scattering could lead to erroneously large values of the critical exponent η if not corrected for in intensity measurements. This work served to dramatize the fact that the effects of multiple-scattering must be correctly accounted for if correlation spectroscopy is to be a useful probe of fluid behavior near the critical point.

3.2 Thought-experiment for double scattering.

We shall start by considering the following experiment. Suppose light is scattered from a system of Brownian particles. The correlation time of the exponential correlation function will be given by Eq. (1.16). Now suppose we collect this light at a given angle, recollimate it, and direct it into another similar system of Brownian particles. What will be the spectrum of light scattered from this second system?

This is the thought-experiment we proposed to ourselves at the beginning of our work on multiple scattering. Its resolution may be obtained if we view

the scattering medium as a randomizing medium which decreases the coherence time of the scattered light. The incident monochromatic laser light can be thought of as completely temporally coherent, so its field correlation function doesn't decay with time. The Brownian particle scatterers act as some sort of chopper which, to a degree, randomize the incident field giving its correlation function a finite decay time. Proceeding to the second Brownian system, the light is randomized further in the second scattering process and the double-scattered field correlation function will have a still faster decay.

We have never performed the experiment suggested above. Interestingly enough, however, after we had completed our work to be described below, we learned of two groups that had performed the above experiment; Bertolotti (1976) at the University of Rome, and Rijswijk and Smith (1976) in Utrecht. Both these groups find experimentally that our conclusions above are correct. However, their work also indicates that if the first and second scattering systems are farther apart than the coherence length of the light scattered from the first system, the second system adds nothing to the spectrum, and the double-scattered spectrum has only the properties of the first scattering event. This distance is of the order of 10cm or more and so will not affect any of our results.

Instead of actually doing the above experiment, we used it to indicate a proper procedure for handling the formalism involved in a double-scattering calculation of the light scattered from a beam incident on one system. We can use the fact that in the above experiment the two scattering regions are completely uncorrelated. This implies that the double-scattered correlation function will be equal to the product of the two single-scattered correlation functions. We also note that the scattering regions are many wavelengths apart and so only far-field scattering is present. This far-field approximation may prove to be a simplifying influence in any calculation of the double-scattered correlation function.

3.3 Electromagnetic wave scattering theory.

With the above thought-experiment in mind, we shall proceed with the equations of electromagnetic theory to derive an expression for the multiple-scattered field correlation function. We have from Born and Wolf (1975)

$$\vec{E}(\vec{r}, t) = \vec{\nabla} \times \vec{\nabla} \times \vec{Z}(\vec{r}, t) + \vec{E}_0(\vec{r}, t) \quad (3.1)$$

$$(\nabla^2 + k_0^2) \vec{Z}(\vec{r}, t) = -4\pi \vec{\alpha}(\vec{r}, t) \cdot \vec{E}(\vec{r}, t) \quad (3.2)$$

where $\vec{E}_0$ is the incident field, $\vec{\alpha}$ is the polarizability tensor, $\vec{k}_0$ is the incident wave vector

$|\vec{k}_0| = k_0 = 2\pi n/\lambda$, and $\vec{Z}$ is the Hertz vector. In Eqs. (3.1) and (3.2) we have left out any terms which do not contribute to the scattered field.

We solve Eqs. (3.1) and (3.2) by use of the Green's function $g(\vec{r}_1, \vec{r}_2)$ where

$$(\nabla^2 + k_0^2)g(\vec{r}_1, \vec{r}_2) = -4\pi\delta(\vec{r}_1 - \vec{r}_2). \quad (3.3)$$

$\delta(\vec{r})$ is the Dirac delta function. Equation (3.3) has the solution

$$g(\vec{r}_1, \vec{r}_2) = \frac{e^{ik_0|\vec{r}_1 - \vec{r}_2|}}{|\vec{r}_1 - \vec{r}_2|} \quad (3.4)$$

Thus, we can easily show

$$\vec{Z}(\vec{r}_1, t) = \int_{\sigma(\vec{r}_1)}^{V_1} d^3r_2 g(\vec{r}_1, \vec{r}_2) \vec{\alpha}(\vec{r}_2, t) \cdot \vec{E}(\vec{r}_2, t). \quad (3.5)$$

In Eq. (3.5), V_1 is the scattering volume and $\sigma(\vec{r}_1)$ is a small volume around $\vec{r}_1$ that is excluded from the integral so that $g(\vec{r}_1, \vec{r}_2)$ won't diverge. From Eqs. (3.1) and (3.2) we have

$$\begin{aligned} \vec{E}(\vec{r}_1, t) = & \vec{E}_0(\vec{r}_1, t) + \int_{\sigma(\vec{r}_1)}^{V_1} d^3r_2 \\ & \vec{\nabla} \times \vec{\nabla} \times [g(\vec{r}_1, \vec{r}_2) \vec{\alpha}(\vec{r}_2, t) \cdot \vec{E}(\vec{r}_2, t)]. \end{aligned} \quad (3.6)$$

The gradient operators in Eq. (3.6) are with respect to $\vec{r}_1$. In arriving at Eq. (3.6) we had to move the

double curl product inside the integral. This resulted in terms not given in Eq. (3.6) which do not contribute to the scattered field, E , at finite scattering angles.

We now evaluate the double curl product. To do this we assign the product $\vec{\alpha} \cdot \vec{E}$ a vector quantity independent of $\vec{r}_1$; we shall call this $\hat{v}$, a unit vector. We then evaluate

$$\vec{\nabla} \times \vec{\nabla} \times [g(\vec{r}_1, \vec{r}_2) \hat{v}]. \quad (3.7)$$

From Eq. (3.4) we may write g as a function of the difference $\vec{r}_1 - \vec{r}_2 = \vec{r}_{12}$ and differentiate with respect to this difference. We find after some vector algebra (see Wills (1958) for various helpful vector identities)

$$\begin{aligned} \vec{\nabla} \times \vec{\nabla} \times [g(\vec{r}_{12}) \hat{v}] &= \frac{e^{ik_0 r_{12}}}{r_{12}} k_0^2 \\ &\left[\hat{v} \left(1 + \frac{i}{k_0 r_{12}} - \frac{1}{k_0^2 r_{12}^2} \right) - \hat{r}_{12} (\hat{v} \cdot \hat{r}_{12}) \right. \\ &\quad \left. \left(1 + \frac{3i}{k_0 r_{12}} - \frac{3}{k_0^2 r_{12}^2} \right) \right]. \end{aligned} \quad (3.8)$$

Which can be written as

$$\vec{\nabla} \times \vec{\nabla} \times [g(\hat{r}_{12}) \hat{v}] = k_0^2 \vec{T}(\hat{r}_{12}) \cdot \hat{v} \quad (3.9)$$

where

$$\begin{aligned} \vec{T}(\vec{r}_{12}) = \frac{e^{ik_0 r_{12}}}{r_{12}} \left[\left(1 + \frac{i}{k_0 r_{12}} - \frac{1}{k_0^2 r_{12}^2}\right) \vec{I} \right. \\ \left. - \left(1 + \frac{3i}{k_0 r_{12}} - \frac{3}{k_0^2 r_{12}^2}\right) \hat{r}_{12} \hat{r}_{12} \right], \end{aligned} \quad (3.10)$$

and $\vec{I}$ is the unit tensor. Equation (3.10) defines the electric dipole field propagator, $\vec{T}(\vec{r}_{12})$. We may then use Eq. (3.5) to give the expression for the scattered field as

$$\vec{E}(\vec{r}_1, t) = k_0^2 \int_{\sigma(\vec{r}_1)} d^3 r_2 \vec{T}(\vec{r}_{12}) \cdot \vec{\alpha}(\vec{r}_2, t) \cdot \vec{E}(\vec{r}_2, t) \quad (3.11)$$

in terms of the electric dipole field propagator. We leave out the integration limit V_1 since it will be implied in our work. We solve Eq. (3.11) by iteration on the field.

$$\vec{E}(\vec{r}_1, t) = \vec{E}_0(\vec{r}_1, t) + \sum_{n=1}^{\infty} \vec{E}_n(\vec{r}_1, t), \quad (3.12)$$

$$\begin{aligned} \vec{E}_n(\vec{r}_1, t) = (k^{[1]})^2 \int_{\sigma_1} d^3 r_2 \vec{T}(\vec{r}_{12}) \cdot \vec{\alpha}(\vec{r}_2, t) \cdot (k^{[2]})^2 \int_{\sigma_2} \dots \\ \cdot (k^{[n]})^2 \int_{\sigma_n} d^3 r_{n+1} \vec{T}(\vec{r}_{n,n+1}) \cdot \vec{\alpha}(\vec{r}_{n+1}, t) \cdot \vec{E}_0(\vec{r}_{n+1}, t). \end{aligned} \quad (3.13)$$

$\vec{E}_n$ represents an electric field that has been scattered n times as shown by Eq.(3.13) and $k^{[n]}$ is the n^{th} scattered wave vector.

In this work we are concerned with the scattered-field correlation function. Using Eq.(3.12) we find this correlation function to be of the form

$$\begin{aligned} \langle (\vec{E}^*(\vec{r}_1, t) \cdot \vec{E}(\vec{r}_1, 0)) \rangle = & \sum_{n=1}^{\infty} \langle \vec{E}_n^*(\vec{r}_1, t) \cdot \vec{E}_n(\vec{r}_1, 0) \rangle \\ & + \sum_{i \neq j} \langle \vec{E}_i^*(\vec{r}_1, t) \cdot \vec{E}_j(\vec{r}_1, 0) \rangle, \end{aligned} \quad (3.14)$$

where we have assumed the field average is stationary in time. The lowest-order term in Eq.(3.14) is the single-scattered correlation function $\langle \vec{E}_1^*(t) \cdot \vec{E}_1(0) \rangle$. The polarization of $\vec{E}_1(t)$ is parallel to the incident polarization and is the lowest-order contributor to the "polarized" scattered component. We will use the usual nomenclature where "polarized" refers to that light scattered with polarization parallel to the incident wave polarization; "depolarized" refers to light scattered with polarization perpendicular to the incident wave polarization.

The next-higher-order term in Eq. (3.14) is $\langle \vec{E}_1^* \cdot \vec{E}_2 \rangle$. This term, as well as any term of the form $\langle \vec{E}_1^* \cdot \vec{E}_m \rangle$, will only be observed in the polarized part of the scattered light because of the inner product with

the $\vec{E}_1$ term, which is solely a polarized component. Thus we need not worry about terms of the form $\langle \vec{E}_1^* \cdot \vec{E}_m \rangle$ if we observe only the depolarized spectrum.

If we assume the individual scattering events are uncorrelated, then all terms of the form $\langle \vec{E}_1^* \cdot \vec{E}_m \rangle$ for $m \geq 2$ are zero. This is because there are $m-1$ extra uncorrelated scattering events in E_m than there are in $\vec{E}_1$. Thus $\vec{E}_m$ and $\vec{E}_1$ are uncorrelated and $\langle \vec{E}_1^* \cdot \vec{E}_m \rangle = \langle \vec{E}_1 \rangle \langle \vec{E}_m \rangle = 0$.

In view of the above arguments, we shall consider the $\langle \vec{E}_2^* \cdot \vec{E}_2 \rangle$ term, the double-scattered term, as the lowest-order contribution to the multiple-scattered field.

3.4 Single scattering.

We shall first use our formalism to find the first-order or single-scattered term. The properties of the single scattered field are well known (see Clark, Lunacek and Benedek (1970)). We will solve Eqs. (3.12) and (3.13) to order $n=1$ and then determine the single-scattered field correlation function. This will help illuminate the procedure to be used when we consider the double-scattered problem.

Truncating Eq. (3.13) and $n=1$ we have

$$\vec{E}_1(\vec{r}_1, t) = k^{-2} \int_{\sigma(\vec{r}_1)} d^3 r_2 \vec{T}(\vec{r}_{12}) \cdot \vec{\alpha}(\vec{r}_2, t) \cdot \vec{E}_0(\vec{r}_2, t) . \quad (3.15)$$

We write the incident electric field as a wave of wave vector k_0 and frequency ω , with polarization

$$\vec{E}_0(\vec{r}_2, t) = \hat{\epsilon} \mathcal{E}_0 e^{i\vec{k}_0 \cdot \vec{r}_2 - i\omega t} \quad (3.16)$$

where $\mathcal{E}_0$ is the wave amplitude.

We shall take the polarizability of the medium to be isotropic. The polarizability tensor may then be written as the diad $\vec{\alpha}(r, t) = a(r, t) \hat{\alpha} \hat{\alpha}$. This isotropy implies that the induced moment will be parallel to the incident field polarization; thus $\hat{\alpha} \cdot \hat{\epsilon} = 1$. From Eqs. (3.15) and (3.16) we then have

$$\vec{E}_1(\vec{r}_1, t) = \mathcal{E}_0 k^{-2} e^{-i\omega t} \int d^3 r_2 a(\vec{r}_2, t) \vec{T}(\vec{r}_{12}) \cdot \hat{\epsilon} e^{i\vec{k}_0 \cdot \vec{r}_2}. \quad (3.17)$$

Since the observation point $\vec{r}_1$ is outside the scattering volume, we need no longer specify the integral in Eq. (3.17) to exclude the volume $\sigma(\vec{r}_1)$.

To proceed further we examine the field propagator, $\vec{T}(\vec{r}_{12})$. In most scattering experiments the detector is many wavelengths distant from the scattering volume and this distance is much larger than the dimensions of the scattering volume. That is, $r_1 \gg 1/k_0$ and $r_1 \gg r_2$. These inequalities imply

$$|\vec{r}_1 - \vec{r}_2| \approx r_1 - \vec{r}_2 \cdot \hat{r}_1, \quad (3.18)$$

which to first order gives

$$|\vec{r}_1 - \vec{r}_2| \approx r_1 \quad (3.19)$$

and

$$|\vec{r}_1 - \vec{r}_2| k_0 \gg 1. \quad (3.20)$$

Equations (3.18), (3.19) and (3.20) describe the far-field approximation (see Jackson, 1962) for a radiating dipole.

In applying the far-field approximation to the field propagation tensor, we use Eq. (3.19) in the magnitude terms of the tensor, but we must use Eq. (3.18) in the phase term in order to evaluate the full effect of the scattered phase. In this approximation, for $\vec{k}' = k' \hat{r}_1$, Eq. (3.10) becomes

$$\vec{T}(\vec{r}_{12}) = \frac{e^{ik'r_1}}{r_1} e^{-i\vec{k}_0 \cdot \vec{r}_2} (\vec{T} - \hat{r}_1 \hat{r}_1) \quad (3.21)$$

Using Eq. (3.21) in Eq. (3.17) we find the single-scattered field to be

$$\begin{aligned} \vec{E}_1(\vec{r}_1, t) = & e_0 k'^2 \frac{e^{ik'r_1}}{r_1} e^{-i\omega t} [\hat{r}_1 \times (\hat{e} \times \hat{r}_1)] \cdot \\ & \int d^3 r_2 a(\vec{r}_2, t) e^{i(\vec{k}_0 - \vec{k}') \cdot \vec{r}_2} \end{aligned} \quad (3.22)$$

We have used the identity $(\vec{a} \times (\vec{b} \times \vec{c})) = \vec{a} \cdot \vec{c} \vec{b} - \vec{a} \cdot \vec{b} \vec{c}$.

Equation (3.22) is the usual result for the single-scattered field with the familiar $1/\lambda^2$ dependence; its strength dies off as $1/r$, and it has the proper dependence on polarization given by the vector products.

Now we consider the case of a system of particles with radius ℓ much less than the wavelength of the incident electric field. Such a particle will scatter light isotropically in the plane perpendicular to the incident polarization. With such a system of scatterers the magnitude of the polarizability is

$$a(\vec{r}, t) = \sigma \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i(t)) , \quad (3.23)$$

where σ is the electric field scattering cross section for one particle.

Substituting Eq. (3.23) into Eq. (3.22) we have

$$\vec{E}_1(\vec{r}_1, t) = e_0 k'^2 \frac{e^{ik' r_1}}{r_1} e^{-i\omega t} [\hat{r}_1 \times (\hat{\epsilon} \times \hat{r}_1)] \sigma \sum_{i=1}^N e^{i(\vec{k}_0 - \vec{k}') \cdot \vec{r}_i(t)} , \quad (3.24)$$

so that the field correlation function in the scattering plane is

$$\begin{aligned} \langle \vec{E}_1^*(\vec{r}_1, t) \cdot \vec{E}_1(\vec{r}_1, 0) \rangle &= e_0^2 k'^4 \sigma^2 r_1^{-2} \\ &\times \left\langle \sum_{i=1}^N e^{-i(\vec{k}_0 - \vec{k}') \cdot \vec{r}_i(t)} \sum_{j=1}^N e^{i(\vec{k}_0 - \vec{k}') \cdot \vec{r}_j(0)} \right\rangle . \end{aligned} \quad (3.25)$$

To evaluate Eq. (3.25) we use the assumption of no correlation between different particles. For no interparticle correlations, the ensemble average on the right hand side of Eq. (3.25) is zero unless $i=j$. If $i=j$ all the terms in the sum are equal. Thus we may write

$$\begin{aligned} \langle \vec{E}_1^*(\vec{r}_1, t) \cdot \vec{E}_1(\vec{r}_1, 0) \rangle \\ = N \epsilon_0^2 k^{-4} \sigma^2 r_1^{-2} \langle e^{i(\vec{k}_0 - \vec{k}') \cdot (\vec{r}_2(0) - \vec{r}_2(t))} \rangle. \end{aligned} \quad (3.26)$$

This is the standard result for the correlation function of the single-scattered electric field. For the case of particles undergoing Brownian motion with a diffusion constant D , Eq. (3.26) gives

$$\langle \vec{E}_1^*(t) \cdot \vec{E}_1(0) \rangle = N \epsilon_0^2 k^{-4} \sigma^2 r^{-2} e^{-D|\vec{k}_0 - \vec{k}'|^2 t}. \quad (3.27)$$

This is the result quoted in the introduction of this thesis, Eq. (1.16).

3.5 Double scattering.

It is a simple matter to generalize the above procedure to obtain the double-scattered field. We start by evaluating Eq. (3.13) to second order

$$\vec{E}_2(\vec{r}_1, t) = k'^2 \int_{\sigma(\vec{r}_1)} d^3r_2 \vec{T}(\vec{r}_{12}) \cdot \vec{\alpha}(\vec{r}_2, t) \cdot k'^2$$

$$\times \int_{\sigma(\vec{r}_2)} d^3r_3 \vec{T}(\vec{r}_{23}) \cdot \vec{\alpha}(\vec{r}_3, t) \cdot \vec{E}_0(\vec{r}_3, t), \quad (3.28)$$

where $\vec{k}'$ is the intermediate scattering wave vector describing the scattering from the first to the second scatterer, and $\vec{k}$ is the wave vector describing the scattering from the second scatterer to the detector. In the first integral we need not worry about the exclusion of the volume $\sigma(\vec{r}_1)$ because we take the observation point $\vec{r}_1$ to be outside the scattering volume. Furthermore, the excluded volume of the second integral $\sigma(\vec{r}_2)$ need not concern us if we only consider double-scattering from two different positions in space.

In the far-field approximation, $\vec{T}(\vec{r}_{12})$ in Eq. (3.28) takes the form given in Eq. (3.21) for the same reasons.

Now we must justify applying the far-field approximation to the tensor $\vec{T}(\vec{r}_{23})$ which describes the scattering of the incident field from the first scatterer to the second scatterer. We make two assumptions:

- 1) $|\vec{r}_3 - \vec{r}_2| k' \gg 1$. This implies that the interparticle separation is on the average greater than the wavelength of the field.
- 2) $r_2 \gg r_3$.

Assumption (1) depends upon the experimental

situation, but is not difficult to satisfy in a real experiment. Assumption (2) can be satisfied if we choose our origin arbitrarily close to the first scatterer at position $\vec{r}_3$. Thus r_3 can be made as small as we wish. Since we are deriving the time correlation function of the scattered field we require assumption (2) to be satisfied for times of the order of the correlation time. For the case of a particle of radius $0.1 \mu\text{m}$ undergoing Brownian motion in water at 20°C , r_3 may change by $0.03 \mu\text{m}$ in a correlation time. Using assumption (1), however, we see that assumption (2) will still hold in general. Thus we may reasonably apply the far-field approximation given by assumptions (1) and (2) to the tensor $\vec{T}(\vec{r}_{23})$. Hence, $\vec{T}(\vec{r}_{23})$ will have the same form as $\vec{T}(\vec{r}_{12})$ given in Eq. (3.21).

With an incident electric field given by Eq. (3.16) and isotropic polarizability, the double-scattered field of Eq. (3.28) takes the form

$$\begin{aligned} \vec{E}_2(\vec{r}_1, t) = & \epsilon_0 \frac{e^{ikr_1}}{r_1} e^{-i\omega t} k^{-2} \int d^3r_2 a(\vec{r}_2, t) e^{-i\vec{k}' \cdot \vec{r}_2} \\ & \frac{e^{ikr_2}}{r_2} k'^{-2} [\vec{I} - \hat{r}_1 \hat{r}_1] \cdot \int d^3r_3 [\vec{I} - \hat{r}_2 \hat{r}_2] \\ & \cdot \hat{e} e^{-i\vec{k}'' \cdot \vec{r}_3} a(\vec{r}_3, t) e^{i\vec{k}_0 \cdot \vec{r}_3}. \end{aligned} \quad (3.29)$$

Here $\vec{k}_0$ is the incident wave vector.

We consider the term $e^{ik''r_2}$ in Eq. (3.29).

Physically, we take $\vec{k}''$ to be the wave vector describing the scattering from the first to the second scatterer, thus $\vec{k}''$ is parallel to $\vec{r}_2 - \vec{r}_3$. By assumption (2) above, $r_2 \gg r_3$, thus $\vec{r}_2 - \vec{r}_3$ and $\vec{k}''$ are nearly parallel to $\vec{r}_2$. Thus, $k''r_2 \approx \vec{k}'' \cdot \vec{r}_2$. With this adjustment Eq. (3.29) becomes

$$\begin{aligned} \vec{E}_2(\vec{r}_1, t) = & e_0 \frac{e^{ik' r_1}}{r_1} e^{-i\omega t} k'^2 k''^2 [\hat{r}_1 \times (\hat{\epsilon}' \times \hat{r}_1)] \\ & \int d^3 r_2 r_2^{-1} a(\vec{r}_2, t) e^{i(\vec{k}'' - \vec{k}') \cdot \vec{r}_2} \\ & \int d^3 r_3 a(\vec{r}_3, t) e^{i(\vec{k}_0 - \vec{k}'') \cdot \vec{r}_3}, \end{aligned} \quad (3.30)$$

where $\hat{\epsilon}'$ is the polarization of the intermediate wave and is given by

$$\hat{\epsilon}' = [\hat{r}_2 \times (\hat{\epsilon} \times \hat{r}_2)] . \quad (3.31)$$

As might have been expected from the approximations we have made, Eq. (3.30) has the form of two completely independent scattering events in succession. Using physically intuitive arguments, such as the thought-experiment proposed above, we could have proposed Eq. (3.30) as the starting point of our theory. However, by proceeding as we have from the elementary

electromagnetic theory, we are more aware of the approximations implicit in Eq. (3.30).

As we did in the case of single-scattering, we examine the particular case of a system of pointlike particles. Using Eq. (3.23) in Eq. (3.30) we have

$$\begin{aligned} \vec{E}_2(\vec{r}_1, t) = & e_0 \frac{e^{ik'r_1}}{r_1} e^{-i\omega t} k'^2 k''^2 \sigma^2 [\hat{r}_1 \times (\hat{e}' \times \hat{r}_1)] \\ & \sum_{i=1}^N \frac{1}{r_{2i}(t)} e^{i(\vec{k}'' - \vec{k}') \cdot \vec{r}_{2i}(t)} \\ & \sum_{\ell=1}^N e^{i(\vec{k}_0 - \vec{k}'') \cdot \vec{r}_{3\ell}(t)}. \end{aligned} \quad (3.32)$$

The time correlation function of the double-scattered field is

$$\begin{aligned} \langle \vec{E}_2^*(\vec{r}_1, t) \cdot \vec{E}_2(\vec{r}_1, 0) \rangle = & \frac{e_0^2}{r_1^2} k'^4 k''^4 \sigma^4 |\hat{r}_1 \times (\hat{e}' \times \hat{r}_1)|^2 \\ & \times \langle \sum_{i,j=1}^N \frac{1}{r_{2i}(0)r_{2j}(t)} e^{i(\vec{k}'' - \vec{k}') \cdot (\vec{r}_{2i}(0) - \vec{r}_{2j}(t))} \\ & \sum_{\ell,m=1}^N e^{i(\vec{k}_0 - \vec{k}'') \cdot (\vec{r}_{3\ell}(0) - \vec{r}_{3m}(t))} \rangle. \end{aligned} \quad (3.33)$$

We now again make the assumption that there is no correlation between any two particles. This allows us to do two things to the expression in Eq. (3.33). First, the ensemble average of the product of the phase terms of the first and second scatterers becomes the product of the ensemble average of each term individually. Second, as in the single-scattering case the average is zero for each term unless $i=j$ or $\ell=m$ for the first or second scatterer respectively, and the sums reduce to N times the argument of the sum. Thus for a noncorrelative system, Eq. (3.33) becomes

$$\begin{aligned}
 \langle \vec{E}_2^*(\vec{r}_1, t) \cdot \vec{E}_2(\vec{r}_1, 0) \rangle &= \frac{e_0^2}{r_1^2} k'^4 k''^4 \sigma^4 \\
 |\hat{r}_1 \times (\hat{e} \times \hat{r}_1)|^2 N^2 \frac{1}{\langle r_2 \rangle^2} &\langle e^{i(\vec{k}'' - \vec{k}') \cdot (\vec{r}(0) - \vec{r}(t))} \rangle \\
 \langle e^{i(\vec{k}_0 - \vec{k}'') \cdot (\vec{r}(0) - \vec{r}(t))} \rangle &.
 \end{aligned} \tag{3.34}$$

In Eq. (3.34) we have taken r_2 to be independent of the phases. We have also dropped the subscripts used to identify the first and second scatterers, since these were only necessary to keep the terms straight while making the averages above. Equation (3.34) is the general result we shall apply to the case of Brownian motion. For such a system each average in Eq. (3.34) yields the usual form for Brownian motion given in

Eq. (3.27). For particles of diffusion constant D , we have

$$\begin{aligned} \langle \vec{E}_2^*(\vec{r}_1, t) \cdot \vec{E}_2(\vec{r}_1, 0) \rangle = & \frac{e_0^2}{r_1^2} k'^4 k''^4 \sigma^4 |\hat{r}_1 \times (\hat{e}' \times \hat{r}_1)|^2 N^2 \\ & \times \frac{1}{\langle r_2 \rangle^2} e^{-D|\vec{k}' - \vec{k}''|^2 t} e^{-D|\vec{k}_0 - \vec{k}''|^2 t}. \end{aligned} \quad (3.35)$$

The comments made after Eq. (3.30) apply here. Equation (3.35) has the form of two distinct and independent scattering events, each event modulates the incident wave and the resultant wave's correlation function is a product of the two individual correlation functions. The conditions we imposed on our result are:

1) The far-field approximation was made twice, once for each scattering event. In particular, the application of the far-field approximation to the first scattering event gives us the condition that the spacing between scatterers be large compared to k^{-1} .

2) We assumed statistical independence of all particles; i.e. we have no long range interactions between particles in the system.

3.6 Integration over the intermediate scattering wave vector.

In this section we will use the results in Eq. (3.35) to derive the correlation function that one would observe in a real experiment on a system of particles. To do this we must realize that while the detector may sit at a particular scattering angle relative to the incident beam, thus defining the final-scattered wave vector $\vec{k}'$, the intermediate-scattered wave vector $\vec{k}''$ may assume any direction in space. Thus to evaluate the correlation function seen in a real experiment we must integrate Eq. (3.35) over all possible directions of $\vec{k}''$. This, of course, is equivalent to averaging over all possible relative positions of the first and second scatterers. In doing this we assume spherical symmetry about the first scatterer. While this is not the most general situation, the experimental conditions can be adjusted so that this symmetry will be satisfied.

To begin we take the final-scattered wave vector to be in the scattering plane. The term "scattering plane" has the usual definition; it is the plane perpendicular to the incident polarization, the x-y plane in Fig. 8. The intermediate scattering wave vector $\vec{k}''$ which is parallel to $\vec{r}_2$ is allowed to assume any direction.

Figure 8. Geometry for double scattering.

From Fig. 8 we can write the following vectors in Cartesian coordinates:

$$\begin{aligned}\hat{k} &= -\hat{1} \\ \hat{\epsilon} &= \hat{3} \\ \hat{k}' = \hat{r}_1 &= \hat{1} \cos\phi_1 + \hat{2} \sin\phi_1 \\ \hat{k}'' = \hat{r}_2 &= \hat{1} \sin\theta_2 \cos\phi_2 + \hat{2} \sin\theta_2 \sin\phi_2 + \hat{3} \cos\theta_2. \quad (3.36)\end{aligned}$$

In Eqs. (3.36) $\hat{1}$, $\hat{2}$ and $\hat{3}$ are the unit vectors in the x, y, and z directions, respectively.

We evaluate the vector cross product $\hat{r}_1 \times (\hat{\epsilon}' \times \hat{r}_1)$ using Eqs. (3.36) and (3.31). This cross product gives the polarization of the scattered field. We separate this term into terms parallel and perpendicular to the incident polarization; these will contribute to the polarized and depolarized spectra, respectively. We find

$$\begin{aligned}|\hat{r}_1 \times (\hat{\epsilon}' \times \hat{r}_1)|_{||}^2 &= \sin^4\theta_2 \\ |\hat{r}_1 \times (\hat{\epsilon}' \times \hat{r}_1)|_{\perp}^2 &= \cos^2\theta_2 \sin^2(\phi_1 - \phi_2) \sin^2\theta_2. \quad (3.37)\end{aligned}$$

Here $||$ and $\perp$ designate parallel and perpendicular to the incident polarization, respectively, i.e., the polarized and depolarized components.

To evaluate the scattered wave vector differences in the exponentials of Eq. (3.35), we make the usual assumption of elastic scattering, $k_0 = k' = k''$. Eqs. (3.36) give us

$$|\vec{k}_0 - \vec{k}''|^2 = k_0^2 (2 + 2\sin\theta_2 \cos\phi_2) \quad (3.38)$$

and

$$|\vec{k}'' - \vec{k}'|^2 = k_0^2 (2 - 2\sin\theta_2 \cos(\phi_2 - \phi_1)) . \quad (3.39)$$

Now we rewrite Eq. (3.35) in terms of θ_2 , ϕ_1 and ϕ_2 ,

$$\begin{aligned} \langle \vec{E}_2^*(t) \cdot \vec{E}_2(0) \rangle = & \frac{\epsilon_0^2}{r_1^2} k_0^8 \sigma^4 N^2 \frac{1}{\langle r_2 \rangle^2} \\ & [(\sin^4 \theta_2)_{||} + (\cos^2 \theta_2 \sin^2(\phi_1 - \phi_2) \sin^2 \theta_2)_{\perp}] \\ & \exp[-Dk_0^2 t (4 + 2\sin\theta_2 (\cos\phi_2 - \cos(\phi_2 - \phi_1)))] , \quad (3.40) \end{aligned}$$

where we have again designated the polarized and depolarized components with a $||$ and $\perp$, respectively.

To find the average field correlation function, we integrate Eq. (3.40) over the volume of the sphere described by r_2 , θ_2 and ϕ_2 and then normalize it with the same integral at $t=0$. We were not able to perform the integral of Eq. (3.40) analytically. However, we can evaluate the slope of the average correlation function at $t=0$. This is the first cumulant as discussed in section 2.3. Since in essence we are summing exponentials, in general we expect a nonexponential spectrum. Nevertheless, the first cumulant will give us a good idea of the behavior of the average double-scattered correlation function. The first cumulant is given by (see Eq. (2.15))

$$K_1 = -\lim_{t \rightarrow 0} \frac{d}{dt} \frac{\langle \langle \vec{E}_2^*(t) \cdot \vec{E}_2(0) \rangle \rangle}{\langle \langle |\vec{E}_2|^2 \rangle \rangle} . \quad (3.41)$$

The second set of angular brackets in Eq. (3.41) indicate the average over $\vec{r}_2$ given by the integration above. Using Eqs. (3.40) and (3.41), and performing the proper integrals we find

$$(K_1)_{\parallel \text{ or } i} = 4Dk_0^2 . \quad (3.42)$$

Equation (3.42) gives us the remarkable result that for either polarization, the first cumulant of the double-scattered field correlation is not a function of

the scattering angle (remember that $\vec{k}_0$ is the incident wave vector). Furthermore, the value of the first cumulant is the same as that obtained for single scattering at a scattering angle of 180° . Intuitively we may picture the double-scattering process as two independent scattering events, each of which may involve scattering at an angle anywhere from 0° to 180° . Since the scattering is isotropic from pointlike particles, all angles are weighted equally, and so we might expect the average scattering angle for each event to be 90° . Two scatterings at 90° yield an effective 180° scattering process.

To get a more exact form of the total field correlation function at all times, we numerically integrated Eq. (3.40) over $\vec{r}_2$ and divided by the proper normalization factor which was determined from a numerical integration of Eq. (3.40) with $t=0$. The double numerical integration was performed with a simple program to compute the integral using trapezoid, midpoint, and Simpson methods. It was found for simple integrals of trigonometric functions which could be solved analytically, that the midpoint method converged fastest to the correct value. Thus the midpoint method was used to evaluate the integrals.

In Figs. 9 and 10 we present plots of the correlation functions versus time of both the polarized and depolarized components of the double-scattered

Figure 9. Polarized correlation function of light double scattered from a system of Brownian diffusing particles.

Figure 10. Depolarized correlation function of light double scattered from a system of Brownian diffusing particles.

light, respectively. Remember that in a scattering experiment, the polarized double-scattered component would not be directly observable due to the much more intense polarized single-scattered component from which it can not be separated. We also plot in Figs. 9 and 10 a line corresponding to the first cumulant or initial slope result of Eq. (3.42). We see that Eq. (3.42) describes the behavior quite well. While there is some scattering-angle dependence of the nonexponentiality of these correlation functions, the first cumulant is independent of the scattering angle in marked contrast to the single-scattered spectrum.

3.7 Scatterers of radius $\ell \lesssim \lambda$.

So far our results apply to the case of pointlike scatterers whose radius ℓ is much less than the wavelength of the incident light ($\ell \ll \lambda$). As the size of the scatterer increases, the scattering from a given particle will become anisotropic with more scattering in the forward direction. In the regime where $\ell \lesssim \lambda$, we expect the results given above will explain the double-scattered field correlation function qualitatively in that there will still be a lack of a major scattering-angle dependence and the correlation time (K_1^{-1}) will in general be shorter than that for single scattering. However, we must also expect that quantitatively the spectrum will be different.

To investigate the double-scattered spectrum of particles of radius $\ell \leq \lambda$, we shall apply the Rayleigh-Debye theory (Kerker, 1969) to our formalism. The Rayleigh-Debye theory describes the scattering of electromagnetic radiation from dielectric spheres when the phase change of the radiation across the spheres is small. This condition is met when (Eq. (2.9))

$$2k_0 \ell (m-1) \ll 1 \quad (3.43)$$

where $\vec{k}_0$ is the incident wave vector, and m is the relative index of refraction of the sphere; m is defined as the index of refraction of the sphere divided by the index of refraction of the medium. To be exact, we should use the full Mie scattering theory of electromagnetic wave scattering from dielectric spheres, but the formalism is too ponderous.

The scattering amplitude in the scattering plane given by the Rayleigh-Debye theory is (Kerker (1969))

$$S(\beta) = \frac{i}{2\pi} k_0^2 (m-1) \ell^3 P(\beta) \quad (3.44)$$

where

$$P(\beta) = \frac{3}{u^3} [\sin u - u \cos u] \quad (3.45)$$

and where

$$u = 2k_0 \ell \sin(\beta/2) \quad (3.46)$$

and β is the scattering angle.

We use $P(\beta)$ of Eq. (3.45) as an attenuation factor to be included in Eq. (3.32). Since there will be two scattering events, there will be two individual scattering angles, β_1 and β_2 . They are the angles between $\vec{k}_0$ and $\vec{k}''$ and $\vec{k}''$ and $\vec{k}'$, respectively, and are given by

$$\begin{aligned} \cos \beta_1 &= \hat{k}_0 \cdot \hat{k}'' \\ \cos \beta_2 &= \hat{k}'' \cdot \hat{k}' \end{aligned} \quad (3.47)$$

From Eqs. (3.36) and the trigonometric identity for half angles we find

$$\sin(\beta_1/2) = \left(\frac{1 + \sin \theta_2 \cos \theta_2}{2} \right)^{1/2}, \quad (3.48)$$

and

$$\sin(\beta_2/2) = \left(\frac{1 - \sin \theta_2 \cos(\phi_2 - \phi_1)}{2} \right)^{1/2}. \quad (3.49)$$

We are now ready to write down the equation for the double-scattered field correlation function for

Rayleigh-Debye scatterers undergoing Brownian motion.

It will have the same form as Eq. (3.35) except that now we must include the factor given in Eq. (3.45) for each of the two scattering events. We have

$$\begin{aligned} \langle \vec{E}_2^*(t) \cdot \vec{E}_2(0) \rangle &= \frac{N^2 A^2 \epsilon_0^2}{r_1^2} k^{-4} k'^{-4} \sigma^4 \\ &\quad |\hat{r}_1 \times (\hat{e}' \times \hat{r}_1)|^2 \frac{1}{\langle r_2 \rangle^2} e^{-D|\vec{k}' - \vec{k}|^2 t} \\ &\quad e^{-D|\vec{k}_0 - \vec{k}'|^2 t} . \end{aligned} \quad (3.50)$$

Where the only difference between Eq. (3.50) and Eq. (3.35) is the attenuation factor A^2 , where

$$A = P(\beta_1) P(\beta_2) . \quad (3.51)$$

We evaluated the first cumulant (initial slope) of the correlation function in Eq. (3.50) using Eq. (3.41) and assuming elastic scattering. The resulting integrals are very complex and thus were performed numerically as described above. We again stress that the first cumulant is in essence the quantity determined experimentally in an experiment; it being the inverse of the correlation time. The nonexponentiality represents

further corrections to the picture the first cumulant gives us.

The results of our calculations are given in Figs. 11 and 12 for the polarized and depolarized double-scattered components, respectively. Here we plot the correlation time ($\tau_c = 1/K_1$) in units of $1/4Dk_0^2$ versus the scattering angle for various values of the particle radius expressed as $2k_0\ell$. Again we see a lack of scattering-angle dependence for the correlation time compared to the single-scattered correlation time dependence of $\tau \propto (\sin\theta/2)^{-2}$. However, there is some scattering-angle dependence as the radius ℓ increases to the order of magnitude of the wavelength of light. We also can see that for all $2k_0\ell$ the correlation times at $\theta = 180^\circ$ are equal. This quality of the double-scattered light was first pointed out by Ferrell (1968).

3.8 The double-scattered intensity.

It is a simple matter to apply our formalism to find the intensity of the double-scattered light. The intensity is merely equal to the correlation function at $t = 0$. For pointlike scatterers ($\ell \ll \lambda$), Eq. (3.27) gives us the single-scattered intensity as

$$I_1(\vec{r}_1) = \frac{\epsilon_0^2}{r_1^2} k_0^4 \sigma^2 N \quad (3.52)$$

Figure 11. General results for the polarized correlation time (inverse of the first cumulant) for light double scattered from a system of Brownian particles.

Figure 12. General results for the depolarized correlation time (inverse of the first cumulant) for light double scattered from a system of Brownian particles.

Similarly, Eq. (3.35) at $t=0$ gives the double-scattered intensity for elastic scattering as

$$I_2(\vec{r}_1) = \frac{e_0^2}{r_1^2} N^2 k_0^8 \sigma^4 |\hat{r}_1 \times (\hat{\epsilon} \times \hat{r}_1)|^2 \frac{1}{\langle r_2 \rangle^2} . \quad (3.53)$$

The ratio of these quantities with the density given by $\rho = N/V$ is

$$\frac{I_2}{I_1} = \rho V k_0^4 \sigma^2 , \quad (3.54)$$

where we have left out the polarization terms and $1/\langle r_2 \rangle^2$. This latter term should vary slowly with the scattering volume. Equation (3.54) has the same form as that given by Oxtoby and Gelbart (1974a) and Reith and Swinney (1975). We see that the double-scattered intensity can be enhanced relative to the single-scattered intensity by increasing the density of the scatterers, a fact we shall make use of later.

If we consider each polarization of the double-scattered light, we may find their relative intensities. Using Eq. (3.40) at $t=0$ and integrating over θ_2 and ϕ_2 for each component we find

$$\frac{I_{2\perp}}{I_{2\parallel}} = \frac{1}{8} . \quad (3.55)$$

So the depolarized component of the double-scattered light is only one-eighth as intense as the polarized part. Thus, if one measures the ratio of the polarized to depolarized intensities in a scattering experiment, one must remember most of the double-scattered light is hidden in the polarized component with the single-scattered light.

For larger particles where $\ell \lesssim \lambda$, we expect the ratio of the total light scattered by the single and double-scattering processes to still vary as shown in Eq. (3.54). However, larger particles no longer scatter isotropically so the scattering ratio of I_2/I_1 may vary with scattering angle. Experimenters have reported that the usual Mie patterns for light scattering from dielectric spheres present in dilute systems of spheres become "washed out" at higher concentrations due to multiple-scattering effects. We can make quantitative predictions of the double-scattered angular dependence using our formalism.

We determine the intensities of the polarized and depolarized components of the double-scattered light as a function of particle radius and scattering angle. This is done by integrating Eq. (3.50) in the prescribed manner at $t = 0$. The results for $2k_c \ell = 2.0$ and 4.0 are plotted in Figs. 13 and 14 for the polarized and depolarized components, respectively. To see the

Figure 13. Intensity versus scattering angle of the polarized double-scattered light for two sizes of particles.

Figure 14. Intensity versus scattering angle of the depolarized double-scattered light for two sizes of particles.

Figure 15. Total double-scattered intensity compared to the single-scattered intensity versus scattering angle.

"washing out" effect we add the polarized and depolarized components and plot this total double-scattered component versus scattering angle along with the single-scattered intensity in Fig. 15. Here we see that the angular dependence of the double-scattered component is greatly reduced relative to that of the single-scattered component.

In Fig. 16 we plot the ratio of the depolarized to polarized double-scattered intensities versus $2k_0\ell$ for various scattering angles. We see that as $2k_0\ell$ increases the polarized component becomes more and more dominant. Again we point out that this implies most of the double-scattered light is irretrievably imbedded within the single-scattered component. A depolarization ratio measurement would imply an erroneously small value of double scattering because, by the results displayed in Fig. 16, the depolarized component is only a small fraction of the double-scattered light. We shall make use of these results in section (3.11) when we consider higher-order scattering.

3.9 Experimental.

Before discussing our own experimental work on double scattering, we compare our theoretical results to the experimental work of Colby, Narducci, Blumel and Baer (1975). In their work, Colby et al. measured the the intensity and intensity correlation of all the light

Figure 16. Ratio of the depolarized to polarized double-scattering intensity, R_2 , versus particle size, $2k_0l$.

scattered from dense systems of Brownian particles. Their intensity measurements showed the "washing out" effect discussed above. Their correlation measurements showed a decrease in correlation time and a lessening of the usual k^2 dependence seen for single scattering. These results are in qualitative agreement with our results above.

To give a stronger case for our theory in view of their data, we plot in Fig. 17 the correlation times for single scattering and polarized double scattering versus $(\sin\theta/2)^{-2}$ for $2k_0\ell=4.3$. We do not plot the depolarized double-scattered correlation time because we have seen (Fig. 16) that this component is much weaker (but not significantly different, compare Figs. 11 and 12) than the polarized double-scattered component. We might expect that as the concentration of scatterers increases, the correlation time will change from behaving like the single-scattered graph to behaving like the double-scattered graph. Also plotted in Fig. 17 are their experimental data for particles of diameter $0.312\ \mu\text{m}$. At their experimental wavelength of $\lambda=6328\text{\AA}$ and the suspending medium index of refraction of 1.33 this gives $2k_0\ell=4.3$. The theory and experiment are seen to be compatible. Further we can even explain their observed nonexponentiality in concentrated systems as the sum of the single-scattered and double-scattered spectra.

Figure 17. Comparison of the data of Colby et al. (1975) to our double-scattering prediction. Particle size is $2k_0 \ell = 4.3$.

To test our results in a quantitative manner, we have measured the depolarized correlation function of light double scattered from systems of Brownian diffusing particles (Sorensen, Mockler and O'Sullivan, 1976a). We used two systems of polystyrene latex microspheres suspended in water. These are the same spheres used in our polydispersity measurements discussed above. The samples are very monodisperse in size thus there should be no nonexponentiality (Koppel, 1972) or scattering angle dependences due to polydispersity effects (section 2.3). The smaller spheres had a radius of $0.055\text{ }\mu\text{m}$ and are barely into the region where finite size must be considered. The larger spheres were of radius $0.117\text{ }\mu\text{m}$ and so are definitely nonpointlike. At this radius one must use the full Rayleigh-Debye treatment discussed above in section 3.7.

We can improve upon the experimental measurements of Colby et al. (1975) by measuring the spectrum of only the depolarized scattered light and not all the scattered light. In this way we separate out the strong single-scattered component. Also, since the depolarized scattered light characterizes the double-scattered light, we may consider its measurement a test of our double-scattering formalism.

Since the depolarized to polarized scattered intensity ratio increases with concentration as shown in

Eq. (3.54), we worked with suspensions of high concentration. However, at large concentrations, polystyrene spheres, which are inherently charged, begin to interact. This violates our condition of noninteracting particles. To determine if a system of microspheres was interacting, we measured the correlation time of the polarized scattered light as a function of concentration. It is known (Pusey, 1974) that the correlation time of the single-scattered polarized component of light scattered from a system of interacting Brownian particles decreases with increasing concentration. If a system was found to be interacting, we diluted it until no further concentration dependence was seen and the correlation time was the same as that measured in the very dilute limit. In this way we chose a concentration of 9×10^{-5} by volume for the $\lambda = 0.055 \text{ } \mu\text{m}$ system, and a concentration of 1.8×10^{-5} by volume for the $\lambda = 0.117 \text{ } \mu\text{m}$ system.

As both Bray and Chang (1975) and Reith and Swinney (1975) have shown, the measured intensity of the depolarized light is a function of the experimental scattering geometry. In deriving our results we have assumed a spherically symmetric distribution of second scatterers about a first scatterer. Equivalently, we could have considered a spherically symmetric distribution of first scatterers about the second scatterer.

This latter situation can be satisfied experimentally if our detector looks at a small region near the center of the illuminated scattering volume. In this way we see second scatterers with a large, isotropic volume of first scatterers around them.

This experiment represents our first attempt to measure the depolarized double-scattered spectrum. Since then we have performed experiments that indicate the spherical scattering geometry can be obtained with a narrow incident beam and a wide field of view for the detector. One can reason that this is equivalent to a spherically symmetric region of second scatterers about the first scatterers. Experimentally, it appears that if in general the scattering volume is of comparable dimensions to the scattering cell or container, the spherical geometry condition will hold. We shall discuss these points and the case where the spherical geometry condition breaks down in section 3.10.

In our experimental situation, as is common, the polarized component of the scattered light is many times larger than the depolarized component. Because of this, special care must be taken to eliminate all the polarized light when measurements on the depolarized light are being carried out. If there is strain in the sample cell, some of the polarized component may be mixed in with the depolarized component causing

erroneous results. We examined our sample cell by placing it between crossed polarizers and found it to be free of strain. However, fingerprints and dust were evident on the wall of the cell. Thus one must take great care that the outside as well as the inside of the cell is clean and dust free in order to avoid mixing the depolarized and polarized components.

In our experimental setup, (also see Chapter V for discussion of our experimental apparatus) we directed the unfocused beam of an Argon-ion laser operating at a wavelength of $\lambda = 5145\text{\AA}$ into our glass scattering cell. The beam diameter was $\sim 5\text{mm}$ and the scattering cell was a glass tube of 21mm I.D. The unfocused beam provided a large scattering region in order to suit the conditions required by the assumption of spherical symmetry as discussed above. Focusing of the beam by the glass cell caused no problems. Before entering the cell, the beam passed through a Glan-Thompson polarizing prism with an extinction ratio of 5×10^{-5} giving the incident beam a vertical polarization. Light scattered in the horizontal plane passed immediately through a small aperture 1.3mm in diameter and then through two more Glan-Thompson polarizers, each of which had an extinction ratio of 5×10^{-5} . These polarizers were adjustable so as to pass either the polarized or depolarized component of the scattered

light. Two polarizers were used to ensure complete filtering of the unwanted component. The light was then collected by a lens of 37mm focal length which focused the image of the 1.3mm aperture onto a 300 μm diameter pinhole.

The magnification of the aperture image by the lens was approximately 0.25. With this configuration we could pick out a small region in the center of the illuminated region. The 300 μm pinhole was one meter from the cathode of a FW130 photomultiplier tube, thus projecting approximately one coherence area of scattered light on the cathode. Pulses from the photomultiplier tube were analysed by our intensity autocorrelator to determine the correlation function of the scattered light. The correlation function was analysed with an on line Nova 800 computer to determine the correlation time using a fitting routine that weights the $t = 0$ part of the spectrum heavily (Lyons, 1973, and see section 5.2).

Our calculations have been concerned with the electric field correlation function of the scattered light. We measured the intensity correlation function of the scattered light in our experiments. These two correlation functions are related in a simple manner, by the Siegert relation, if the scattered electric field is Gaussian (Pike, 1974). Since we are considering

scattering from many different pairs of events, this Gaussian assumption should be satisfied for double scattering. Kelly (1973) discusses this point and finds that the scattered field will be Gaussian for a large number of scatterers. Colby et al. (1975) found experimentally that the light scattered from their dense systems was Gaussian. Furthermore both Bertolotti (1976) and Rijswijk and Smith (1976) found that the light coherently scattered from their double systems was Gaussian. For these reasons we shall take the double-scattered field to be Gaussian and, therefore, assume the Siegert relation holds.

Care had to be taken to adjust the polarizers to the correct polarization angle during depolarized spectrum measurements or else erroneous results were obtained. Both the polarization of the incident beam and the detected light had to be adjusted to better than $\pm 0.3^\circ$. Our procedure was to measure the count rate as a function of both the incident and detection polarization angles to find a minimum in the count rate. As an example, in Fig. 18 we plot the count rate and the measured correlation time as a function of the detection polarization angle. This data was taken from the $0.117 \mu\text{m}$ system at a scattering angle of 30° . The minimum in the count rate and the correlation time are at the same angle. We also know from our theoretical

Figure 18. Count rate and correlation time as a function of the detection polarization angle.

work that at $\theta = 30^\circ$ the depolarized double-scattered correlation time is much less than the single-scattered correlation time. Thus, it is reasonable to interpret Fig. 18 as indicating the polarization angle at which the single-scattered component has been filtered out; that angle being the angle at which τ_c and the count rate are at minimum. As can be seen the minimum angle could be defined to better than $\pm 0.3^\circ$. In our experimental results to be described below, it is conceivable that we were not always successful in finding this minimum or in completely filtering out all of the polarized component. However, from data like those in Fig. 18, we believe that the resulting error in the measured correlation time was probably limited to $\leq +3\%$.

In Figures 19 and 20 we plot the results of our experiments along with our theoretical predictions as given by Eq. (3.50). The correlation times are normalized to 20°C from our experimental condition of $T=23.5\pm 0.3^\circ\text{C}$ assuming a normal viscosity temperature dependence. Figure 19 shows our results for the $\lambda=0.055\mu\text{m}$ system. The upper curve shows the experimental results and the theoretical prediction for the polarized component. The bulk of this polarized component is due to single scattering and indeed we see the characteristic $\sin^2(\theta/2)$ dependence. The datum

Figure 19. Comparison of theory and experiment for light scattering from the $\lambda=0.055\mu\text{m}$ system.

Figure 20. Comparison of theory and experiment for light scattering from the $\lambda=0.117\mu\text{m}$ system.

point for $\theta=30^\circ$ ($\tau_c = 1.59$ msec) runs off the graph on this scale and was not plotted. In marked contrast is the correlation time behavior for the depolarized component plotted in the lower part of Fig. 19. Obviously the large scattering-angle dependence seen in the polarized component is gone in the depolarized component. The dashed line in Fig. 19 is the prediction of Eq. (3.42) for $\ell \ll \lambda$ and is seen to be inadequate to explain the data, being $\sim 10\%$ too low. The solid line nearest the depolarized data represents the results obtained from the numerical integration of Eq. (3.50) which takes into account the Rayleigh-Debye scattering from a particle of radius $\ell=0.055\mu\text{m}$. The agreement between theory and experiment is seen to be good.

Figure 20 presents our results for the system of $\ell=0.117\mu\text{m}$ particles. The assumption of $\ell \ll \lambda$ would result in a predicted correlation time of $\tau_c=0.257$ msec for the depolarized scattered light, by Eq. (3.42). This is obviously not the case and we must again use Eq. (3.50). Numerical integration of Eq. (3.50) gives the dashed line in Fig. 20. While the fit is much closer, it is still inadequate. We must remember, however, that the Rayleigh-Debye theory is only an approximation and it begins to lose validity when Eq. (3.43) is poorly satisfied. What is really needed is the exact

Mie theory, but as mentioned earlier this would be very unwieldy. To get a better fit, we compared the predictions of the Rayleigh-Debye scattered intensity versus angle for various sized particles near $\ell=0.117\mu\text{m}$ to the exact Mie theory for particles for radius $\ell=0.117\mu\text{m}$. These comparisons were made to fit the experimental conditions where $m=1.20$ for polystyrene in water, $\lambda=5145\text{\AA}$ and the index of refraction of water is 1.33. It was found that the Rayleigh-Debye formula using a particle radius of $\ell=0.123\mu\text{m}$, agreed very well with the tabulated (Denham, Heller and Pangonis, 1963) Mie results for the true particle radius of $\ell=0.117\mu\text{m}$. Thus we rederived our theoretical prediction using Eq. (3.50) and a particle radius of $\ell=0.123\mu\text{m}$. We may consider this prediction to be the same as that which would be given by the exact Mie theory for a particle radius of $\ell=0.117\mu\text{m}$, the true particle radius. This result is the solid line in Fig. 20 and is seen to agree quite well with the data. We conclude that our theory is good for particles when the condition $\ell \ll \lambda$ is no longer satisfied, if the proper scattering function is known for the particle.

3.10 The spherical scattering geometry condition.

Our results of Eqs. (3.42) and (3.50) which were applied successfully to our data as seen in Figs. 19 and 20, apply to the particular experimental situation of a spherical scattering geometry. By this we mean that there is either: (1) a spherically symmetric region of observed second scatterers surrounding a given first scatterer, or (2) there is a spherically symmetric region of first scatterers surrounding the observed second scatterers. As we discussed in the last section, our experimental setup was designed to satisfy the second condition.

We may imagine a situation in which the assumption of a spherical scattering geometry is no longer valid. In Fig. 21a we see a typical scattering setup where laser light is incident from the left and light scattered out at some angle is detected by the photomultiplier tube, PMT. If we look in along the direction of the incident beam, we would see the situations drawn in Figs. 21b and 21c. In Fig. 21b we have an incident wide beam geometry. Scatterers numbers 1, 2, and 3 are all viewed by the detector. Scatterer number 1 may receive light from any other scatterer in the illuminated region to be a second scatterer. We can see that scatterer number 1 has essentially a spherically symmetric region of first scatterers around it. Similarly,

Figure 21. Typical scattering geometries for wide and narrow incident beams.

we may argue that scatterers numbers 2 and 3 have right and left hemispheres of first scatterers about them. The combined effect of this is complete spherical symmetry. From such reasoning, we can justify the spherical scattering geometry for an incident beam of width comparable to the dimensions of the container.

In Fig. 21c we draw a narrow incident beam. Again, for scatterers numbers 1, 2, and 3 we may make the arguments above for a spherical scattering geometry. However, now we have scatterers such as numbers 4 and 5 which no longer have first scatterers in a finite region above or below them. The spherical scattering geometry does not hold for these scatterers.

We can characterize the lack of spherical geometry by the angle α in Fig. 21c. There are no first scatterers for the second scatterers numbers 4 and 5 above an angle α out of the scattering plane. Thus to see how our theory is affected, we limit our integration over the intermediate scattering angle to only this region defined by α . That is, when we integrate (or average) over the relative positions of the scatterers, we integrate over all r_1 (0 to ∞) all ϕ_1 (0 to 2π) but only over θ_1 in the range $90^\circ - \alpha \leq \theta_1 \leq 90^\circ + \alpha$ (see Fig. 8). In this way, we exclude some of the first scatterers above and below the second scatterers simulating the nonspherical geometry of Fig. 21c.

In table I we give the results of correlation measurements using the techniques described in the last section only for various incident beam diameters. The $\ell=0.117 \mu\text{m}$ system was used. We see that as the incident beam is narrowed the correlation time increases from the wide beam limit by as much as 23%.

In Fig. 22 we plot these experimental values along with our theoretical predictions using the ideas above and Eq. (3.50) for $2k_0\ell=4.0$. We parameterize our theoretical curves on the angle α . While we can not hope for a quantitative fit, we do find qualitative agreement; the correlation time increases with the loss of the spherical scattering geometry. Oddly enough, the theoretical correlation time at first decreases at $\alpha=45^\circ$ but then, as $\alpha \rightarrow 0$, increases monotonically. Whether this effect is real is doubtful, but we have not investigated it. In any event, it appears our formalism is flexible enough to account for less symmetric scattering geometries.

We go back to Fig. 21c. Here we draw a possible wider detection region by the dashed lines. It can now be reasoned that such a geometry would be spherical because there is now a spherically symmetric region of second scatterers about the first (condition number 1 at the beginning of this section). This is indeed the case. We have found experimentally that a narrow incident beam

TABLE I

Effect of narrowing the incident beam on the measured correlation time of the depolarized light scattered from the $\lambda=0.117\text{ }\mu\text{m}$ system. Beam diameters greater than 5 mm showed no change in τ_C .

θ (deg.)	Beam diam (mm)	τ_C (msec)
60	5	0.524
	2.5	0.600
	1.6	0.650
90	5	0.447
	5	0.473
	1.6	0.505

Figure 22. Comparison of theory and experiment for a narrow incident beam scattering geometry.

will exhibit the spherical geometry results if our detection region is big.

We now stress the fact that while it may be possible to adjust the integrating procedures for most geometries, in particular the more conventional narrow beam and narrow detection region geometry, the wide beam or wide detection region geometry is significantly more tractable for predicting theoretical results. Thus, we would recommend that future work concerned with double scattering or its effects use the wide beam or wide detection region configuration. There is no drawback to these methods, and its favorable qualities make adoption of the procedure worthwhile.

3.11 Higher-order scattering.

Up to this point, our discussion has been concerned with double scattering, the lowest-order contribution to the multiple-scattered field. It is obvious that an explicit calculation of the higher-order terms in Eq. (3.14) would be extremely difficult and tedious. In this section, we shall discuss these higher-order terms in a qualitative manner, based on what we have learned from our double-scattering work. This will help us estimate the effects of these higher-order terms in any experiments we may perform.

We may include higher-order terms of the multiple-scattered light by not truncating the series

in Eq. (3.14) at $n=2$. The next-lowest-order term, after the double-scattered term is $\langle \vec{E}_2^* \cdot \vec{E}_3 \rangle$. We shall again use the assumption of noninteracting particles. We shall also assume the n^{th} and m^{th} scatterers are not the same scatterer when $m \neq n$. For the case of $\langle \vec{E}_2^* \cdot \vec{E}_3 \rangle$ this excludes the possibility that light might scatter from the first to the second and back to the first scatterer to yield the triple-scattered term, $\vec{E}_3$. Under these assumptions, $\langle \vec{E}_2^* \cdot \vec{E}_3 \rangle$ is zero because at least one scattering event in $\vec{E}_2$ and $\vec{E}_3$ is random (see section 3.3) relative to the other events. Thus, all such terms of the form $\langle \vec{E}_i^* \cdot \vec{E}_j \rangle$ where $i \neq j$ are zero. We recognize that there is a finite probability for scattering twice from the same scatterer in a sequence as described above, but this scattering is much less probable and therefore much less intense than a nonrepeating series of scattering events. It should also be pointed out that these conclusions will not be valid for strongly interacting systems.

With this reasoning Eq. (3.14) loses its cross terms. The next-lowest-order term is the triple-scattered term, $\langle \vec{E}_3^* \cdot \vec{E}_3 \rangle$. We may apply our formalism in a straight-forward manner to the calculation of this triple-scattered or any n -scattered term to find the correlation function. We merely extend our results of independent scattering to n events. Thus, we have that

the correlation function of the n -scattered light is found by considering n single-scattering events in succession. Actual calculation of such an n -scattered correlation function would require keeping track of the polarizations and intermediate scattering wave vectors and then integration over the $n-1$ relative position vectors. Such an integration appears to be far too complex to pursue except for the double-scattering case where $n=2$.

We may however approach the problem on a non-analytic level and come up with some qualitative predictions concerning higher-order scattered light. We showed in section 3.6 that for pointlike particles undergoing Brownian diffusion the double-scattered spectrum was independent of the scattering angle and had a correlation time equal to the single-scattered correlation time at a 180° scattering angle. This is equal to one half the single-scattered correlation time at 90° . We may visualize that each scattering event might have a scattering angle anywhere from 0° to 180° . For pointlike particles the scattering is isotropic. Thus, there is no preferred direction, and we might expect an average scattering angle of 90° for each event. On the average each event contributes a correlation time equal to that for single scattering at 90° . Two such events would give half this time; the spectrum that is indeed predicted and

observed. Thus, we have a simple picture of the double-scattering process.

We now generalize this argument for n scattering events. Each of the n events contributes a correlation time equal to that for single scattering at 90° ; call this $\tau_1(90^\circ)$. Then the n^{th} order correlation time will be

$$\tau_n = \frac{\tau_1(90^\circ)}{n}, \quad (3.56)$$

and again independent of the scattering angle.

We may extend this argument to large particles where $\ell \leq \lambda$. For these particles we developed the Rayleigh-Debye modified formalism of Eq. (3.50). For such particles the scattering is no longer isotropic; there being more scattering in the forward direction. Thus, the average scattering angle would be weighted more heavily by the forward angles. That is, we expect an average scattering angle of less than 90° per event due to this smaller angle weighting, and this average scattering angle will drop as $2k_0\ell$ increases. This picture predicts no scattering-angle dependence which we have seen to be false (Fig. 20); but it also predicts double-scattered correlation times larger than those for pointlike particles which we do know to be true. We may then rewrite Eq. (3.56) as

$$\tau_n = \frac{\tau_1(\bar{\theta})}{n} \quad (3.57)$$

with $\bar{\theta}=90^\circ$ for $2k_0\ell \ll 1$ and $\bar{\theta}$ decreasing for $2k_0\ell$ increasing. While Eq. (3.57) is not exact, we may use it as an estimate of higher-order correlation times.

We would also like to evaluate the relative intensities of the higher-order scattered light. It is easy to show that Eq. (3.54) for the ratio of the double to single-scattered light can be generalized to the n^{th} and $(n+1)^{\text{th}}$ order scattered light as

$$\frac{I_{n+1}}{I_n} \propto \rho V k_0^4 \sigma^2. \quad (3.58)$$

Obviously, the sum of all the I_n terms, $\sum I_n$, diverges unless $I_n/I_{n+1} < 1$. Our Eqs. (3.12) and (3.13) represent a Born series for the scattered intensity. Such a series is good only for a small scattering cross section implying $I_n/I_{n+1} \ll 1$ (Merzbacher, 1967). We emphasize here that while the intensities predicted by Eqs. (3.12) and (3.13) may be wrong in the limit of large scattering, the correlation times will be correct. They are not affected by the absolute amount of scattering but only by the temporal characteristics of the scattering process.

In the optically dense limit, the limit where higher-order scattering is quite probable, we can not expect the Born series represented by Eq. (3.58) to still hold. In this intensely scattering case, we shall

consider the scattering as a random process. The characteristics of this process are such that each scattering event is independent of the next. Also, while the probability of any one scattering event is small, there are many possible events so that the average number of actual events is finite (say one or two). Such a random process is described well by the Poisson distribution (Melissinos, 1966). A Poisson distribution is derived from a Gaussian distribution in the limit of small probability per event but many events, exactly our conditions in multiple scattering. The probability of having n scattering events will be, by the Poisson distribution

$$P(n) = \frac{\bar{n} e^{-\bar{n}}}{n!} . \quad (3.59)$$

Here we use $\bar{n}$ to denote the average number of scattering events. Note that $P(n)$ is normalizable to one; $\sum P(n) = 1$. We shall take the intensity of the n^{th} order scattered light to be proportional to $P(n)$

$$I_n \propto P(n) . \quad (3.60)$$

With the above reasoning, we can characterize the multiple-scattering process with the parameter $\bar{n}$, the average number of scattering events. We can then calculate the effective correlation times for the polarized

and depolarized scattered light in the case of higher-order scattering using Eqs. (3.56) and (3.57). These effective correlation times will be the average correlation times, weighting the averages with the Poisson distribution. Before these averages can be evaluated, however, we must determine $\bar{n}$ experimentally.

We can determine $\bar{n}$ experimentally by measuring the ratio of the depolarized to polarized scattered light intensities. This ratio is called the depolarization ratio and is zero for no scattering of higher order than first for an isotropic system. We write the depolarization ratio, R , as

$$R = \frac{I_{\perp}}{I_{\parallel}} = \frac{\sum_{n=1}^{\infty} I_{n\perp}}{\sum_{n=1}^{\infty} I_{n\parallel}} . \quad (3.61)$$

$I_{n\perp}$ and $I_{n\parallel}$ are the depolarized and polarized parts of the n^{th} -order scattered light and

$$I_n = I_{n\parallel} + I_{n\perp} \propto P(n) . \quad (3.62)$$

We shall also require the depolarization ratio of the n^{th} order scattered light, R_n

$$R_n = \frac{I_{n\perp}}{I_{n\parallel}} . \quad (3.63)$$

We have calculated this ratio for $n=2$ and the results for general particle radius are given in Fig. 16. In this higher-order scattering derivation to be presented here, we shall consider only the case of $\ell \ll \lambda$ so that $R_2 = 0.125$ (Eq. (3.55)).

For higher order than $n=2$, determination of R_n becomes very difficult. A lengthy derivation for $n=3$ gives $R_3 = 0.26$ (Sorensen, unpublished). For $n \gg 1$ we expect the polarization to be completely randomized relative to the incident polarization and $R_n = 1$ for $n \gg 1$.

We may use Eqs. (3.62) and (3.63) to find

$$I_{n||} \propto \frac{1}{1+R_n} P(n) \quad (3.64)$$

and

$$I_{n\perp} \propto \frac{R_n}{1+R_n} P(n) \quad (3.65)$$

In the proportionalities in Eqs. (3.64) and (3.65), the proportionality constants are all equal. Thus, from Eqs. (3.61), (3.64) and (3.65) we find

$$R = \frac{\sum_{n=1}^{\infty} \frac{R_n}{1+R_n} P(n)}{\sum_{n=1}^{\infty} \frac{1}{1+R_n} P(n)} \quad (3.66)$$

We evaluate this expression numerically for $R_1=0$, $R_2=0.125$, $R_3=0.26$, $R_4 \approx 0.5$ (this is an estimate) and $R_n=1$ for $n \geq 4$ for various $\bar{n}$. The results are plotted in Fig. 23. By measuring R and using Fig. 23, we can determine $\bar{n}$ for a given experimental situation.

We now calculate the average correlation time for the depolarized and polarized scattered light when higher-order scattering is present. We do this for the case when $\ell \ll \lambda$ and $\theta=90^\circ$ using Eq. (3.56). The average correlation time is given by

$$\bar{\tau}_{\perp \text{or} \parallel} = \frac{\sum_{n=1}^{\infty} I_{n\perp \text{or} \parallel} \tau_n}{\sum_{n=1}^{\infty} I_{n\perp \text{or} \parallel}}. \quad (3.67)$$

Using Eqs. (3.56), (3.64) and (3.65) in Eq. (3.67), we have

$$\bar{\tau}_{\perp} = \tau_1 \frac{\sum_{n=1}^{\infty} \frac{1}{n} \frac{R_n}{1+R_n} P(n)}{\sum_{n=1}^{\infty} \frac{R_n}{1+R_n} P(n)} \quad (3.68)$$

and

$$\bar{\tau}_{\parallel} = \tau_1 \frac{\sum_{n=1}^{\infty} \frac{1}{n} \frac{1}{1+R_n} P(n)}{\sum_{n=1}^{\infty} \frac{1}{1+R_n} P(n)}. \quad (3.69)$$

Figure 23. Average number of scattering events $\bar{n}$ versus the depolarization ratio R .

We evaluate these expressions numerically for the same R_n used above. The results are plotted in Fig. 24 where we plot $\bar{\tau}_{||}/\tau_1$ and $\bar{\tau}_1/\tau_2$ ($\tau_2=\tau_1/2$, and is the lowest-order depolarized correlation time) versus $\bar{n}$. The curves are nearly identical.

As has become characteristic procedure in this thesis, once we have a theoretical result, we put it to the test of experiment. We performed polarized and depolarized correlation time measurements on the $\ell=0.055\mu\text{m}$ system at $\theta=90^\circ$. Our procedures were similar to those described in section 3.9. We have seen that the condition $\ell \ll \lambda$, while not perfectly satisfied for this system, gives reasonable results for the depolarized spectrum when higher-order effects should be small.

To vary the average number of scattering events $\bar{n}$, we varied the concentration of the microspheres. As we have discussed above, the polystyrene microspheres are inherently charged and may interact at high concentrations. We have not calculated the effect such a possible interaction might have. Efforts to screen the interactions with the addition of an ionic salt failed. We found for a concentration of 3.3×10^{-5} by volume microspheres in water a 0.017M solution of NaCl caused coagulation of the microspheres. Lower concentrations of NaCl are not practical to obtain. Thus, we shall neglect any possible effects of these interactions and

Figure 24. Comparison of theory and experiment for the polarized and depolarized scattered light correlation times of light multiple scattered from a system of Brownian particles.

see how well our data and theory agree.

Plotted in Fig. 24 along with our theory for $\tau_{||}$ and $\tau_{\perp}$ is our data. $\bar{n}$ was determined from depolarization ratio measurements on the system and Fig. 23. As can be seen, theory and data for the polarized correlation time agree quite well. The polarized correlation time is, of course, dominated by the single-scattered component and is often considered as a sole result of single scattering. Here we see that the effects of higher-order scattering are not only important but can be calculated using the ideas described here.

The depolarized correlation function does not agree well with our theoretical prediction. At this time we can not explain this discrepancy. If we take our theory's success in explaining the polarized correlation function as indicating our depolarized theory is correct, we must conclude that another effect is entering into the depolarized correlation function. While we can offer no proof, this extra effect may be the interactions between the diffusing charged microspheres.

Finally, in Fig. 25 we have plotted $\bar{n}$ versus the concentration. Here we see a reasonably linear dependence as we might have expected.

Figure 25. The average number of scattering events $\bar{n}$ determined from depolarization ratio measurements and Fig. 23 versus the concentration of microspheres.

CHAPTER IV

DOUBLE SCATTERING FROM CRITICAL FLUID SYSTEMS

4.1 Introduction.

The problem of multiple scattering from fluid systems near their critical point has an unusual history. Unusual in the fact that despite the intense activity in light-scattering studies on such systems in the past ten years few workers, experimental or theoretical, have given more than casual concern to this problem. This is more unusual in the light of the extreme critical opalescence observed in such phenomena in the region near the critical point, the most interesting region.

A few reasons for this casual concern might be identified. First, the apparent complexity of the theoretical problem has deterred most workers from attacking it. Second, the fortunate, apparently coincidental, fact that the light-scattering data has fit reasonably well to the single-scattering theories. Thus, the reasoning is, a posteriori, that the multiple scattering must not have a significant effect. We need not mention how dangerous such a procedure is.

Recently, there has been some work on the intensity of the double-scattered light from fluids near

their critical point. Oxtoby and Gelbart (1974a) were the first to develop a formalism for this double-scattered intensity. They showed (Oxtoby and Gelbart, 1974b) that near the critical point one would have more than single scattering alone. This extra scattering due to multiple-scattering effects could be erroneously interpreted as due to the critical exponent η . Bray and Chang (1975) developed this point of view for a particular experimental scattering geometry. In other work, Reith and Swinney (1975) gave experimental verification of Oxtoby and Gelbart's work when they measured the depolarization ratio of light scattered from xenon near its critical point.

Work concerning the effects of double or higher-order scattering on the correlation function of the scattered light is much less complete. Essentially no theoretical development has been presented on this problem except for the short note by Ferrell (1968). As we discussed in section 3.7 above, this is a particular solution of our work and represents in no way a complete solution.

Some workers have pursued the problem experimentally (Theil et al., 1975 and Volochine and Berge, 1970). Since it is reasoned that the amount of multiple-scattered light depends on the scattering volume, their procedure was to vary the scattering volume geometry and try to measure a change in the correlation

time of the scattered light. No changes were found, and the conclusion was drawn that multiple scattering has little or no effect.

Our concern for the effects of multiple scattering on the critical fluid light-scattering spectrum arose when we were studying the shape of the spectrum. The droplet model predicts a nonexponentiality of the single-scattered correlation function. Our measurements had shown a good exponential spectrum down to $T - T_C = 8\text{m}^\circ\text{C}$; below this temperature the spectra were nonexponential. Our problem then was what was the reason for this non-exponentiality? Was it a consequence of the droplet model or was it due to multiple scattering? This problem had to be solved.

With the formalism developed in Chapter III for Brownian particle systems, our task should be relatively simple. We shall retain the basic assumption of independent scattering events. With this assumption, the results of Chapter III might be simply stated as: If we know the single-scattered intensity and spectrum, we can calculate the multiple-scattered intensity and spectrum. We know the intensity and spectrum of light scattered from critical fluids (Eqs. (1.7) and (1.15)). From this we shall calculate the double-scattered intensity and spectrum.

4.2 Calculation of the double-scattered field.

In this section, we follow the development of Sorensen, Mockler and O'Sullivan (1976b). In evaluating the double-scattered correlation function for Brownian diffusing particles, we made several assumptions concerning the nature of the particle suspension and the scattered light. We must consider these assumptions when applied to a critical fluid system and determine if they are still valid.

We assumed that the individual particles did not interact, thus their motion was uncorrelated. Similarly, we shall assume for light double scattered from a critical fluid that the first and second scattering regions are uncorrelated. For a critical fluid the Ornstein-Zernike correlation length ξ gives a measure of the distance over which regions of fluid are correlated. Usually $\xi \leq 1\mu\text{m}$ for most experimental situations ($T - T_C \geq 1\text{m}^\circ\text{C}$). Since a typical illuminated scattering volume may measure at least $100\mu\text{m}$ on a side, we expect in general any two scattering regions to be uncorrelated.

We assumed the particles were on the average separated by a distance r such that $k_0 r \gg 1$ (remember $k_0 = 2\pi n/\lambda$). This was a result of the far-field approximation. From the reasoning in the last paragraph, we expect on the average $r > 1\mu\text{m}$ for any two scattering regions. Thus $k_0 r \gg 1$ will hold for a typical scattering geometry.

We derived our result for a spherically symmetric scattering geometry. We shall do so again here. When we examine our system experimentally, we will use the wide beam or wide detection region scattering geometry as discussed in section 3.10. We may also use our experimental and theoretical conclusions regarding the narrow beam geometries to gain understanding of the effects of double scattering on the experimental results of others, where the spherical scattering geometry assumption may not hold.

Lastly, we derive the field correlation function, whereas experimentally, as for example in the case of homodyne detection, we measure the intensity correlation function. Thus, we will again assume Gaussian statistics so that these two quantities will be related in a simple manner by the Siegert relation (Pike, 1974). As discussed in section 3.9, the Gaussian assumption should be good because of the large number of double-scattering events.

We will consider systems where the scattering is not too great, such that $|\vec{E}_n| > |\vec{E}_{n+1}|$ for all n . Also, since the different scattering regions are not correlated, $\langle \vec{E}_1^* \cdot \vec{E}_m \rangle$ terms are zero for $m \neq 1$ (see section 3.3). We then take the double-scattered correlated function, $\langle \vec{E}_2^* \cdot \vec{E}_2 \rangle$, to be the lowest-order contribution to the multiple-scattered light.

We found for light scattering from Brownian motion systems that the double-scattered field was a result of two independent single-scattering processes when the assumptions above were made. As stated in the introduction of this chapter: if we know the single-scattering properties, we may calculate the double-scattering properties. We thus combine the single-scattering results of Eqs. (1.7) and (1.15), both experimentally verified forms, with the usual polarization factors (e.g. Eq. (3.24)) to arrive at a general expression for the single-scattered field correlation function for light scattered from a critical fluid system

$$\langle \vec{E}_1^*(t) \cdot \vec{E}_1(0) \rangle = A |\hat{r} \times (\hat{\epsilon} \times \hat{r})|^2 \frac{e^{-Dk^2(1+\xi^2k^2)^{1/2}t}}{(k^2+\xi^{-2})^{1-\eta/2}} \quad (4.1)$$

Here we use the usual notation, where $\vec{k} = \vec{k}_0 - \vec{k}'$; $\vec{k}'$ is the scattered-light wave vector, and $\vec{k}$ is the scattering wave vector, $k = (4\pi n/\lambda) \sin(\theta/2)$. The incident polarization is $\hat{\epsilon}$ and $\hat{r} = \hat{k}'$. A is a constant which includes factors not pertinent to our development.

We now consider the double-scattering process. Light is incident on the first scattering region with polarization $\hat{\epsilon}$ and wave vector $\vec{k}_0$. It elastically scatters to a new wave vector $\vec{k}''$, the

intermediate-scattered wave vector, and new polarization $\hat{\epsilon}' = \hat{r}'' \times (\hat{\epsilon} \times \hat{r}'')$ where $\hat{r}'' = \hat{k}''$. The correlation function is given by Eq. (4.1). This scattered light is then incident on a second scattering region where it scatters to a new wave vector $\hat{k}'$, the final-scattered wave vector, and new polarization given by $\hat{r}' \times (\hat{\epsilon}' \times \hat{r}')$ where $\hat{r}' = \hat{k}'$. This second scattering event again modulates the spectrum of the scattered light by the rule of Eq. (4.1). Thus, we write the double-scattered correlation function as

$$\langle \vec{E}_2^*(t) \cdot \vec{E}_2(0) \rangle = A^2 |\hat{r}' \times (\hat{\epsilon}' \times \hat{r}')|^2$$

$$\frac{e^{-Dk_1^2(1+k_1^2\xi^2)^{1/2}}}{(k_1^2+\xi^{-2})^{1-\eta/2}} \frac{e^{-Dk_2^2(1+k_2^2\xi^2)^{1/2}}}{(k_2^2+\xi^{-2})^{1-\eta/2}} \quad (4.2)$$

where

$$\vec{k}_1 = \vec{k}_0 - \vec{k}''$$

$$\vec{k}_2 = \vec{k}'' - \vec{k}' \quad (4.3)$$

and

$$\hat{\epsilon}' = \hat{r}'' \times (\hat{\epsilon} \times \hat{r}'') \quad (4.4)$$

Equation (4.2) is equivalent to Eqs. (3.35) or (3.50) in our Brownian particle theory.

We now wish to average Eq. (4.2) over all possible relative positions of the first and second scattering regions. In doing this we assume the relative positioning is spherically symmetric; thus, we have again our spherical scattering geometry. The averaging is done by integrating Eq. (4.2) over $\vec{r}''$ and dividing by the same integral at $t=0$. We do this with the help of the geometrical factors given in Eqs. (3.36)-(3.39). The complete expression is ridiculously complicated so we reserve its complete writing for an appendix (see appendix I).

4.3 The intensity of light double scattered from a critical fluid system.

We performed the integrals over $\vec{r}''$ using the numerical integration methods mentioned above and the exponent $\eta=0$. The intensity is the correlation function at $t=0$.

In Figs. 26 and 27 we present graphs of the ratio of the double-scattered polarized and depolarized intensities, respectively, to the single-scattered intensity given by the Ornstein-Zernike form, Eq. (1.7), in arbitrary units. We plot these for two scattering angles, 30° and 90° , versus $k_0\xi$. We stress that k_0 is the incident wave vector. Most graphs of light-scattering results for critical phenomena are plotted versus $k\xi$ where k is the scattering wave vector. We do not do so

Figure 26. Ratio of the polarized double-scattered to single-scattered light intensity of light scattered from a critical fluid mixture.

Figure 27. Ratio of the depolarized double-scattered to single-scattered light intensity of light scattered from a critical fluid mixture.

for double scattering because a change in θ is not equivalent to a change in λ in the double-scattered spectrum as it is in the single-scattered spectrum. Figs. 26 and 27 show us the expected behavior, namely that the light intensity ratios decrease as one leaves the critical region ($k_0 \xi \gg 1$). We shall have occasion to compare Figs. 26 and 27 to our experimental data later.

In Fig. 28 we plot the ratio of the depolarized to polarized double-scattered light versus $k_0 \xi$ for the scattering angles 30° and 90° (again $\eta=0$). This is similar to our Fig. 16 for scattering from Brownian particle systems. Notice that in the $k_0 \xi \rightarrow 0$ limit, we find the hardly surprising result that $I_{2\perp}/I_{2\parallel} \rightarrow 1/8$ just as for pointlike particles in a Brownian motion system (Eq. (3.55)).

As discussed in sections 3.8 and 3.11, this figure is of some importance when evaluating the relative magnitude of the double-scattered light. In section 3.11 we call this ratio R_2 , the ratio of the depolarized to polarized double-scattered light intensities.

In section 3.11 we developed a procedure to calculate the effects of higher-order scattering on the correlation times of the scattered light. This procedure was good for only $\ell \ll \lambda$, or equivalently in critical fluids, $k_0 \xi \ll 1$. Thus, we can not use our method in section 3.11 in general for $k_0 \xi \geq 1$.

Figure 28. Ratio of the depolarized to polarized light intensity double scattered from a critical fluid system.

To get another picture of the extent of multiple scattering from critical fluids, we consider the following technique good to second order. We write the depolarization ratio as

$$R = \frac{I_{2\perp}}{I_{1\parallel} + I_{2\parallel}} \quad (4.5)$$

where we have neglected scattering of higher order than double ($n=2$). Figure 28 gives us the ratio $R_2 = I_{2\perp}/I_{2\parallel}$. Thus using $I_2 = I_{2\parallel} + I_{2\perp}$ we can easily show

$$\frac{I_2}{I_1} = \frac{R(1+R)}{R_2 - R} \quad (4.6)$$

We can use Eq. (4.6) to evaluate the ratio of the double to single-scattered light intensities when the higher-order scattering is small. This condition is equivalent to $I_2/I_1 \ll 1$.

As an example of the use of Eq. (4.6) we can use the depolarization ratio measurements of Reith and Swinney (1975). They found at $T - T_C = 0.1^\circ\text{C}$ for xenon, a depolarization ratio of 1.7×10^{-3} to 9×10^{-3} for various scattering geometries. Naively, one might take these ratios as indicating very little double scattering is present because they are very close to zero. However, using Eq. (4.6), and from Fig. 28 an R_2 of 0.125, we find the ratio of the total double to single-scattered

light is 1.6×10^{-2} to 8.7×10^{-2} . This is a significant fraction not obvious from the depolarization measurement itself.

We also plot, in Figs. 29 and 30, the polarized and depolarized double-scattered intensities versus angle for a few values of $k_0 \xi$. Also drawn in each Figure is the Ornstein-Zernike single-scattered result, Eq. (1.5). We see a similar "washing out" effect as described for Brownian particle systems in section 3.8.

4.4 Critical fluid double-scattered correlation function.

We now use Eq. (4.2) to calculate the double-scattered correlation functions scattered from a critical fluid. The integral over $\vec{r}''$ is performed numerically as before. These integrals proved quite time consuming due to their complexity.

We present our results for the double-scattered correlation functions versus time in Figs. 31-34. Figures 31 and 32 are for the polarized component at scattering angles 30° and 90° , respectively. Figures 33 and 34 are our results for the depolarized component, again at scattering angles 30° and 90° , respectively. The figures are parameterized on $k_0 \xi$, each $k_0 \xi$ curve normalized to the same $t=0$ slope or first cumulant. Also included in these figures is the straight line

Figure 29. Comparison of the polarized double-scattered and single-scattered intensities of light scattered from a critical fluid system versus the scattering angle.

Figure 30. Comparison of the depolarized double-scattered and single-scattered intensities of light scattered from a critical fluid system versus the scattering angle.

Figure 31. Polarized correlation function of light double scattered from a critical fluid system. $\theta_{\text{SCAT}} = 30^\circ$.

Figure 32. Polarized correlation function of light double scattered from a critical fluid system. $\theta_{\text{SCAT}} = 90^\circ$.

Figure 33. Depolarized correlation function of light double scattered from a critical fluid system.
 $\theta_{\text{SCAT}} = 30^\circ$.

Figure 34. Depolarized correlation function of light double scattered from a critical fluid system.
 $\theta_{\text{SCAT}} = 90^\circ$.

representing the first cumulant of all the curves. This first cumulant was evaluated in the usual way using Eqs. (3.41) and (4.2).

For both the polarized and depolarized components, the first cumulant characterizes the correlation function reasonably well at a scattering angle of 90° . However, at 30° in each case the first cumulant becomes progressively insufficient to describe the correlation function as $k_0\xi$ increases; the spectra for large $k_0\xi$ being very nonexponential.

This behavior will lead to difficulties in analyzing our data in terms of the theory. We have seen for Brownian particle systems that the first cumulant could be experimentally extracted from the data, and successfully compared to the first cumulant calculations of our double-scattering theory. This was possible because the spectra were only slightly nonexponential ($K_2/K_1^2 \sim 0.07$). Thus, we might expect the same sort of results when dealing with critical fluid double-scattering at a scattering angle of 90° , for all $k_0\xi$, and at a scattering angle of 30° for $k_0\xi < 1$. However at $\theta = 30^\circ$ and $k_0\xi > 1$ we probably will not be successful in extracting the first cumulant from the data due to the extraordinary large amount of nonexponentiality.

We need a second parameter other than the first cumulant with which to characterize the decay rate. We

shall make the choice of defining the decay time as that time at which the correlation is $1/e$ (e =base of natural logarithms, 2.718...) times its $t=0$ value. This is reasonable, since for an exponential decay this is the decay time. Furthermore, such a definition will reflect the apparent lengthening of the decay due to the non-exponentiality. We emphasize however that this is only a means of describing the general behavior of the decay time that might be measured in a double-scattering experiment.

We now plot the depolarized linewidth ($1/\tau$) versus k parameterized on the scattering angles 30° and 90° in Fig. 35. The linewidth is expressed in terms of the scaled linewidth defined in Eq. (1.17) of our introduction, rewritten here as

$$\Gamma_2^* = \frac{6\pi\eta_s}{k_B T} \Gamma_2 / k_0^3. \quad (4.8)$$

Γ_2^* , the calculated scaled linewidth, is plotted in two forms. The solid line of Fig. 35 represents the first cumulant value, the dashed line represents the time-at- $1/e$ value. The curves have a general behavior similar to that for single scattering (see Fig. 1) but now a change in scattering angle is not equivalent to movement along the $k_0 \xi$ axis. Notice that the k_0^3

Figure 35. Depolarized scaled linewidth of light double scattered from a critical fluid system versus $k_0\xi$. The solid line is for the linewidth determined from the first cumulant of the correlation function; the dashed line for the $1/e$ value of the correlation function.

behavior is retained in the large $k_0\xi$ region as in single scattering.

Until we have data to compare to our graphs in Fig. 35, Fig. 35 is only of casual interest. For now, a much more interesting result of our calculation is to compare the double-scattered correlation time to the single-scattered correlation time. In this way, we may estimate the effects of double scattering on the single-scattered Rayleigh linewidth measurements near the critical point. In Figs. 36 and 37 we plot the ratio of the double to single-scattered correlation time, τ_2/τ_1 , for both polarizations of the double-scattered component. Figure 36 is for 30° and Fig. 37 is for 90° scattering angle. As before we give the first cumulant correlation time as the solid line and the $1/e$ correlation time as the dashed line. In each case we find that the polarized component, which is by far the more intense component, of the double-scattered light (see Fig. 28) has a correlation time approximately equal to the single-scattered correlation time in the critical region where $k_0\xi > 5$. This is exactly the region in which double scattering should have its largest effect. Thus we find the remarkable result that in the critical region double scattering should have little or no effect on the assumed single-scattering Rayleigh linewidth measurements. We now understand theoretically why workers such as

Figure 36. Ratio of the double to single-scattered correlation times of light scattered from a critical fluid system. $\theta_{\text{SCAT}} = 30^\circ$.

Figure 37. Ratio of the double to single-scattered correlation times of light scattered from a critical fluid system. $\theta_{\text{SCAT}} = 90^\circ$.

Theil et al. (1975) and Volochine and Berge (1970) didn't observe any effects of double scattering in their linewidth measurements. We also can now understand why Rayleigh linewidth data and single-scattering theory agree well in the very opalescent region $k_0 \xi > 1$; the single and double-scattered spectra are nearly the same in this region. Thus, this ten year old problem is at last understood.

These conclusions apply to our spherical scattering geometry. We have discussed in section 3.10 how this geometry is not difficult to obtain. Thus, we might suppose that most workers had scattering arrangements that satisfied this geometry. We have also seen that when this geometry is not satisfied the correlation time for Brownian diffusion may increase by more than 20%. Such an increase due to nonspherical scattering geometries on critical fluid light-scattering experiments would only affect our conclusions above slightly. Also, the error bars on the linewidth in this region for most experiments are at least 10% so it is doubtful a scattering geometry effect could be seen.

It is possible that the double-scattered intensity will be a significant fraction of the total light scattered in the region where $k_0 \xi < 5$. In this region τ_2 and τ_1 are becoming significantly different. If this were so, we might expect the measured correlation time

in this region to be a little less than that predicted by the single-scattering theories, Eqs. (1.11), (1.14) or (1.15), due to double-scattering effects. Very far from the critical point where there will be very little double-scattering we again expect agreement between single-scattering theory and the data. Indeed, such a deviation from theory has been observed by many other workers in the region $k_0 \xi \sim 1$; sometimes resulting in a deviation of as much as 20% (Swinney and Henry, 1973). As yet this deviation is unexplained, but it is conceivable in the light of our work, that it is here, and ironically, not in the extreme critical region, that the effects of double scattering become important.

We conclude this section and chapter by reminding our reader that we have only solved the double-scattered field, not the multiple-scattered field. We might make arguments, similar to those in section 3.11, that since the double-scattered and single-scattered correlation times are nearly equal then the next-higher-order term, the triple-scattered term, has a correlation time about the same as the double-scattered term. Such an argument may be none too shabby. However, it is an argument and not an exact result. Of course, we can always argue, as those before us, that the next-higher-order term isn't important. Fortunately, being an experimentalist, I have a way

out of all these arguments. We shall measure the depolarized intensities, and using the results of section 4.3 determine experimentally the magnitude of the higher-order-terms.

CHAPTER V

EXPERIMENTAL TECHNIQUES AND PROCEDURES

5.1 Introduction.

In this chapter we shall briefly discuss some of the equipment in our laboratory which were used in our light-scattering experiments. We will review the capabilities and limits of the equipment. We will discuss the temperature control cell which holds the binary fluid system and controls its temperature. We will evaluate its design in terms of the temperature stability it has achieved. In this way, we will gain insight into the problems of attaining precision temperature control. We shall also describe our light-scattering techniques and the actual data taking process from our binary fluid system. We will discuss our laser heating measurements, sample preparation, and viscosity measurements on the binary fluid system.

5.2 The Spectrometer.

The detailed workings and design of our spectrometer are described elsewhere (Lyons, 1973). The spectrometer relies on digital electronics to measure the time interval between successive photon pulses arriving

from the amplified and discriminated output of the detection photomultiplier tube. The time interval is measured in units of 200 nsec; thus, this defines the limit of our time resolution to 200 nsec or, in frequency space, 5 MHz. This time record is fed into an on-line Nova 800 minicomputer which is programmed to calculate the photon correlation function of the light.

In actual practice our time resolution is limited to measuring correlation times of approximately 5 μ sec or greater because of noise problems. The exact nature of these problems is unknown, but is probably a ringing effect somewhere in the electronics. In any event, this limit had no effect on the light-scattering measurements described herein, where the correlation times were 6 μ sec or longer.

The spectrometer is controlled through a teletype terminal. Three basic command parameters are available. One may pick the basic unit of time of the measurement in units of 200 nsec. This command is the channel length designated by C. The actual channel length is given by $200 \text{ nsec} \cdot 2^C$. The second parameter is the run length R. This parameter determines the number of channels or points in a spectrum. The number of channels is 2^R . The third parameter is the clip level L. Actually, the machine is not a true clipped autocorrelator but rather a scaled autocorrelator (Pike, 1974).

For our purposes either is suitable, but the scaled autocorrelator is preferable when dealing with non-Gaussian statistics.

The data analysis routine used in the minicomputer fits the spectra, which are all exponential or nearly exponential, to a form

$$\langle I(t)I(0) \rangle = B + e^{-at+bt^2}. \quad (5.1)$$

B is a background term which can be varied for a best-fit by the operator, a is the first cumulant equal to the reciprocal of the correlation time, and b is a measure of the nonexponentiality equal to one half of the second cumulant. Thus, Eq. (5.1) represents a two cumulant fit. We have found in practice that a two cumulant fit is sufficient for any nearly exponential spectrum. In general, even if higher-order cumulants are needed, the fit isn't improved significantly by their use.

The fitting procedure fits the spectrum by weighting the points by their value above the background. The weighting function of the fit is

$$W(n) = S(n) - B \quad (5.2)$$

where $W(n)$ is the weighting function of the n^{th} channel, and $S(n)$ is the total number of counts in the n^{th} channel. The important point is that the fitting procedure

yields a correlation time which tends to reflect the initial or $t \rightarrow 0$ part of the spectrum.

5.3 Optical arrangement.

Figure 38 gives an overhead drawing of our optical arrangement for light-scattering experiments.

Our laser is an Argon-ion laser, Spectra Physics model 165. We generally operated it at wavelengths of $5145\text{\AA}$ or $4579\text{\AA}$ in multimode configuration.

The laser beam is directed down a short length of optical bench which is tied to our optical table. Secured to this optical bench is a large aluminum protractor with another longer length of optical bench attached so as to pivot about the center of the aluminum protractor. In this way, we select various scattering angles. Experience indicates that a scattering-angle accuracy of $\pm 1^\circ$ is possible. A versatile x-y-z translation stage is mounted over the center of the aluminum protractor to act as an adjustable sample holder.

The photomultiplier tube is an ITT FW 130. In our experiment, it operated at the ambient room temperature of $\sim 23^\circ\text{C}$ with a dark count of < 30 counts/sec. Our experimental count rates were high enough (> 800 counts/sec) so as not to warrant cooling the tube. A one meter long, two and one half cm in diameter tube is positioned in front of the cathode of the photomultiplier. At the end of this tube closest to the sample is a $300\text{ }\mu\text{m}$

Figure 38. Overhead drawing of our optical arrangement for light scattering.

pinhole. Since our light has a wavelength of $\sim 5000\text{\AA}$, simple wave optics will tell us that this pinhole will project a coherence area 0.2 cm in diameter onto the cathode one meter away. Since the photocathode is 0.25 cm in diameter, we will have approximately one coherence area on the photocathode. This is the condition for optimal signal/noise (Cummins and Swinney, 1970). In front of this pinhole, we have the capability to place entrance apertures of various diameters. The ray optics described by these apertures and the pinhole determines the field of view for the photocathode.

The optical benches provide for easy insertion of various optical devices into the light path. Thus lenses, filters, polarizers and stops are easily included to make the arrangement quite adaptable.

This whole arrangement is mounted on an aluminum slab 4'x8'x4" thick weighing one ton. This slab is the top of a table which rests on an isolation pad in the center of our laboratory. This isolation pad keeps vibrations from other events in our lab, such as vacuum pumps and personal movement, from affecting the spectrum being measured on the table. Furthermore, our entire lab is isolated from the rest of the building thus insuring against extraneous signals due to vibrations.

5.4 Temperature controllers.

In our temperature control work, the temperature sensors are Yellow Springs Instruments (YSI) 44004 precision thermistors. These thermistors have a resistance of 2250 ohms at 25°C and 984 ohms at 45°C, the temperature of our critical point. Individual thermistors are rated to be interchangeable to $\pm 0.2^\circ\text{C}$. We have found that it is possible to achieve a temperature resolution of at least $0.03\text{m}^\circ\text{C}$ with these thermistors. (This value is limited not by our thermistors but by our detecting bridge). The thermistors were found to drift with time, however, and in particular we show in Fig. 39 the relative critical temperature of our binary fluid mixture versus time as measured by the control thermistor in our experiment. This particular thermistor has drifted uniformly at a rate of $\sim 1.5\text{m}^\circ\text{C}/\text{month}$ for a period of several months. Other thermistors have been found to drift in a similar manner. To measure the resistance and hence the temperature of our thermistors, we used a four lead AC Kelvin double bridge. We used two such bridges; one operating at 22Hz and the other at 33Hz. Two different frequencies eliminate any "cross talk" noise problems. The bridges are balanced by adjusting both a ratio arm resistance and a quadrature or phase value. The resistance on the ratio arm at balance gives the resistance of the thermistor and hence the

Figure 39. The drift of our control thermistor with time.

temperature. Details of the construction of these bridges are given by Lyons (1973).

One of the AC bridges controls a current source which is connected to heater wires in the temperature control cell. This control bridge monitors the temperature and adjusts the current to the heater to keep the temperature constant. The other AC bridge is used to measure the temperature of other thermistors in the cell to measure thermal gradients.

Besides these two AC bridges, we use a DC bridge which is capable of measurement and control to $\pm 5\text{m}^\circ\text{C}$. This bridge is used to control, with another current supply, the shield in the control cell. As we shall see, this shield acts as a controlled environment for the more sensitive and highly controlled inner portion of the cell.

5.5 The temperature control cell.

We wish to place stringent limits on the capabilities of our temperature control cell. Prior to our experiment, no careful data had been obtained on the Rayleigh linewidth scattered from critical fluids in the region $k\xi > 20$, very close to the critical point. One of the goals of our experiment is to go well into the large $k\xi$ region. To do so we need extremely good temperature control and stability. For instance, at a scattering angle of 90° and a wavelength of $5145\text{\AA}$ the scattering

wave vector for our binary fluid system, methanol and cyclohexane, is $23.83 \mu\text{m}^{-1}$. At $T-T_C=0.2\text{m}^\circ\text{C}$, the correlation length ξ for typical values of $\xi_0=2.5\text{\AA}$ and $\nu=0.63$, is $\xi=1.95\mu\text{m}$. Thus, $k\xi=46$. We see that control much better than $1\text{m}^\circ\text{C}$ is necessary to explore this region; control approaching $0.1\text{m}^\circ\text{C}$ or better is required.

Our cell was built on a cylindrical symmetry. We used a basic design comprised of three "cans": the outer can, the shield can, and the inner can. The outer is the can exposed to the environment. It is not temperature controlled. The shield is the next can inside the outer can. It is controlled by the DC bridge to $\pm 5\text{m}^\circ\text{C}$ and isolates the more precisely controlled inner can from the external environment. The inner can holds the test tube or sample cell containing the binary fluid mixture and is temperature controlled as precisely as possible. Its temperature determines the temperature of the fluids.

Our first consideration in construction of the cell was what type of insulation to use. We may use either physical packing or a vacuum. To determine which is better we compared the vacuum to polystyrene which is a good insulator. To calculate the energy transport through the polystyrene, we used the heat transport equation

$$E = \Lambda VT \quad (5.3)$$

where E is the energy transport, VT is the temperature

gradient and Λ is the thermal conductivity. Λ for polystyrene is $\sim 10 \times 10^{-4}$ (j/sec)/(cm $^{\circ}\text{C}$ /cm) (Materials in Design Engineering Vol. 58, No. 5, 1963, p.240). We used the Stephan-Boltzman equation for radiating thermal bodies to determine an effective thermal conductivity for a vacuum (Halliday and Resnick, 1962)

$$E = e\sigma (T_1^4 - T_2^4) \quad (5.4)$$

Here $\sigma = 5.67 \times 10^{-12}$ j/sec cm^2 ($^{\circ}\text{C}$) 4 is the Stephan-Boltzman constant, e is the emissivity of the radiating bodies, $0 \leq e \leq 1$, and T_1 and T_2 are the temperatures of the radiating bodies. We differentiate Eq. (5.4) with respect to one of the temperatures and obtain

$$dE = 4e\sigma T^3 \delta T \quad (5.5)$$

This equation is similar to Eq. (5.3) except that for a vacuum heat flow is proportional to the temperature difference δT , not the temperature gradient ∇T . For unit thickness (1cm) we may then compare Λ to $4e\sigma T^3$. For a vacuum at 300 $^{\circ}\text{K}$ we find

$$4e\sigma T^3 = e 6.1 \times 10^{-4} \text{ (j/sec)/(cm}^2\text{ }^{\circ}\text{C)} \quad (5.6)$$

Thus, even for the maximum emissivity of $e=1$ the vacuum is a slightly better insulator. For thinner regions the

vacuum is better since ∇T will increase while δT stays constant. (Don't forget the converse is also true). This is an important fact since the size of the cell should be kept to a minimum for light-scattering purposes. Also, the emissivity can be made quite small with white or mirrored surfaces. For these reasons we chose a vacuum to thermally insulate our cell.

In Fig. 40 we give our first design for our temperature control cell. This cell was actually built and tested. The inner can was made of a large aluminum cylinder. Its large mass gave it a large thermal capacity, and thus, a large thermal inertia to resist temperature changes. The inner can was supported by the shield can with three connecting nylon posts at the top of the cans. Both cans had heater wires of number 26 gauge nichrome wire wrapped uniformly about the sides of the cans. Both cans were anodized black to cut down possible internal light reflections. This has the disadvantage of making the emissivity nearly unity. The shield can was connected by three more nylon posts to the top of the outer can. The outer can was made of brass and lined with shiny aluminum foil to reduce the emissivity, thereby increasing the overall insulation. The lid of the outer can had 18 electrical lead-throughs for various thermistor and heater wire connections. The whole system was evacuated with a vacuum pump.

Figure 40. First design of our temperature control cell.

We evacuated the cell to a pressure of $\sim 50\mu\text{m(Hg)}$ and began testing the control possible near 45°C . We found that our short term (hours) stability was good to $\pm 0.1\text{m}^{\circ}\text{C}$ and our long term (12 hours) stability was good to $\pm 0.25\text{m}^{\circ}\text{C}$. Our temperature control overnight or over weekends was very poor ($\sim 1\text{m}^{\circ}\text{C}$). These periods reflected the general change in temperature of the laboratory because the temperature control of the whole building was turned off. The temperature control of the cell was at best marginally satisfactory for our purposes.

Most significant, was our measurement of the thermal gradient on the inner can. To measure this, two thermistors were placed side by side in good thermal contact in the inner can. The cell was then assembled and controlled at several temperatures with the third, control thermistor. In such a configuration, we may take the two side by side thermistors as being at the same temperature. Thus, we calibrate these thermistors relative to each other. Once this was done, the cell was disassembled, and one of the thermistors moved to a new position on the inner can. The cell was then reassembled, controlled, and the temperature difference between the two parts of the inner can measured.

Following this procedure, we found thermal gradients from the middle to the upper end of the inner can, a distance of 4.4cm, of $14\text{m}^{\circ}\text{C/cm}$ to $20\text{m}^{\circ}\text{C/cm}$ depending on the relative temperature of the three cans.

The gradient was such that the upper portion of the inner can was cooler than the lower, middle portion. This indicated a significant heat loss out of the top of the cell. Also, we could not rid the cell of the gradient by varying the relative temperatures of the cans. Such large gradients could well cause problems in both determining the true temperature of the fluids and through possible (and unknown) effects a gradient could have on the light-scattering spectrum. We had to find the cause of the gradient and correct for it.

Examination of Fig. 40 shows that the coolness of the upper portion of the inner can might well be due to the direct heat loss through the nylon supporting posts to the cooler external environment. Another possible heat leak is through the wire leads to the thermistors and heater coils. These wire leads proceed out the top of each can and might well conduct a significant amount of heat. To see if these possible explanations for the gradient are reasonable, we calculated the heat losses due to radiation through the vacuum, conduction through the supporting posts, and conduction through the lead wires, and compared their relative magnitudes.

Radiative heat loss is governed by the Stephan-Boltzman equation (5.4). Using an emissivity of one, a temperature difference of 2°C between the inner can and

the shield, and the average surface area of these two cans, Eq. (5.4) gives a heat loss due to radiation of 82 milliwatts (mW).

Whereas the inner can sees only the shield can via the radiative loss, we considered the two sets of nylon posts as a direct heat path from the external environment to the inner can. The heat flow through these posts for a temperature difference of 22°C (45°C inner can temperature minus the 23°C room temperature) using $\Lambda(\text{nylon}) = 23 \times 10^{-4} \text{ (j/sec)/(cm}^2\text{C/cm)}$ (Materials, p.214) is 4mW, small compared to the radiative loss.

The loss through the copper lead wires connected from the external environment to the inner can for $\Lambda(\text{Cu}) = 4 \text{ (j/sec)/(cm}^2\text{C/cm)}$ (Handbook of Chemistry and Physics, Vol. 54, (1973-1974)) and for 14 wires of 26 gauge was found to be 92mW, easily as much as the radiative loss.

We concluded from the above values that conduction through the wires represented a major heat loss and may have been responsible for the thermal gradient. It was conceivable that the nylon posts also add to this gradient. Overall stability might be improved by shielding the inner can better from the outer cans. With what we had learned from calculations such as these, we redesigned the temperature control cell.

Figures 41-44 show in detail our second cell.

Figure 41. General view of the temperature control cell.

8/5 Scale

Figure 42. Temperature control cell detail: shield can and radiation shield.

4/3 Scale

Figure 43. Temperature control cell detail: inner can.

Figure 44. Temperature control cell detail: top view.

This was the cell that was used in our experiments on critical phenomena. The outer can was the same brass can used before in our first cell. It had epoxied glass windows at 0° , 30° , 60° , 90° and 180° . To aid in lowering the emissivity of the inner wall, it was lined with shiny aluminum foil as before.

The shield can was black anodized aluminum with lucite (methyacrylate plastic) windows again at 0° , 30° , 60° , 90° , and 180° . Actual windows are better than holes because they form an infrared radiation barrier against heat loss. It was supported as before by three nylon posts connected to the outer can lid. The heater wire was wound over the entire surface of the shield including both the top and bottom. In this way, we hoped to eliminate cold end regions and gain more uniform heating. The circumference of the top lid of the shield was turned down on a lathe so that when the lid was attached to the rest of the shield a groove $1/8$ " deep and $1/4$ " wide resulted. Lead wires from the inner can circled this groove before continuing to the outer can lead-throughs. In this way the lead wires equilibrated to the warmer shield temperature before they continued on to the inner can. This procedure should reduce the heat loss from the inner can to the outer can via the lead wires.

The most extensive changes were made on the inner can. A large, massive aluminum lid was made for this

can. The upper most section of this lid was a square cross section post which holds binding terminals for the lead wires. This allowed us to assemble and disassemble the control cell easily by merely loosening the screws holding the wires. This convenience was often appreciated. The lead wires, which had already been equilibrated to the shield temperature, typically about 2°C below the inner can temperature, then proceeded to a spool on the inner can lid directly below the terminal posts. Here the lead wires become equilibrated to the inner can temperature by passing a few times around this spool. Thus, by the time the lead wires pass into the inner can itself, they were well equilibrated to the inner can temperature.

The whole of the inner can was covered by a stainless steel radiation shield. This stainless steel shield was polished in an electrolytic acid bath to obtain a mirror-like surface. Hence, its emissivity should be quite small and the radiation loss from the inner can was as small as possible. (The shield can is still anodized black, however).

The stainless steel radiation shield had another important use. To eliminate the direct heat path through the two sets of nylon supports in our first design, we removed the nylon supports between the inner can and the shield can. Our supporting mechanism for the inner can

was comprised of four stainless-steel-pointed nylon set screws (see detail in Fig. 42) mounted in the shield can. One was at the center of the bottom lid and the other three were placed at 120° around the circumference of the shield can more than half way up. These upper three set screws beared directly against the stainless steel shield of the inner can. The bottom set screw beared against a stainless steel insert in the bottom of the inner can. The set screws had a fine point so that the actual surface area of contact between the hard stainless steel points and shield was very small. Since the heat conduction is directly proportional to the cross sectional surface area, this arrangement should result in very little heat loss. Also, stainless steel is a very poor metallic heat conductor. Perhaps most importantly, with this arrangement there was no longer a direct heat path from the inner can to the outer can and the environment.

The heater wire for the inner can was, as for the shield can, wrapped on the top lid and bottom as well as on its sides. There was an entrance window at 180° and a large window extending from 0° to 90° . These windows were made of lucite. The control and measurement thermistors were placed at the level of these windows between the 90° and 180° positions. The gradient detection thermistor was placed 4.4cm above these thermistors.

All the thermistors were in deep holes and caulked in with Apeizon Q for easy removal. Lastly, the lead wires were number 40 gauge copper wire thus again reducing the heat loss through the lead wires.

This design was assembled, evacuated and controlled near 45°C . We found essentially no thermal gradient on the inner can. The temperature difference between the measurement and gradient thermistors, 4.4cm apart, was $0.2\text{m}^{\circ}\text{C}$. This is an excellent value.

The cell was found to be capable of excellent temperature stability. No drift to $0.05\text{m}^{\circ}\text{C}$ over periods of heating loss in our laboratory such as nights or weekends were found. The short time (hours) behavior seemed to be better than $\pm 0.03\text{m}^{\circ}\text{C}$, the estimated limit of our temperature precision. In Fig. 45 we give the monitored output of our measurement bridge for a 24 hour period. One can see stability to better than $0.03\text{m}^{\circ}\text{C}$.

In conclusion we feel our design for the temperature control cell combined with the bridge controlling system described in section 5.4 gives excellent temperature stability and gradient control. Good enough for measurements to values of $T - T_{\text{C}} = 0.1\text{m}^{\circ}\text{C}$.

Figure 45. Monitored output of detection bridge showing temperature stability of our cell.

5.6 Laser heating.

Since we had achieved temperature control for our binary fluid mixture good to $0.1\text{m}^{\circ}\text{C}$, we had to be concerned with other heating effects which otherwise might be taken as quite small. In particular, the incident laser beam was capable of heating the scattering volume in the fluid. We knew of no other work concerning this problem; however, we felt that if the experiment were to be done properly, the actual heating of the fluids by the laser had to be measured.

We consider Eq. (1.5) for the intensity of the light scattered from a critical fluid.

$$I = \frac{A}{(k^2 + \xi^{-2})} . \quad (5.7)$$

A is a constant independent of temperature. By Eq. (1.6), $\xi = \xi_0 t^{-\nu}$, as the temperature approaches T_C , the scattering intensity in Eq. (5.7) increases.

Now suppose the laser beam is incident on the critical fluid. It will illuminate a cylindrical region in the fluid, the scattering volume. We shall take our fluid to be at a temperature slightly above the critical temperature. As the incident beam heats up the fluid in the scattering volume, the scattered intensity from this volume will decrease. We shall assume that there is little mixing of fluid in and out of the scattering

volume. This is reasonable if the fluid is not physically disturbed. Also, we expect convection effects due to density changes to be small because we expect heating of the order of only a few millidegrees. Even if there is some mixing, we shall take the measured heating as some average involving the mixing.

For a small amount of heating in such a tiny volume, we do not expect our temperature controllers to be affected. The temperature controller controls the large, thermally massive, inner can as well as all of the fluid. Thus, the small amount of heat added to the small scattering volume will not be seen by the controller.

We shall use the change in scattering intensity as a measure of the change in temperature due to the laser heating. From Eq. (5.7) we find

$$\frac{dI}{I} = \frac{2}{(k^2 + \xi^{-2})} \xi^{-2} \frac{d\xi}{\xi} . \quad (5.8)$$

From $\xi = \xi_0 t^{-\nu}$ where $t = (T - T_C)/T_C$

$$\frac{d\xi}{\xi} = \frac{-\nu}{T_C} \left(\frac{T - T_C}{T_C} \right)^{-1} dT . \quad (5.9)$$

thus,

$$\frac{dI}{I} = \frac{-2\nu}{(1 + k^2 \xi^2)} \frac{dT}{T - T_C} . \quad (5.10)$$

We may use Eq. (5.10) to calculate the fractional change in intensity due to a change in temperature. Notice that this fractional change is linear in the temperature change, dT , for small dT .

The largest change in Eq. (5.10) occurs for the smallest k . To optimize the effect we will use our smallest experimental k value. This is when $\theta=30^\circ$ and $\lambda=5145\text{\AA}$ then $k=8.72\mu\text{m}^{-1}$. We have calculated dI/I for this k value using Eq. (5.10) for a range of values of $T-T_C$ for a laser heating dT of $1\text{m}^\circ\text{C}$. The results are plotted in Fig. 46.

In Fig. 46 we see that even millidegree heating may cause about a two percent decrease in the scattered intensity. In the region $T-T_C=10\text{m}^\circ\text{C}$ the effects are the largest, there being a 2.6% decrease in scattered intensity for every millidegree of heating. An effect of this size should be easily measured.

To measure the laser heating, we directed the beam of the laser into the temperature control cell containing our binary fluid mixture (methanol and cyclohexane). The beam may be focused to varying degrees. The more focused the beam, the more power per unit volume will result, and thus, the more heating per unit incident power. The incident power was monitored with a photocell and beamsplitter arrangement as shown in Fig. 47. The scattered intensity was detected by another photocell

Figure 46. Laser heating effect at $k = 8.72\mu\text{m}^{-1}$.

Figure 47. Experimental arrangement to measure laser heating.

placed at the 30° window of the temperature control cell. The output of this photocell, the scattered intensity, was monitored with a strip chart recorder.

Figure 48 shows the results of two typical experimental runs. We can see that the scattered intensity decays rather exponentially to a new value in approximately one hour. This new intensity represents the new temperature in the scattering volume. The change in intensity gives us, with the help of Fig. 46, the laser heating. In Figure. 49 we plot the results of a run to determine the laser heating. For this particular temperature ($T - T_C = 0.2\text{m}^\circ\text{C}$) and beam diameter ($\sim 1.5\text{mm}$) there was $1.5\text{m}^\circ\text{C}$ of heating for each milliwatt of incident laser power. This is a large value and the result casts some doubt on the temperature accuracy of all previous light-scattering experiments that didn't recognize the magnitude of the laser heating. We have made use of this knowledge in our light-scattering work to obtain an accurate temperature determination for our experiment.

5.7 Viscosity measurement.

As can be seen in Eq. (1.15), the shear viscosity plays an important role in determining the critical Rayleigh linewidth of a fluid. For this reason, we require an independent measurement of the shear viscosity of our binary fluid mixture. We have performed the following experiment to determine this viscosity.

Figure 48. Decrease in scattered intensity at $k=8.72\mu\text{m}^{-1}$ due to laser heating.

Figure 49. Experimental results of a laser heating measurement.

We prepared a mixture of methanol and cyclohexane. Both fluids were of Spectrographic grade quality. The fluids were mixed under a dry nitrogen atmosphere in a dry box. The mixture had a concentration of $29.00 \pm 0.02\%$ methanol. This is very close to the value of 29.0 given by Huang and Webb (1969).

Our viscometer was a Poiseuille flow viscometer. We measured the viscosity of the mixture by timing its flow through the capillary tube of the viscometer. The viscometer had been calibrated with other liquids of known viscosity. It was found that for our viscometer the shear viscosity is given by

$$\eta = Atp \quad (5.11)$$

A is a constant which for our viscometer is 8.21×10^{-3} c.p. $\text{cm}^3/\text{sec gm}$, t is the time of flow and ρ is the density.

The fluids were sealed inside the viscometer which was immersed in a large water bath held at constant temperature controlled to $\pm 0.05^\circ\text{C}$ by a heater-thermostat type of arrangement. Flow times at a number of different temperatures were measured with a stop watch. The precision of the time measurement was usually ± 0.1 sec. For a typical flow time of ~ 80 sec this corresponds to $\pm 0.1\%$ precision.

Equation (5.11) also requires a knowledge of the

the density of the fluid system. To measure the density we calibrated a 25ml volumetric flask. The flask was filled to the fiducial mark with distilled water, sealed and immersed in the water bath. The rise due to thermal expansion of the water at various temperatures was measured with a traveling microscope. By obtaining the density of the water from standard tables (Handbook of Chemistry and Physics Vol. 54 (1973-1974)), we calibrated the flask volume to the height above the fiducial mark.

We made another mixture of methanol and cyclohexane using the precautions described above. The concentration was $29.0 \pm 0.1\%$ methanol. The ground glass stopper of the flask was sealed with RTV adhesive but it appeared to leak with time. The leak was small and should not affect the accuracy of the density measurement significantly.

Due to these leaking problems only three data points were obtained which were considered of suitable accuracy. These are given in Table II. The value at 46.0°C of $\rho=0.7497 \text{ gr/cm}^3$ agrees quite well with that of Timmermans (1950) at that temperature of $\rho=0.7504 \text{ gr/cm}^3$.

We are now ready to use Eq. (5.11) to determine the viscosity of our critical mixture from our flow time measurements. The viscosity is given in Table II and plotted in Fig. 50. The characteristic anomaly of a transport coefficient is readily seen.

TABLE II

Viscosity and density of the binary mixture methanol and cyclohexane at the critical concentration.

$T(^{\circ}\text{C})$	$T-T_c(^{\circ}\text{C})$	$\eta(\text{c.p.})$	$\rho(\text{gr/cm}^3)$
61.1	15.1	0.444	-
60.8	14.8	-	0.7346
60.0	14.0	0.461	-
59.2	13.2	0.466	-
58.2	12.2	0.474	-
56.8	10.8	0.485	-
56.0	10.0	-	0.7391
55.4	9.4	0.496	-
54.3	8.3	0.505	-
53.1	7.1	0.517	-
52.0	6.0	0.528	-
51.0	5.0	0.539	-
50.1	4.1	0.549	-
49.5	3.5	0.556	-
49.1	3.1	0.562	-
48.4	2.4	0.573	-
47.6	1.6	0.588	-
47.4	1.4	0.596	-
46.8	0.8	0.609	-
46.2	0.2	0.654	-
46.0	0	-	0.7497

Error on $T-T_c$ is $+0.0, -0.1^{\circ}\text{C}$ due to uncertainty in T_c .

Figure 50. Viscosity versus temperature for the critical mixture methanol and cyclohexane. Solid line represent the Arrhenius form for the background viscosity.

To determine the background viscosity, we fitted the seven points farthest from T_C to an Arrhenius form (Lyons, 1973)

$$\log \eta = A + B/T . \quad (5.12)$$

These seven points were chosen by visual inspection of the plot of $\log \eta$ versus $1/T$ in Fig. 50. On such a plot the background Arrhenius behavior should appear as a straight line, as these seven points did. The fit yielded the values of $A=-2.667$ and $B=775^\circ\text{K}$. Equation (5.12) for these values is plotted with the data in Fig. 50.

We analyse our data using the form for the critical part of the viscosity given by Perl and Ferrell (1972a, see also Oxtoby and Metiu, 1976),

$$\Delta\eta = \eta_s - \eta_b = \bar{\eta}_s A \ln q_D \xi . \quad (5.13)$$

Perl and Ferrell show that $A=8/15\pi^2=0.051$, $\bar{\eta}_s$ is an effective viscosity approximately equal to the viscosity in the critical region (see Swinney and Henry, 1973) and q_D is a cutoff parameter. We plot the difference $\eta_s - \eta_b$ obtained from our data (Fig. 50) versus the log of $T-T_C$ in Fig. 51. The data for $T-T_C < 4^\circ\text{C}$ are described by a straight line on this graph, consistent with Eq. (5.13). From this straight-line fit, we find

$$A=0.0524 \pm 0.03 \quad (5.14)$$

Figure 51. Critical viscosity, $\eta_s - \eta_b$, versus $T - T_c$ for the critical mixture methanol and cyclohexane. Solid line is the best fit of the Perl and Ferrell form for the critical viscosity.

and

$$\ln q_D \xi_0 = -2.74 \pm 0.2, \quad (5.15)$$

where these values are for $\bar{\eta}_s = 0.584 \text{ c.p.}$ and $v = 0.65$.

Our value of A is in good agreement with the value of $A = 0.051$ predicted by Perl and Ferrell. Also our value for $\ln q_D \xi_0$ seems representative when compared to values for other fluids (Swinney and Henry, 1973).

5.8 Sample preparation.

The sample cell was a glass test tube approximately $5\frac{1}{2}$ in. long and $\frac{1}{2}$ in. I.D. It was sealed first with a tight fitting teflon stopper. The teflon is unreactive and should have no effect on the critical properties of the binary mixture. A glass cap fitted over the stopper and was sealed with an "O" ring seal. In this way the fluids were doubly sealed in the glass cell. (For details of this cell see Lyons (1973)). In practice we found no leakage to $\pm 2 \text{ mg}$ when the filled cell was held at various temperatures up to 60°C for nearly three months in a vacuum.

Before filling, the tube and stoppers were washed and sonarated in hot Alconox detergent, rinsed in water, washed again with a hot $\text{H}_2\text{SO}_4/\text{K}_2\text{Cr}_2\text{O}_7$ solution, rinsed well with distilled water, spectrographic grade methanol and dried overnight in an oven at 100°C . Upon removal from the oven, they were placed in a

desiccated dry box under a nitrogen atmosphere.

Our sample was prepared from freshly opened bottles of spectrographic grade reagents obtained from Fisher Chemical Company. All procedures such as opening the bottles and the filling of the cell were done under a nitrogen atmosphere in a desiccated dry box. In this way water contamination was kept at a minimum. The masses of the methanol and cyclohexane were

$$\text{mass methanol} = 2.4910 \pm 0.0002 \text{ gr}$$

mass total

$$(\text{methanol \& cyclohexane}) = 8.5786 \pm 0.0002 \text{ gr}$$

Thus

$$\% \text{ mass methanol} = 29.035 \pm 0.004\%$$

This is very close to the critical concentration value given by Huang and Webb (1969) of 29.0% methanol by weight.

The critical temperature of this fluid mixture was found by observing the meniscus between the two fluids; no meniscus is present when $T > T_C$. Our procedure was to agitate the whole temperature control cell by hand to mix the fluids well. If a meniscus formed, this meant we were still below T_C . Usually a meniscus formed within twelve hours after agitation when $T - T_C \geq 0.8^\circ\text{C}$. When $T - T_C < 0.8^\circ\text{C}$ times of as long as 48 to 60 hours were required for the meniscus to form.

Even then the meniscus was quite delicate and hard to see. This process of temperature change followed by agitation was continued until no meniscus formed, at that point we were above T_C .

As we have shown in Fig. 36, our control temperature had a constant drift of $\sim +0.05\text{m}^\circ\text{C}/\text{day}$. This drift limited the precision with which we could determine T_C . Obviously if we waited 60 hours for a meniscus to form after agitation the temperature had drifted $0.125\text{m}^\circ\text{C}$. Our measurements where we claim $T - T_C = 0.155 \pm 0.07\text{m}^\circ\text{C}$ (see Table III) were made by finding a value of T at which the meniscus formed, then agitating the cell without readjusting the temperature, and then finding no meniscus reformation after 60 hours. In this time our constant drift in temperature had changed enough to change the temperature from a value just below to one just above T_C . The value of $T - T_C = 0.155\text{m}^\circ\text{C}$ was the closest we could get to T_C using this method to account for the drift in temperature.

CHAPTER VI

LIGHT SCATTERING MEASUREMENTS ON A CRITICAL FLUID MIXTURE

6.1 Introduction.

In this chapter we discuss our light-scattering measurements on a critical fluid mixture. We have scattered light from the binary mixture methanol and cyclohexane at the critical concentration at various temperatures above the critical or consolute point of this mixture in the range $6.3^{\circ}\text{C} > T - T_c > 0.155\text{m}^{\circ}\text{C}$. Using photon autocorrelation techniques, we have measured the Rayleigh linewidth of light scattered from this system not taking precautions against the effects of multiple scattering. In this way, we simulated the Rayleigh linewidth measurements of others before us. We also measured the depolarized scattered linewidth and the depolarization ratio of the scattered intensity. The former of these measurements tests our results of Chapter IV where we found a theoretical result for the depolarized double-scattered linewidth. The latter measurement allows us to use our methods in section 3.11 and Chapter IV to evaluate the magnitude of the multiple-scattered light. With this knowledge, we re-examine both our Rayleigh linewidth and our depolarized

spectral measurements accounting for multiple-scattering effects.

We compare our Rayleigh linewidth measurements to the three theoretical forms for the linewidth: the mode-mode form, Eq. (1.11), the decoupled mode form, Eq. (1.14) and the dynamic droplet model form, Eq. (2.18). Least-squares fits of theory to data are performed for the decoupled mode and droplet model theories. We evaluate the relative fits of the data to the theories. We find that multiple-scattering effects become important in the nonhydrodynamic region ($k\xi > 1$), and a critical test of the theories can not be made. We do not, however, make the mistake of assuming that the extent of multiple scattering is small.

We also measured the shape of the scattered Rayleigh line and found it to be exponential in conflict with the dynamic droplet model prediction.

6.2 Measurement of the Rayleigh linewidth.

Throughout this chapter, we shall use the term "Rayleigh linewidth" to mean the linewidth of all the light scattered from a critical fluid mixture. Precisely speaking, this term should only apply to the linewidth of the single-scattered light. We use this operational definition because workers before us have done so in not accounting for the possibility of higher-order scattering. We might say that this is an

experimental definition because, in a real experiment, we are not at liberty to remove all but the single-scattered component. In this section, we describe our Rayleigh linewidth measurements.

Our fluid system was the binary fluid mixture of methanol and cyclohexane. A binary fluid was used instead of a single component fluid because of the difficulties in using a single component fluid. These difficulties include the need for high pressure cells and the large compressibility of the fluid near the critical point. One need only mix the binary fluid mixture at the proper concentration and the mixture is ready for use. Methanol and cyclohexane were used because they can be obtained commercially in high purity, their critical temperature is at 45°C , a reasonable temperature, and they had been used in other critical phenomena experiments in our laboratories (Hartley, 1974 and Jacobs, 1976).

The fluid mixture was prepared as described in section 5.8. The glass tube containing the fluids was placed in our temperature control cell and the cell mounted in our optical arrangement. The incident laser beam first passed through a 333mm focal length lens. Just after the lens was a Glan-Thompson polarizing filter positioned so as to insure a vertical polarization of the incident light. The beam then passed into the 180° window of the temperature control cell, through

the sample cell containing the fluids, and then out the 0° window. The sample cell center was $\sim 240\text{mm}$ distant from the lens, thus, since the laser beam had a diameter of $\sim 5.5\text{mm}$, the beam diameter in the cell was $\sim 1.5\text{mm}$. In this configuration, light scattered at 30° , 60° and 90° could be detected.

Before actual runs on the critical system were made, the cell was calibrated by placing a dilute Brownian microsphere suspension in it and measuring the scattered-light correlation function. An $\lambda = 0.117\mu\text{m}$ monodisperse polystyrene system was used. It was found that at all angles the spectra were very exponential ($K_2/K_1^2 < 0.03$) as they should have been. The measured correlation times in and out of the cell agreed to 1%. Thus, we felt that accurate measurements of the spectral shape and correlation time could be made on systems inside the temperature control cell.

Our first measurements concerned the laser heating effects. These measurements for the incident beam diameter 1.5mm and a wavelength of $5145\text{\AA}$ have already been discussed in section 5.6 (see Fig. 49). Similar measurements were made for the wavelength $\lambda = 4579\text{\AA}$ which was also used in our Rayleigh linewidth measurements. For $\lambda = 5145\text{\AA}$ the heating was 1.5°C/mW , and for $\lambda = 4579\text{\AA}$ the heating was 2°C/mW . Having determined the extent of laser heating for our particular scattering geometry,

we accounted for this heating in our $T-T_C$ determination.

At the majority of temperatures used in this experiment, six scattering wave vectors, k , were used. This was possible using both wavelengths $\lambda=4579\text{\AA}$ and $5145\text{\AA}$ and the three scattering angles, 30° , 60° and 90° . In this way, a wide range in k was obtained.

The estimated error in our correlation time measurements was $\pm 2\%$. This reasonable value was obtained by, in some cases, making several runs at a given $T-T_C$ and k and then evaluating the scatter in the correlation time data. For $T-T_C \leq 8\text{m}^\circ\text{C}$ the error was a bit larger, $\sim \pm 3\%$, due to some nonexponentiality in the spectra.

It was also determined that the scattering angle could be adjusted to better than $\pm 1^\circ$. This value was arrived at from our cell calibration measurements described above and from general experience. This error in the scattering angle causes an error of $\pm 1\%$ to $\pm 3\%$ in k at scattering angles of 90° to 30° .

The temperature was always evaluated in terms of its value relative to T_C , $T-T_C$. Three thermistors on the inner can gave values for T_C of 45.31°C , 45.36°C and 45.25°C , respectively. These values are in reasonable agreement with that given by Huang and Webb (1969) of $T_C=45.14^\circ\text{C}$. The precision of T_C was generally known to $\pm 0.3\text{m}^\circ\text{C}$ when $T-T_C > 30\text{m}^\circ\text{C}$ and known to $\pm 0.1\text{m}^\circ\text{C}$ when we

were closer to T_C (see the description of $T-T_C$ determination very close to T_C in section 5.8). Conversion of the thermistor resistance measurements to temperature were done with data supplied by the manufacturer of our thermistors.

The data are presented in Table III. The first column " $T-T_C$ " is the relative temperature of the inner can. The third column "actual $T-T_C$ " is the relative temperature of the fluid in the scattering volume determined from the sum of the inner can $T-T_C$ and the laser heating. The wave vector k is determined from $k=(4\pi n/\lambda)\sin(\theta/2)$ with the index of refraction of the mixture $n=1.380$ (Jacobs, 1976).

6.3 Comparison of the Rayleigh linewidth data to the dynamic droplet model.

Our first concern was to check the shape of the light-scattered correlation function of the Rayleigh line. The dynamic droplet model predicts a large non-exponentiality of $K_2/K_1^2 \sim 0.15$ independent of $T-T_C$ (Wonica et al., 1976). We found for the range $6.3^\circ\text{C} > T-T_C > 8\text{m}^\circ\text{C}$ the spectra were all very exponential having a second cumulant $K_2/K_1^2 < 0.03$. This is in conflict with the prediction of the dynamic droplet model. For values of $T-T_C \leq 8\text{m}^\circ\text{C}$, we found the spectra were non-exponential with $K_2/K_1^2 \sim 0.07$ or possibly greater. Our fitting routine (see section 5.2) is unable to

TABLE III

Rayleigh line measurements.

Cell $T-T_C$ ($m^{\circ}C$)	Laser Heat ($m^{\circ}C$)	Actual $T-T_C$ ($m^{\circ}C$)	λ ($\text{\AA}$)	θ (deg)	k (μm^{-1})	τ (μsec)
4162.	-	4162.	5145	90	23.83	8.67
"	-	"	"	60	16.85	15.93
"	-	"	4579	"	18.94	14.0
2066.	-	2066.	"	30	9.80	80.
"	-	"	5145	"	8.72	118.
"	-	"	4579	60	18.94	23.5
"	-	"	5145	"	16.85	26.0
"	-	"	"	90	23.83	14.45
"	-	"	"	"	"	14.25
1031.	-	1031.	"	"	"	23.1
"	-	"	4579	"	26.78	17.1
"	-	"	"	60	18.94	34.2
"	-	"	5145	"	16.85	40.6
"	-	"	"	30	8.72	175.
"	-	"	4579	"	9.80	136.
6300.	-	6300.	5145	60	16.85	11.8
"	-	"	"	90	23.83	6.27
"	-	"	"	"	"	6.28
4692.	-	4692.	"	"	"	7.8
3109.	-	3109.	"	"	"	10.8
"	-	"	"	60	16.85	19.1

TABLE III (Continued)

Cell $T-T_C$ ($m^{\circ}C$)	Laser Heat ($m^{\circ}C$)	Actual $T-T_C$ ($m^{\circ}C$)	λ ($\text{\AA}$)	θ (deg)	k (μm^{-1})	τ (μsec)
1754	-	1754.	5145	90	23.83	16.5
"	-	"	"	60	16.85	29.1
721.	-	721.	"	90	23.93	31.7
"	-	"	"	"	"	32.8
"	-	"	"	60	16.85	56.2
"	-	"	"	"	"	55.9
310.	-	310.	"	90	23.83	46.1
"	-	"	"	"	"	45.1
313.	-	313.	"	"	"	45.0
"	-	"	4579	"	26.78	33.5
"	-	"	"	30	9.80	301.8
"	-	"	5145	30	8.72	374.7
"	-	"	"	60	16.85	88.0
"	-	"	4579	"	18.94	68.9
166.	-	166.	5145	90	23.83	57.5
"	-	"	"	60	16.85	120.
105.	-	105.	"	90	23.83	69.9
63.	-	63.	5145	90	23.83	77.5
"	-	"	4579	"	26.78	55.6
"	-	"	5145	60	16.85	160.1

TABLE III (Continued)

Cell $T-T_C$ ($m^{\circ}C$)	Laser Heat ($m^{\circ}C$)	Actual $T-T_C$ ($m^{\circ}C$)	λ ($\text{\AA}$)	θ (deg)	k (μm^{-1})	τ (μsec)
28.	-	28.	4579	90	26.78	62.3
"	-	"	5145	"	23.83	85.3
"	-	"	"	"	"	86.2
"	-	"	"	60	16.85	216.
"	-	"	"	"	"	217.
20.4	-	20.4	"	90	23.83	86.3
"	-	"	4579	"	26.76	59.7
"	-	"	"	60	18.94	149.
"	-	"	5145	"	16.85	222.
"	-	"	"	30	8.72	1396.
"	-	"	"	"	"	1417.
"	-	"	4579	"	9.80	1010.
12.3	0.3	12.6	5145	90	23.83	91.2
"	"	"	4579	90	26.78	65.9
"	0	12.3	"	30	9.80	1362.
"	"	"	"	"	"	1350.
"	"	"	5145	"	8.72	1808.
"	"	"	4579	60	18.94	178.
"	"	"	5145	"	16.85	244.
8.2	0.3	8.5	5145	90	23.83	82.5
"	"	"	"	"	"	87.7

TABLE III (Continued)

Cell T-T _C (m°C)	Laser Heat (m°C)	Actual T-T _C (m°C)	λ $\text{\AA}$	θ (deg)	k (μm^{-1})	τ (μsec)
8.2	0.3	8.5	4579	90	26.78	63.5
"	0	8.2	5145	60	18.85	262.
"	"	"	"	30	8.72	1772.
"	"	"	4579	"	9.80	1492.
6.1	-	6.1	5145	60	16.85	266.
"	-	"	"	"	"	269.
"	-	"	"	90	23.83	93.
"	-	"	4579	"	26.78	75.6
5.2	0.3	5.5	5145	"	23.83	90.2
"	"	"	4579	"	26.78	68.8
"	0	5.2	"	60	18.94	204.
"	"	"	5145	"	16.85	266.
"	"	"	"	30	8.72	2052.
"	"	"	4579	"	9.80	1548.
"	0.3	5.5	5145	90	23.83	93.4
2.9	0.3	3.2	"	"	23.83	89.5
"	"	"	4579	"	26.78	70.0
"	0	2.9	"	60	18.94	200.
"	"	"	5145	"	16.85	281.
"	"	"	"	30	8.72	2040.
"	"	"	4579	"	9.80	1514.

TABLE III (Continued)

Cell $T-T_C$ ($m^{\circ}C$)	Laser Heat ($m^{\circ}C$)	Actual $T-T_C$ ($m^{\circ}C$)	λ $\text{\AA}$	θ (deg)	k (μm^{-1})	τ (μsec)
1.35	0	1.35	5145	30	8.72	1861.
"	"	"	"	"	"	1798.
"	"	"	4579	"	9.80	1305.
"	"	"	"	60	18.94	193.
"	0.1	1.45	5145	"	16.85	284.
"	"	"	"	90	23.83	96.1
"	"	"	"	"	"	96.4
"	"	"	"	"	"	95.0
"	"	"	4579	"	26.78	68.3
0.6	0	0.6	5145	30	8.72	1900.
"	"	"	4579	"	9.80	1476.
"	0.15	0.75	"	60	18.44	179.
"	0.2	0.80	5145	"	16.85	252.
"	0.14	0.74	"	90	23.83	95.
"	"	"	"	"	"	99.
"	"	"	4579	"	26.78	69.9
"	"	"	"	"	"	67.7
0-0.33	0.1	.26 $\pm$ 0.2	5145	"	23.83	93.5
0-0.13	0.1	.165 $\pm$ 0.07	"	"	"	96.7
0-0.13	0.08	.155 $\pm$ 0.07	4579	"	26.78	70.3
"	"	"	5145	30	8.72	2035.
"	"	"	4579	"	9.80	1660.
"	"	"	"	"	"	1482.
"	"	"	5145	60	16.85	290.
"	"	"	4579	"	18.94	192.

accurately measure larger second cumulants. At first we thought this nonexponentiality was due to polydispersity effects consistent with the dynamic droplet model, but we realized that multiple-scattering effects could also be responsible. In fact, this was one of our motives to study multiple scattering. As we shall see, multiple scattering is significant in this region, and is undoubtedly the cause of the observed nonexponentiality in this region. We conclude that the single-scattered Rayleigh lineshape is exponential in disagreement with the prediction of the dynamic droplet model. Similar results for xenon 18m°C from T_C were subsequently found by Wonica, Swinney and Cummins (1976) (see the discussion in section 2.4).

In analysing our linewidth data in Table III, we shall ignore multiple-scattering effects for reasons we discussed at the beginning of the last section. We analyse the data using a least-squares fitting program called MINUIT developed at CERN. This program is capable of a ten parameter fit, and we found it to give reliable results with our data.

To fit the data, we use Eq. (2.18) for the linewidth result of the dynamic droplet model. The form of Eq. (2.18) can be written as

$$\Gamma = \gamma^{-1} D k^2 \quad (6.1)$$

where

$$D = \frac{k_B T}{6\pi\eta_b \xi} (1+k^2\xi^2)^{\frac{1}{2}}. \quad (6.2)$$

The factor γ , of order unity, was dependent on the fitting technique used in measuring the correlation time of the predicted nonexponential correlation function (Ackerson et al., 1975 and Sorensen et al., 1976).

Since we know experimentally that the correlation function is exponential, the meaning of the factor γ becomes unclear. We might reason that $\gamma=1$, but until we develop a droplet model that correctly predicts an exponential scattered-light correlation function, we can not theoretically predict the value of γ . In general, we shall use γ as an adjustable parameter of order unity in our fitting procedure.

When fitting the predictions of the droplet model, Eqs. (6.1) and (6.2), to the data, we shall have three adjustable parameters: γ , ξ_0 and v . The parameters ξ_0 and v determine the correlation length ξ by Eq. (1.6).

The program uses Eq. (1.17) to find the scaled linewidth of both the theory and data. The droplet model scaled linewidth is given by

$$\Gamma^* = \frac{1}{k\xi} (1+k^2\xi^2)^{\frac{1}{2}}. \quad (6.3)$$

The scaled linewidth for the data is given by

$$\Gamma^* = \gamma \frac{6\pi\eta_b}{k_B T} \frac{1}{k^3} \frac{1}{2\tau} \quad (6.4)$$

where η_b is the background viscosity and τ is the measured correlation time. We use the value of the background viscosity given by Eq. (5.12) with $A=-2.667$ and $B=775^\circ\text{K}$ as determined by our viscosity measurements. The average error in the data scaled linewidth is taken to be $\pm 5\%$ as determined from the errors in τ and k .

All 108 data points are fit to the droplet model form. A "best fit" of $\chi^2=212$ (sum for all 108 data points) with values of $\gamma=1.037$, $\xi_0=2.48\text{\AA}$ and $\nu=0.649$ is found. Examination of the fit showed eight data points which had individual $\chi^2>10$. Since these points do not corroborate the rest of the data, we shall discard these points from the data set. We fit the remaining 100 points and find a best fit at $\gamma=1.037$, $\xi_0=2.38\text{\AA}$ and $\nu=0.654$ with (sum) $\chi^2=150$. An error analysis in the MINUIT program gave errors (standard deviations) of $0.026\text{\AA}$ and 0.002 for ξ_0 and ν , respectively. This fit is plotted in Fig. 52.

We may also analyse the data as two separate groups. One group in the region $k\xi>7$ is not dependent on ξ_0 and ν and essentially determines the parameter γ . Averaging Γ^* for all points for which $k\xi>7$ gives

Figure 52. Scaled Rayleigh linewidth of light scattered from the critical fluid system methanol and cyclohexane. Solid line represents the best fit for all 100 data points to the dynamic droplet model. Values of $\xi_0 = 2.38\text{\AA}$, $\nu = 0.654$ and $\gamma = 1.037$ were found for this fit.

$\Gamma^* = 0.963 = \gamma^{-1}$ corroborating with the value of $\gamma = 1.037$ obtained from our least-squares fit.

The second group of data are for $k\xi < 0.8$. This is the region which determines ξ_0 and ν . The 33 data points in this region are fit with the program for $\gamma = 1.00$ and the values $\xi_0 = 2.46\text{\AA}$ and $\nu = 0.655$ with $\chi^2 = 21$ are found. Again in reasonable agreement with the fit to all the data.

The values ξ_0 and ν are quite reasonable when compared to other values for other systems (Swinney and Henry, 1973, Table VII). If anything the exponent may be a bit large, the value 0.62 to 0.63 being more common. Fig. 52 shows the data are well described by the theory even in the region $k\xi \sim 80$. We point out that this is the largest value of $k\xi$ reported to date for a light-scattering experiment on a critical fluid.

6.4 Comparison of the dynamic droplet model to the Rayleigh linewidth data of others.

Perl and Ferrell (1972b) were the first to suggest that the form Eq. (1.15) or (2.18) would fit the Rayleigh linewidth of light scattered from a critical fluid system well. Thus, it should be no surprise to us that our data fits this form well too. The fit depends on the three parameters γ , ξ_0 and ν . ξ_0 and ν can be independently determined from light-scattering intensity measurements. Unfortunately, we have not made

any such measurements, and therefore, can not compare our values to other independently determined values. Our values for ξ_0 and ν are quite reasonable, however, so there appears to be no need for objection here.

The parameter γ is peculiar to our droplet model, and its physical meaning is unclear. We shall find γ from other light-scattering measurements by finding the average $\bar{\Gamma}^*$ in the region $k\xi \gg 1$ and compare these values.

We have found three systems in the literature for which both Rayleigh linewidth measurements and the background viscosity in the critical region have been determined. These systems are 3-methylpentane and nitroethane (Chang et al., 1971 and Tsai et al., 1973), 2,6-lutidine and water (Gulari et al., 1972) and aniline and cyclohexane (Berge et al., 1970 and Arcovito et al., 1969). Using η_b at T_C and the linewidth data we find $\gamma^{-1} = \bar{\Gamma}^*$ at $k\xi \gg 1$. These values are:

$$\gamma = 1.09, \text{ 3-methylpentane and nitroethane}$$

$$\gamma = 1.18, \text{ 2,6-lutidine and water}$$

$$\gamma = 1.12, \text{ aniline and cyclohexane}$$

$$\gamma = 1.037, \text{ methanol and cyclohexane.}$$

We find an average of $\bar{\gamma} = 1.08$.

It is in the large $k\xi$ region where we expect multiple-scattering effects to be largest. We have seen in Figs. 36 and 37 that the double-scattered linewidth

is equal to the single-scattered linewidth in this region to $\pm 10\%$. Thus, we might reasonably assume that this $\pm 10\%$ effect can account for the variation of γ from fluid to fluid.

However, as we shall see we expect multiple scattering to increase the total linewidth slightly, not decrease it as the values of $\gamma > 1$ indicate. Also, the system 3-methylpentane and nitroethane has a very small scattering cross section. Hence, we expect little multiple scattering from this system, yet it has an intermediate value of γ relative to the other three, more highly scattering liquids. Thus, we conclude that while multiple scattering may well have effects in this region these effects may not be the whole story on the factor γ .

We can also consider the possibility that the background viscosity is not the proper viscosity to use to describe the diffusion of the droplets in the critical region. Notice that if the background viscosity η_b were increased to $\eta_s = \gamma \eta_b$, we could consider the droplets as diffusing in this larger viscosity η_s . It is not unreasonable to assume that the diffusing droplets feel some sort of critical viscosity. The full macroscopic critical viscosity is too large, however, being $\sim 50\%$ larger than η_b in the critical region ($k\xi \sim 10$). It is possible that the diffusing droplets do feel each

others presence, and thus, diffuse in a microscopic viscosity slightly larger than η_b . Such a possibility is of interest in regards to the work of Lyons, Mockler, and O'Sullivan (1973) on diffusion in a critical fluid. Such an effective critical viscosity might be a necessary addition to the droplet model.

6.5 Comparison of the Rayleigh linewidth data to the mode theories.

We now fit our data to the decoupled mode theory of Perl and Ferrell (1972). This form is given in Eq. (1.14). Swinney and Henry (1973) show that to a good approximation (good to 0.5%) the scaled linewidth of the decoupled mode theory is given by (see their Eq. (45))

$$\Gamma^* = \frac{K_0(k\xi)}{(k\xi)^3} \left\{ 1 + \frac{\bar{\eta}_s A}{\eta_b} \left[\frac{1}{2} \ln(1+k^2\xi^2) - \tau(k\xi) \right] \right\}, \quad (6.5)$$

for the critical exponent $\eta=0$. The value $\bar{\eta}_s A$ was determined from our viscosity measurements to be 0.0306cp (section 5.7). $K_0(k\xi)$ is given in Eq. (1.12). The function $\tau(x)$ is a numerically determined quantity. Some values given by Swinney and Henry (1973) are $\tau(100) \approx \tau(\infty) = 0.09$, $\tau(2) = -0.189$, $\tau(1) = -0.357$ and $\tau(0.1) \approx \tau(0) = -0.492$.

When comparing the decoupled mode theory to the data we use

$$\Gamma^* = \frac{6\pi\eta_s}{k_B T} \frac{1}{k^3} \frac{1}{2\tau} \quad (6.6)$$

for the data scaled linewidth. This is identical to Eq. (6.4) for the droplet model only now we use the full macroscopic critical viscosity, η_s . This critical viscosity can be calculated from our results in section 5.7 using Eq. (5.13) as

$$\eta_s = \eta_b - 0.0306(2.74 + v \ln t). \quad (6.7)$$

Using Eqs. (6.5), (6.6) and (6.7) in the MINUIT fitting program we analyse the data. For the first 33 data points for which $k\xi < 0.8$, we find fitting on ξ_0 and v only, $\xi_0 = 2.85 \text{ \AA}$ and $v = 0.627$ with $\chi^2 = 21.7$. These values are both about 5% different than the values found for the droplet model. One reason for the smaller value of v is that the critical viscosity increases faster for increasing ξ than the background viscosity. This tends to make the slope of the Γ^* versus $T - T_C$ curve in the region $k\xi < 0.8$ smaller. This slope, however, is equal to the critical exponent v . Thus, the major reason for a smaller exponent is the use of the critical viscosity in the mode theory.

Upon fitting all 100 data points to the decoupled mode theory, we find a best fit for $\xi_0 = 2.30\text{\AA}$, $\nu = 0.664$ with a total $\chi^2 = 313$. This is a poor fit, corresponding to an average deviation of theory and data of $\sim 9\%$ per point. Examination of the fit shows that in the region $k\xi > 5$ the data consistently fall 10% to 14% below the theory. In another comparison, we compare the fit to the first 33 data points described above, to all the data. Again, the data for $k\xi > 5$ fell 10% to 16% below the theory. This fit is plotted in Fig. 53.

In order to improve the fit of all the data, and to be fair in comparing the fits to those obtained for the droplet model, we use the adjustable parameter γ as before. We point out that the decoupled mode theory does not allow for such an adjustable parameter. We find a very good fit for $\xi_0 = 2.77\text{\AA}$, $\nu = 0.616$ and $\gamma = 1.085$ with a total $\chi^2 = 138$. We plot this fit in Fig. 54. The values of ξ_0 and ν corroborate well with those obtained from the fit to the first 33 data points.

We see that if we are allowed three parameters, γ , ξ_0 and ν , in our fit we can achieve a fit as good as that for the droplet model.

In Fig. 53 we have also plotted the prediction of the mode-mode theory of Kawasaki and Lo (1972) and Lo and Kawasaki (1973) (Eq. (1.11)). The mode-mode and decoupled mode theories are essentially equal in the

Figure 53. Scaled Rayleigh linewidth of light scattered from the critical fluid system methanol and cyclohexane. Solid line represents the best fit of the first 33 data points for which $k\xi < 0.8$ to the decoupled mode theory. Dashed line corresponds to the mode-mode theory fit to these same points. Values of $\xi_0 = 2.85\text{\AA}$ and $\nu = 0.627$ were found for these fits.

Figure 54. Scaled Rayleigh linewidth of light scattered from the critical fluid system methanol and cyclohexane. Solid line represents the best fit for all 100 data points to the decoupled mode theory. Values of $\xi_0 = 2.77\text{\AA}$, $\nu = 0.616$ and $\gamma = 1.085$ were found for this fit.

$k\xi < 1$ region. Thus, we can consider the fit obtained to the $k\xi < 0.8$ points for the decoupled mode theory equivalent to that which we would obtain for the mode-mode theory, and compare the theory and experiment in Fig. 53. As can be seen, the mode-mode theory deviates significantly from the data in the large $k\xi$ region. We must not, however, consider this a test of either mode theory until we investigate the effects of multiple scattering in this region.

6.6 Measurement of the depolarized light-scattering linewidth and intensity.

The experimental procedures used in obtaining the depolarized light-scattering linewidths are very similar to those used in our Rayleigh linewidth measurements. The incident laser beam first passed through a Glan-Thompson polarizing prism of extinction ratio 5×10^{-5} . The prism was arranged to pass only vertically polarized light. No lens was used to narrow the beam. By using the full beam width, we obtained a spherical scattering geometry as discussed in section 3.10. We used this arrangement before subsequent work indicated that such a geometry could be obtained with a narrow incident beam if we viewed a large region about the beam. In any event, a wide beam (~5mm diameter) ensured a spherical scattering geometry to fit our theoretical conditions.

The light scattered from the fluid mixture first passed through a second, similar Glan-Thompson polarizing prism. This polarizer could be adjusted to pass either the polarized or depolarized component of the scattered light. Directly after this polarizer was an entrance aperture and pinhole leading to the photomultiplier tube (section 5.3).

We measured the laser heating for this wide beam geometry using the methods of section 5.6. Because the beam is wider than in the Rayleigh linewidth experiment, the heating is smaller. We found heating of $0.36\text{m}^\circ\text{C}/\text{mW}$ for $\lambda=5145\text{\AA}$ and $0.50\text{m}^\circ\text{C}/\text{mW}$ for $\lambda=4579\text{\AA}$.

The depolarized spectra proved to be very laborious to obtain. The depolarized scattered intensity is much less intense than the polarized scattered intensity. Hence, accumulation times are much longer. The incident power had to be kept low so that laser heating effects would be moderate. Run times for a single spectrum ranged from 12 hours near T_C to as much as 48 hours far from T_C . Even after such long accumulation times, the spectra had more scatter than those obtained for the polarized, Rayleigh component.

The depolarized correlation function also proved to be highly nonexponential. This was expected from our theoretical results shown in Figs. 33 and 34. Our fitting routine described in section 5.2, did not

always yield a good fit to these spectra, especially in the $\theta=30^\circ$ case. Hence, we expect a fairly large uncertainty in the determination of the first cumulant from these spectra. At a scattering angle of 30° it appeared that errors of 20% to 30% may have resulted in our first cumulant determination. At 90° , where the spectra were more nearly exponential, an error of 10% may have resulted.

Because of the large amount of time required in obtaining the depolarized spectra, runs were not made at $\theta=60^\circ$. Thus, only runs at $\theta=30^\circ$ and 90° and $\lambda=4579\text{\AA}$ and $5145\text{\AA}$ were made. This should lend us enough information to test our theoretical results of Chapter IV.

For each experimental run, the detection polarizer was adjusted to obtain a minimum in the count rate. This technique was developed and proved successful in our depolarization measurement on Brownian particle systems described in section 3.9 and illustrated in Fig. 18.

The depolarization ratio measurement was made by measuring the polarized and depolarized scattered intensities at a given $T-T_C$, θ , λ and incident power. These measurements are fairly simple and take only a few minutes; the estimated error on these measurements is $\pm 5\%$.

In Table IV we present our depolarized correlation time and ratio measurements for the light scattered from our binary fluid mixture. The headings in this table are similar to those in Table III.

6.7 Analysis of the depolarized light-scattering data.

Our first concern is the magnitude of the multiple-scattered light. We have seen in sections 3.11 and 4.3 how depolarization ratio measurements can be used to determine this quantity. In section 3.11 we developed a method to determine the average number of scattering events, $\bar{n}$. A knowledge of $\bar{n}$ with the use of Eq. (3.60) gives us the relative magnitudes of all the orders of the scattered light.

We shall not use the method of section 3.11 for our critical fluid depolarization ratio. This method is good only for $k_0 \xi \ll 1$ which corresponds to $k_0 \xi \ll 1$ for critical fluids. Our data is not limited solely to this region. Extension of the method into the $k_0 \xi > 1$ region requires the knowledge of the values

$R_n = I_{n\perp} / I_{n\parallel}$ (see Eq. 3.63) in this region. Also the techniques in section 3.11 were successful in determining the average polarized and depolarized correlation times because the higher-order correlation functions for light scattering from Brownian particle systems were well described by the first cumulant. We have seen in section 4.4 that this is not the case for

TABLE IV

Depolarized correlation time and ratio measurements.

Cell $T-T_C$ ($m^{\circ}C$)	Laser Heat ($m^{\circ}C$)	Actual $T-T_C$ ($m^{\circ}C$)	λ $\text{\AA}$	θ (deg)	τ (μsec)	R ($\times 10^2$)
313.	3.0	316.	5145	30	39. $\pm$ 2	0.54
"	4.0	317.	4579	"	21. $\pm$ 2	0.76
"	4.5	317.5	"	90	20. $\pm$ 1	0.87
"	4.5	317.5	5145	"	25.7	0.64
156.	1.0	157.	5145	30	34. $\pm$ 3	0.62
"	1.2	157.2	4579	"	32.5 $\pm$ 2	0.79
"	1.0	157.	"	90	22.5 $\pm$ 1	1.67
"	1.0	157.	5145	"	32. $\pm$ 4	1.19
104.	0.6	104.6	5145	30	52. $\pm$ 7	1.23
"	0.8	104.8	4579	"	32. $\pm$ 3	0.88
"	0.8	104.8	"	90	20. $\pm$ 2	2.14
"	1.0	105.	5145	"	27. $\pm$ 4	1.5
57.	0.6	57.6	"	30	56. $\pm$ 4	1.25
"	"	"	4579	"	39. $\pm$ 5	1.39
"	"	"	"	90	32. $\pm$ 5	3.52
"	"	"	5145	"	32.5 $\pm$ 3	2.41
32.	0.5	32.5	4579	30	54. $\pm$ 4	1.53
"	"	"	5145	"	60.5 $\pm$ 1	1.45
"	"	"	"	90	48. $\pm$ 5	4.46
"	"	"	4579	"	35.5 $\pm$ 1	5.01
15.4	0.6	16.	"	30	62.6 $\pm$ 1	1.68
"	"	"	5145	"	89. $\pm$ 5	1.76

TABLE IV (Continued)

Cell $T-T_C$ (m°C)	Laser Heat (m°C)	Actual $T-T_C$ (m°C)	λ $\text{\AA}$	θ (deg)	τ (μsec)	R ($\times 10^2$)
15.4	0.6	16.	4579	30	62.6 $\pm$ 1	1.68
"	"	"	5145	"	89. $\pm$ 5	1.76
"	"	"	"	90	47.5 $\pm$ 3	5.85
"	"	"	4579	"	37.7 $\pm$ 1	6.11
8.3	0.5	8.8	4579	90	40. $\pm$ 1	6.62
"	"	"	5145	"	52. $\pm$ 2	4.4
"	"	"	"	30	86. $\pm$ 4	1.14
"	"	"	4579	"	58. $\pm$ 2	1.61
4.2	0.5	4.7	"	90	43. $\pm$ 4	7.04
"	"	"	5145	"	57. $\pm$ 2	4.92
"	"	"	"	30	105. $\pm$ 5	1.32
"	"	"	4579	"	78. $\pm$ 6	1.81
2.2	0.5	2.7	"	90	46. $\pm$ 2	7.16
"	"	"	5145	"	59. $\pm$ 3	5.53
"	"	"	"	30	112. $\pm$ 5	1.19
"	"	"	4579	"	75. $\pm$ 4	2.02
1.02	0.5	1.7	"	90	42. $\pm$ 3	7.93
"	"	"	5145	"	59. $\pm$ 4	5.97
"	"	"	"	30	138. $\pm$ 8	1.85
"	"	"	4579	"	87. $\pm$ 5	2.75
0.2	0.5	0.7	5145	90	66. $\pm$ 3	-
"	"	"	4579	"	36. $\pm$ 3	8.16
"	0.9	1.1	"	"	54. $\pm$ 5	8.4
"	0.5	0.7	5145	30	122. $\pm$ 8	1.19
"	"	"	4579	"	85. $\pm$ 5	1.89

double scattering from critical fluid systems. This lack of a good quantitative parameter makes the extension of these techniques to critical fluid scattering difficult.

In section 4.3 we use Eq. (4.6) to give us an estimate of the ratio of the single to double scattered intensity. This is a second-order expression, however, and is good only when I_2/I_1 is small. This is when the depolarization ratio $R \ll R_2$ in Eq. (4.6). When I_2 is a significant fraction of I_1 , Eq. (4.6) breaks down (e.g. when $I_2/I_1 = \frac{1}{2}$, $\bar{n}=1$ so $\Sigma I_n/I_1 = 0.218$ for $n \geq 3$). As R approaches R_2 , $I_2/I_1 \rightarrow \infty$. This, of course, isn't happening but a value of R of the same order or larger than R_2 indicates the breakdown of the second-order theory and the onset of higher-order-than-second effects on the light-scattering intensity and spectra measurements.

To use this R compared to R_2 technique, we plot our depolarization ratio measurements and the calculated value of R_2 from our theory in Chapter IV together versus $k_0 \xi$ in Fig. 55. To determine ξ we used the values of $\xi_0 = 2.46 \text{ \AA}$ and $\nu = 0.655$ obtained from the dynamic droplet model fit to the data in the $k\xi < 0.8$ region. As we shall see, in this region the effects of multiple scattering should be small.

Figure 55. Depolarization ratio measurements for light scattered from the critical fluid system methanol and cyclohexane. Solid lines are $R_2 = I_{2\perp} / I_{2\parallel}$ as shown in Fig. 28.

In the region $k_0 \xi \lesssim 1$, $R < R_2$ and so we expect the second-order Eq. (4.6) to hold. Using the depolarization ratio data and the values of R_2 for the experimental $k_0 \xi$ in Eq. (4.6), we generate Table V for the ratio of the double to single-scattered light. Inspection of Table V shows that double scattering becomes large ($I_2/I_1 \sim 15\%$ to 20%) when $k_0 \xi \geq 1.1$ for $\theta = 30^\circ$ and $k_0 \xi \geq 0.8$ when $\theta = 90^\circ$. We stress here that these results are very system dependent, depending on the absolute cross section of the fluids and the scattering geometry.

In the region $k_0 \xi \geq 5$, $R \geq R_2$ indicating that double scattering is no longer sufficient to describe the depolarization ratio. In this region higher-order scattering effects are dominant and as yet these effects are not clearly understood for critical fluid systems. Thus, we see how Fig. 55 indicates the regions of solely single, single plus double and multiple scattering.

Some general features of Fig. 55 should be pointed out. First we see that R increases with $k_0 \xi$ similar to the double-scattered result predicted in Fig. 27. This increase in R levels off in the region $k_0 \xi \gg 1$. $k_0 \xi \gg 1$ implies $k^2 \gg \xi^{-2}$ for our scattering angles. From Eq. (1.5) for the scattering amplitude, we see that under this condition the scattering amplitude doesn't increase for increasing ξ . Thus the

TABLE V

Ratio of the total double to single-scattered light scattered from our critical fluid system.

Actual $T - T_C$ ($^{\circ}\text{C}$)	λ ($\text{\AA}$)	θ (deg)	$k_0 \xi$	I_2/I_1 ($\times 10^{-2}$)
316.	5145	30	0.40	5.15
317.	4579	"	0.45	7.3
317.5	5145	90	0.40	6.2
317.5	4579	"	0.45	8.4
156.	5145	30	0.62	6.4
157.2	4579	"	0.69	8.0
157.	5145	90	0.62	11.2
157.	4579	"	0.69	15.
104.6	5145	30	0.84	17.
104.8	4579	"	0.94	12.
105.	5145	90	0.84	17.5
104.8	4579	"	0.94	27.
57.6	5145	30	1.21	26.
57.6	4579	"	1.35	29.
57.6	5145	90	1.21	38.
57.6	4579	"	1.35	65.

extent of multiple scattering is constant in this region.

The depolarization ratio is larger for $\lambda=4579\text{\AA}$ than for $\lambda=5145\text{\AA}$. Equation (2.13), which gives the full expression for the scattering cross section, shows us that the scattering is proportional to λ^{-2} in the critical region in qualitative agreement with observation.

The two sets of depolarization ratio data for 30° and 90° are nearly equal in the region $k_0\xi < 0.5$. This is expected since in this region both I_1 and I_2 have very little scattering-angle dependence. As $k_0\xi$ increases, I_1 develops a $(\sin\theta/2)^{-2}$ dependence. Figure 30 shows us that I_2 also begins to scatter more in the forward direction for $k_0\xi > 1$, but not as much as I_1 . Higher-order scattering intensities are fairly isotropic for large order. Thus, we expect R to vary as $(\sin\theta/2)^x$ where $0 < x < 2$. From our data in Fig. 55, it appears $x \sim 0.8$.

We may summarize by saying that depolarization ratio measurements with the use of Eq. (4.6) and Fig. 55 are effective indicators of the degree of multiple scattering. These effects are dependent on the system used and the light-scattering geometry. For our system and wide beam geometry we found the double-scattered intensity became large for $k_0\xi \geq 0.8$. We also found that multiple (higher order than double) scattering became important in the region $k_0\xi \geq 3$. We also saw that our

double-scattering theory for light scattering from critical fluids provided a reasonable qualitative description of the depolarization ratio measurement.

Now we consider our depolarized light-scattering correlation time measurements. As discussed in Chapter IV, the double-scattered spectrum can be found if we know the single-scattered spectrum. Thus, barring the possibility of correlations between the first and second scattering regions in the fluid, there is no new physics in the double-scattered light. This implies that we may use any single-scattering theory that describes the single-scattered data well to predict the proper form of the double-scattered intensity and linewidth. In Chapter IV we used the dynamic droplet model form for the single-scattered correlation function. Since we have found this form fits our Rayleigh linewidth data well, we can expect it to predict the proper form for the double-scattered linewidth. The fit to the $k\xi < 0.8$ points, where, as we have seen above, multiple-scattering effects are minimal, yielded values of $\xi_0 = 2.46 \text{ \AA}$ and $\nu = 0.655$. We shall use these values in analysing the fit of data and theory for our depolarized scattered light.

We present our data versus theory comparison in Figs. 56 and 57 for $\theta = 30^\circ$ and 90° , respectively. We plot the scaled linewidth versus $k_0 \xi$ (remember, k_0 is

Figure 56. Depolarized scaled linewidth of light scattered from the critical fluid system methanol and cyclohexane at $\theta_{\text{SCAT}} = 30^\circ$.

Figure 57. Depolarized scaled linewidth of light scattered from the critical fluid system methanol and cyclohexane at $\theta_{\text{SCAT}} = 90^\circ$.

is the incident wave vector). The theoretical curve for the linewidth represents the first cumulant of the scattered-light correlation function. To a first approximation, the double-scattering theory is successful in describing the data. The $\theta=30^\circ$ data fit quite well, but the data for $\theta=90^\circ$ show a systematic deviation, being approximately 25% greater than the theory for $k_0\xi>2$.

Our theoretical curves in Figs. 56 and 57 are for the first cumulant of the scattered-light correlation function. Our calculations of the total correlation function in section 4.4 indicated that, while at $\theta=90^\circ$, the first cumulant described the decay of the correlation function well, the correlation function at $\theta=30^\circ$ was very nonexponential and was not well characterized by the first cumulant for $k_0\xi>2$. Using our fitting routine (section 5.2), the correlation time measured from such nonexponential spectra might be 20% to 50% larger (thus, the linewidth is smaller) than the first cumulant value. These considerations, lead us to conclude that the 90° data accurately reflect a deviation of data and theory in the $k_0\xi>2$ region; whereas, the 30° data erroneously indicate an agreement of theory and experiment. If we did consider a 25% systematic error in our $\theta=30^\circ$ measurements due to the nonexponentiality, a correction for this would in

effect move all the 30° linewidth data up in Fig. 56 and lead to a deviation of theory and experiment similar to that observed in the $\theta=90^\circ$ measurements. Notice that the $\theta=30^\circ$ data at $k_0\xi < 1$, which without such a correction deviate from the theory, would now tend to agree with the theory as does the $k_0\xi < 1$ data at $\theta=90^\circ$. We conclude theory and experiment do not agree in the $k_0\xi > 2$ region for both scattering angles.

Our depolarization ratio measurements and analysis indicate the cause of this disagreement in theory and experiment. We found from this analysis that the second-order double-scattering theory began to fail because of higher-order scattering in the region $k_0\xi \gtrsim 3$. This corroborates well with the failure of the double-scattering theory to explain the depolarized linewidth data in the region $k_0\xi > 2$. Furthermore, throughout our work on multiple scattering, we have seen that, in general, each higher-order correlation time is progressively smaller (see section 3.11). Thus, each higher-order linewidth is larger. Because of this, we expect the linewidth to be larger than the double-scattered prediction in the region where multiple scattering effects are important, which indeed they are. Also we see that the deviation is constant with $k_0\xi$ above $k_0\xi > 2$. This is expected for we found with our depolarization ratio measurements that the relative

magnitudes of the higher-order scattered light don't increase with $k_0\xi$ in the $k_0\xi \gg 1$ region. We conclude that multiple scattering describes, or at least accounts for, the depolarized spectrum of light scattered from critical fluid systems.

Before we leave the subject of depolarized double-scattering, we point out that inspection of Table III for the Rayleigh or polarized correlation times and Table IV for the depolarized correlation times, shows that in the region $T - T_C < 10\text{m}^\circ\text{C}$ at $\theta = 90^\circ$ the depolarized correlation times are approximately 60% to 70% of the polarized correlation times, i.e.

$\tau_{21}/\tau_{11} \approx 0.6$ to 0.7 . This corroborates well with our comparison results of Chapter IV plotted in Fig. 37, being a bit low due, as we have seen, to higher-order scattering effects. Hence, we can expect that the polarized part of the double plus higher-order scattered spectra would corroborate well with the τ_2/τ_1 results in Figs. 36 and 37 if they could be measured being, if anything, 10% to 20% smaller than predicted because of higher-order scattering effects.

6.8 Reevaluation of the Rayleigh linewidth data accounting for multiple scattering.

We are now in a position to apply our knowledge of multiple scattering of light from critical fluids to evaluate its effects on the Rayleigh linewidth measurements.

We have seen that the multiple-scattered intensity begins to get large for $k_0 \xi \gtrsim 0.5$. This result, however, applies to the wide beam geometry used in our depolarized light-scattering measurements. In our Rayleigh linewidth measurements, we used a narrower incident beam. We expect the amount of multiple scattering at a given $k_0 \xi$ to be significantly less in this narrow beam configuration. We made our Rayleigh linewidth measurements before we had developed our multiple-scattering theories; hence, we did not measure the depolarization ratios for this narrow beam configuration.

Even if we had results of these depolarization ratio measurements, it is unlikely that they would be of much help. We have seen in Figs. 36 and 37 that the effects of double scattering on the linewidth are small, and because of the nonexponentiality of the correlation functions, difficult to characterize in a quantitative way. Thus, the insidious effects of multiple scattering would be difficult to remove quantitatively from our

Rayleigh linewidth measurements even if the relative intensity of the multiple scattering were known.

We are left with only qualitative observations of these effects. We first observe that the general conclusions made concerning Figs. 36 and 37 (see also Sorensen, Mockler and O'Sullivan 1976b) are correct. The effects of double and, to a lesser extent, multiple scattering on the true single-scattered Rayleigh linewidth are small. This is why we, as well as experimenters before us, have observed agreement between the single-scattering theories and the data. Multiple scattering is there, perhaps even in large amounts, but its effects on the linewidth measurements are small.

Beyond having no observable effect, the multiple-scattered linewidths tend to be a bit larger than the single-scattered linewidths. Thus, if we were to account for this in our measurements, our linewidths would be corrected in such a way as to make them perhaps 5% to 10% smaller. This would mean that in our droplet model fit the parameter γ would have to be larger, say $\gamma=1.1$, to obtain a good fit. Recalling our discussion in section 6.4, this would imply that γ is reflecting some sort of critical viscosity seen by the diffusing droplets that is roughly 10% larger than the background viscosity in the critical region.

Another effect of multiple scattering is to drastically reduce any k -dependence seen in the single-scattered linewidth. This is most dramatically illustrated in Fig. 19 where we plot the single and double-scattered correlation time versus the scattering angle. In Fig. 19 the single-scattered correlation time has a strong $\sin^2(\theta/2)$ dependence, whereas, the double-scattered correlation time is nearly independent of θ . Colby et al. (1975) see similar effects in their multiple-scattering systems. Thus, it is easy to see how the slightly different k -dependences of the mode-mode, decoupled mode and dynamic droplet models in the extreme critical region, $k\xi \gg 1$ (Fig. 1 or Fig. 53) might be washed out by the multiple scattering. This is why we can not consider our results in Fig. 53 as a test of the theories in this region.

Lai and Chen (1973) reported measurements of the Rayleigh linewidth to $k\xi \sim 50$ which purports to support the mode-mode theory results. Their system was the binary fluid mixture *n*-hexane and nitrobenzene. These fluids have a very large index of refraction mismatch of $\Delta n = 0.18$. In way of comparison, our fluid system has a mismatch of 0.098. Thus, we could expect twice as much multiple scattering in their system as ours for a given scattering geometry. They took no precautions against the effects of multiple scattering, probably

because these effects have always been neglected or underestimated. Furthermore, they claimed measurements to $T-T_C=0.3\text{m}^\circ\text{C}$, but they did not know the extent of the incident laser beam heating of the fluids. We have seen that for reasonable beam powers of 1mW heating effects of $0.3\text{m}^\circ\text{C}$ to $1\text{m}^\circ\text{C}$ may result. Certainly, we can see the need for more and careful work in this large $k\xi$ region.

We can be reasonably sure that our Rayleigh linewidth data for $k\xi < 0.8$ are free from multiple-scattering effects. These 33 data points were used in our fitting program to determine ξ_0 and ν for the dynamic droplet model and the mode theories. Since there is no multiple scattering for these data points, we may consider these data as giving accurate values of ξ_0 and ν for the binary system methanol and cyclohexane. The values obtained for the dynamic droplet model fit were

$$\xi_0 = 2.46 \pm 0.1 \text{ \AA}$$

$$\nu = 0.655 \pm 0.01 .$$

The values obtained for the mode theory fit were

$$\xi_0 = 2.85 \pm 0.1 \text{ \AA}$$

$$\nu = 0.627 \pm 0.01 .$$

CHAPTER VII

SUMMARY AND OUTLOOK

7.1 A summary of our results.

From our early attempts to model critical fluid light-scattering behavior with emulsions has evolved a new theory of critical phenomena, The Dynamic Droplet Model. We have shown how our light-scattering experiments on emulsions and other polydisperse systems led us to the concept of a k -dependent diffusion constant due to polydispersity. This polydispersity induced k -dependence was the key factor missing in a Brownian diffusion picture of the critical fluctuations.

The dynamic droplet model as it now stands is successful in predicting the behavior of the Rayleigh linewidth of light scattered from critical fluids as we have seen in this thesis (also, Ackerson et al., 1975 and Sorensen et al., 1976). It has also been successfully applied to an understanding of critical viscosity (Oxtoby and Metiu, 1976) and critical fluid sound absorption (Sorensen, unpublished).

We have shown, however, that the droplet model incorrectly predicts the shape of the scattered-light correlation function to be nonexponential. Our data

indicate that this correlation function is exponential within the limits of our experimental uncertainty. This result is corroboration of the result of Wonica et al. (1976) who measured the scattered-light correlation function of xenon.

We have theoretically determined the form of the intensity and spectrum of light double scattered from a system of noninteracting Brownian particles. Starting with the fundamental equations of electromagnetic wave scattering theory, we derived the double-scattered spectrum for the case of independent scattering events. We have given our predictions for the double-scattered spectrum and intensity for particles of both size $\ell \ll \lambda$ and $\ell \lesssim \lambda$.

From the idea of independent scattering events, we have extended our results to scattering of any order, multiple scattering. For particles of radius $\ell \ll \lambda$ we theoretically determined the polarized and depolarized light-scattering correlation time of all the light scattered from a Brownian diffusional system.

We also developed a means to determine the extent of multiple scattering from depolarization ratio measurements. This quantity was expressed by $\bar{n}$, the average number of scattering events, and is proportional to the absolute cross section of the scattering process.

This multiple scattering formalism was put to the test of experiment. Measurements of the depolarized correlation time of light scattered from two different Brownian motion systems were found to be in excellent agreement with our double-scattering predictions. Correlation times for denser systems of particles, where scattering of higher order than double was important, gave agreement with our multiple-scattering theory for the polarized component. The depolarized correlation time of such dense systems was not in agreement with our theory. The nature of this discrepancy was not identified but inherent interactions between the individual particles was mentioned as the possible cause.

Having successfully solved the double scattering problem for light-scattering correlation measurements from diffusional systems, we applied our results to light scattering from critical fluids. The assumption of noninteracting scattering events was retained. We found theoretically that in the critical region, $k\xi \geq 5$, the single and double scattered correlation times were nearly equal ($\pm 10\%$). This remarkable result served to indicate why the effects of multiple scattering were never detected in spectral light-scattering measurements on such systems.

We discussed our temperature control and cell design. We also described a new method to measure the

heating effects of the incident laser beam on a critical fluid system. With this method, and by taking advantage of the excellent temperature control in our cell, we were able to make light-scattering measurements on a critical fluid system to almost $T-T_C \approx 0.1\text{m}^\circ\text{C}$.

In our final series of light-scattering measurements, we measured the polarized and depolarized correlation times of light scattered from our critical fluid system, methanol and cyclohexane. The polarized correlation time which can be identified with the Rayleigh linewidth in the absence of multiple scattering was measured deep into the critical region to $k\xi \approx 80$. Agreement of these data and the dynamic droplet model was found.

Our depolarized correlation time measurements represent the first such measurements reported on a critical fluid system. We found a qualitative agreement of this data to the prediction of our double-scattering theory.

We also measured the depolarization ratio of the light scattered from the critical fluid system. These measurements along with our multiple-scattering theory indicated that multiple scattering was important in the region $k\xi \geq 1$.

With this knowledge of the degree of multiple scattering, we were able to explain the discrepancy of

our depolarized correlation time data with the second-order, double-scattered theory. We furthermore, were able to show that because of the large amount of multiple scattering in the critical region the Rayleigh linewidth data, while appearing to agree with the single-scattering theories, could not be trusted to give a quantitative test of the light-scattering theories in this region.

7.2 Outlook and future work.

Our work on the correlation function of light double scattered from a system of Brownian diffusing particles has been very successful. Our extension of this work to multiple scattering (all orders of scattering) should prove very helpful to workers confronted with the necessity of dealing with highly scattering systems. Such systems are encountered when studying interacting particle diffusion and critical opalescence.

Our work discussed in section 3.11 represents only our first attempts at understanding the multiple-scattered light. Extension of this work to systems where the radius of the particles $a \lesssim \lambda$ would broaden the applicability of this work.

This discrepancy of the multiple-scattered depolarized correlation time with the theory in Fig. 24 is as yet not understood. The very real possibility that this discrepancy is due to correlated Brownian

diffusion of interacting particles is intriguing. Such a result could mean that the multiple-scattering spectrum would prove to be a very useful probe of interacting systems. This problem should be easy to explore experimentally because systems exist for which the interactions can be varied. The noninteracting assumption in our formalism in Chapter III is explicit; thus theoretically, we should be able to go back and find the consequences of not making this assumption.

It would also be useful to develop a multiple scattering theory for light scattering from critical fluid systems. As discussed in Chapter VI however, this problem is complicated by the large degree of non-exponentiality of the double-scattered correlation function at small scattering angles and large $k_0 \xi$. Because of this, the first cumulant does not characterize these spectra well and can not be used in a multiple-scattering theory, such as that in section 3.11. We point out that such work is of interest if we are successful in developing a method for measuring interactions in the depolarized spectrum from Brownian particle systems. This method and a knowledge of multiple-scattering effects could allow us to measure possible interactions between diffusing droplets of the dynamic droplet model.

The most pressing issue for the droplet model is its discrepancy with the observed exponentiality of the light-scattered correlation function. The polydispersity, while being key to the k -dependent diffusion constant, is the cause of the predicted nonexponentiality. How can the good quality be retained, and the bad quality be removed? It appears that some property of the system must negate the effects of polydispersity on the shape of the correlation function.

The droplet model was derived under the assumption that the droplets neither grow nor decay during the correlation time of the scattered light. We have tried methods to include the growth and decay of the droplets. Using droplet model dynamical theories of others (Binder, Stauffer and Muller-Krumbhaar, 1975), we have found that the shape of the correlation function can be changed by including a growth and decay term. However, we are as yet unsuccessful in finding the correct recipe for an exponential correlation function.

Another possible area of improvement, that was indicated by the data, is to include a critical viscosity term. We saw in section 6.4 that the background viscosity in the critical region might have been ~10% too small to accurately describe the data. Use of the full macroscopic critical viscosity would over compensate for this effect. Thus, it appears that the diffusing

droplets are experiencing some sort of semimicroscopic critical viscosity, the true microscopic viscosity being the background viscosity. These ideas are similar to those of Lyons (1973) who studied diffusion of $0.3\mu\text{m}$ microspheres in a binary critical fluid. It might be possible to use the methods developed by Lyons to understand this semimicroscopic viscosity.

One definite problem we would like to pursue is the measurement of the single-scattered Rayleigh line deep into the critical region. Such a measurement would give us an accurate critique of the relative merits of the mode and droplet model theories in this region where these theories no longer give the same results (see Fig. 1). Our knowledge of multiple scattering and our ability to determine the relative higher-order scattered intensities from depolarization ratio measurements can be applied, as we already have, to this problem. It is unfortunate that our system of methanol and cyclohexane, with an index of refraction difference of $\Delta n = 0.0978$, showed strong multiple-scattering effects. Needless to say, when we began our work, it was not possible to estimate the effects or intensity of the higher-order scattered light. Thus, our system was picked for other reasons.

We would propose a similar experiment, as that described in Chapter VI, on the system 3-methylpentane

and nitroethane. For this system $\Delta n = 0.0152$ about one sixth that of our current system. With this system and by making the scattering volume as small as possible, there should be very little multiple-scattered light. The extent of multiple scattering can be determined with depolarization ratio measurements and our analysis techniques. We can control our temperature to $0.03\text{m}^\circ\text{C}$ and measure the effects of the laser heating. Thus, it should be possible to go deep into the critical region, measure the Rayleigh linewidth and verify that the multiple-scattered intensity is small.

Other work would be to extend the droplet model to the understanding of critical phenomena other than light scattering. Oxtoby and Metiu (1976) have been successful in explaining the critical viscosity using the droplet model. The author has shown how sound absorption may be explained in this picture. Other work on the thermal conductivity and the index of refraction has been done with promising, although nonquantitative, success. Such a program of extending the physical picture of the droplet model to other phenomena might lead to further insight into the model itself.

Lastly, the model's relation to other theories of critical phenomena should be reviewed. We have discussed some of our ideas in section 2.5. The possible relationship to the current and highly successful

renormalization group approach to critical phenomena might prove very useful. As yet, this approach is not founded on first principles or observation. If our ideas in section 2.5 were extended, such a foundation, at least so far as observation is concerned, may lie in the droplet model. In any event, reasoning such as that in section 2.5 might add to our understanding and physical picture of all these phenomena which is, after all, the purpose of science.

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APPENDIX

APPENDIX I

We wish to write out the full expression for the correlation function of light double scattered from a critical fluid system. From Eq. (4.2) we have

$$\langle \vec{E}_2^*(t) \cdot \vec{E}_2(0) \rangle = A^2 |\hat{r}' \times (\hat{\epsilon}' \times \hat{r}')|^2$$

$$\frac{e^{-Dk_1^2(1+k_1^2\xi^2)^{\frac{1}{2}}}}{(k_1^2+\xi^{-2})^{1-\eta/2}} \frac{e^{-Dk_2^2(1+k_2^2\xi^2)^{\frac{1}{2}}}}{(k_2^2+\xi^{-2})^{1-\eta/2}} \quad (A.1)$$

where

$$\vec{k}_1 = \vec{k}_0 - \vec{k}'' \quad (A.2)$$

$$\vec{k}_2 = \vec{k}'' - \vec{k}' \quad (A.3)$$

and

$$\hat{\epsilon}' = \hat{r}'' \times (\hat{\epsilon} \times \hat{r}'') \quad (A.4)$$

We have evaluated the polarization term in Eq. (A.1) in terms of $r_1, r_2, \phi_1, \phi_2, \theta_1$ and θ_2 (Fig. 8) as given in Eq. (3.37). We shall assume the scattering is elastic; thus, $k_0 = k' = k''$. We write the scattering wave vectors as $\vec{k}_1 = k_0 \cdot \hat{k}_1$ and $\vec{k}_2 = k_0 \cdot \hat{k}_2$. We then have

$$\hat{k}_1 = 2 \sin(\beta_1/2) \quad (A.5)$$

$$\hat{k}_2 = 2 \sin(\beta_2/2) \quad (A.6)$$

where β_1 and β_2 are given by Eqs. (3.47).

From Eqs. (3.48) and (3.49) we see that

$$\hat{k}_1 = [\frac{1}{2}(1 + \sin\theta_2 \cos\theta_2)]^{\frac{1}{2}} \quad (\text{A.7})$$

$$\hat{k}_2 = [\frac{1}{2}(1 - \sin\theta_2 \cos(\phi_2 - \phi_1))]^{\frac{1}{2}}. \quad (\text{A.8})$$

Thus, Eq. (A.1) can be written as

$$\begin{aligned} \langle \vec{E}_2^*(t) \cdot \vec{E}_2(0) \rangle = & A^2 \{ (\sin^4 \theta_2)_{||} \\ & + (\cos^2 \theta_2 \sin^2(\phi_1 - \phi_2) \sin^2 \theta_2)_{\perp} \} \\ & \times \frac{e^{-Dk_0^2 \hat{k}_1^2 (1 + \xi^2 k_0^2 \hat{k}_1^2)^{\frac{1}{2}}}}{(k_0^2 \hat{k}_1^2 + \xi^{-2})^{1-\eta/2}} \\ & \frac{e^{-Dk_0^2 \hat{k}_2^2 (1 + \xi^2 k_0^2 \hat{k}_2^2)^{\frac{1}{2}}}}{(k_0^2 \hat{k}_2^2 + \xi^{-2})^{1-\eta/2}} \end{aligned} \quad (\text{A.9})$$

where $\hat{k}_1$ and $\hat{k}_2$ are given in Eqs. (A.7) and (A.8).

This expression is parameterized on $k_0 \xi$.