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**ON THE SCALE OF DIFFUSION LENGTHS OBSERVABLE BY
NEUTRON REFLECTION: APPLICATION TO POLYMERS**

A. Karim, A. Mansour and Gian P. Felcher
Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

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and

T. P. Russell
IBM Research Division
Almaden Research Center
San Jose, CA 95120

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ON THE SCALE OF DIFFUSION LENGTHS OBSERVABLE BY NEUTRON REFLECTION: APPLICATION TO POLYMERS.

A. Karim, A. Mansour and G.P. Felcher Argonne National Laboratory, Argonne, IL 60439,
T.P. Russell, IBM Research Division, Almaden Research Center, San Jose, CA 95120.

ABSTRACT

A systematic approach has been applied to neutron reflectivity data to study interdiffusion across an interface. It is shown that with this technique it is possible to probe interface broadening from $\sim 10\text{\AA}$ to upward of $200\text{\AA}$, the upper limit being already within the range of observation of other techniques such as Rutherford backscattering spectrometry (RBS), forward recoil spectrometry (FRES) and secondary ions mass spectroscopy (SIMS). As example is analyzed the interdiffusion of a bilayered polymer system: a deuterated polystyrene (d-PS) layer on protonated polystyrene (h-PS).

Introduction

Neutron reflectivity¹ has emerged as a useful technique to probe interface broadening caused by diffusion across an interface on the nanometer scale. The technique relies on the contrast of the neutrons scattering length densities of the layers facing the interface. The quantity obtained in such experiments is the reflectivity (R) of the sample: this is a function of the component of the neutron momentum perpendicular to the surface, k_z . $R(k_z)$ is an optical transform of the scattering length density, as measured as a function of the depth z from the surface. In this paper, we define the range of interface widths measurable by neutron reflectivity, by taking the reflectivity curves at subsequent times of the diffusion process.

Limits of resolution

Consider a homogeneous layer of thickness z_2 on an infinitely thick lower layer; the indices 1, 2 and 3 indicate the vacuum above, homogeneous material and lower layer respectively. Then the reflectivity R is given by^{2,3}

$$R = \frac{r_{12}^2 + \rho_{23}^2 + 2r_{12}\rho_{23}\cos 2k_2z_2}{1 + r_{12}^2 + \rho_{23}^2 + 2r_{12}\rho_{23}\cos 2k_2z_2} \quad (1)$$

The reflectance at the $i, i+1$ boundary is:

$$r_{i,i+1} = \frac{k_i - k_{i+1}}{k_i + k_{i+1}} \quad (2)$$

where $k_i = [k^2 - (b/v)_i]^{1/2}$ and $(b/v)_i$ = scattering length density of the i^{th} layer, while $k = 2\pi \sin\theta/\lambda$. If symmetric interdiffusion^{4,5} occurs between layers 2 and 3,

$$\rho_{23} = r_{23} \exp -2k_2 k_3 \sigma^2 \quad (3)$$

In conventional diffusion, the diffusion coefficient D is a function of the width $\sigma^2(t)$ and of time, namely⁶

$$D = \frac{\sigma^2(t)}{4t} \quad (4)$$

In this paper we would like to examine how to obtain σ^2 systematically from the experimental data in order to obtain the measurable range of diffusion coefficients.

The z_2 averaged expression for the reflectivity [eq(1)], is :

$$\langle R \rangle = \frac{r_{12}^2 + \rho_{23}^2 - 2r_{12}\rho_{23}}{1 - r_{12}^2 \rho_{23}^2} \quad (5)$$

which for large values of k can be approximated by the expression:

$$\begin{aligned} \langle R \rangle &\sim r_{12}^2 + \rho_{23}^2 \\ &\sim [\pi^2/k_1^4] [(b/v)_2^2 + ((b/v)_3 - (b/v)_2)^2 \exp -4k_1^2 \sigma^2] \quad (6) \end{aligned}$$

Thus Rk^4 vs k tends, for large values of k , to an asymptotic value. This value is different for an infinitely sharp 2,3 interface compared to when some interdiffusion has occurred across such a boundary; the decay to the new asymptote reaches a value $1/e$ for $k_1 = (1/4\sigma^2)^{1/2}$.

It is easy to see that the determination of σ becomes progressively ill defined for large σ . This is because the $1/e$ point occurs for smaller values of k_1 . Even if the more correct eq. (5) is used, rather than its asymptotic form, the relation between the experimental resolution, Δk , the precision by which σ can be determined:

$$dk/k = -d\sigma/\sigma \quad (7)$$

shows that extremely stringent requirements are progressively important on the angular resolution and the wavelength definition of the incident beam. Practically speaking, this method of analysis is convenient for values of σ less than $150\text{\AA}$. However it is possible to monitor diffusion over significantly longer distances by using derivatives of the reflectivity. In the normalized difference analysis, the infinitesimal changes in R with σ^2 is given by $R^{-1}(dR/d\sigma^2)$. Rather than giving the rather cumbersome - but easily derivable - complete expression, it is worthwhile to point out that the z -averaged expression of $R^{-1}(dR/d\sigma^2)$ is simply zero. On this flat base line, the envelope between the maxima and the minima of the reflectivity becomes:

$$\Delta\left(\frac{\partial R}{\partial \sigma^2}/R\right) = 4r_{12}\rho_{23}k_2k_3 \left[\frac{1}{r_{12}^2 - \rho_{23}^2} - \frac{1}{1 - r_{12}^2 \rho_{23}^2} \right] \quad (8)$$

the exponential term which gives the broadening of the interface is now contained in the linear expression of ρ_{23} at the numerator of eq.(8); which means that the range over which σ can be measured is extended by a factor of $1/\sqrt{2}$.

In practical terms the difference between the reflectivities at times t' , t'' can be taken. It is easy to see that the relation holds:

$$\frac{R(t'') - R(t')}{R(t'') + R(t')} = 2D \left(\frac{\partial R}{\partial \sigma^2}/R \right) (t'' - t') \quad (9)$$

where D is the diffusion coefficient as measured in the $t'' - t'$ interval.

Interdiffusion of polymers

We would like to apply directly this method of analysis to the study of the interdiffusion between two polymers. Neutron reflection can readily observe diffusion even over short time, when eq.(9) is not applicable. It is worthwhile then to compare the value of D obtained after relatively long annealing time with neutron reflectivity with that obtained by other techniques which have intrinsically less spatial resolution. Unfortunately, it has not been possible yet to apply directly eq.(9) on two accounts: the instrumental resolution has to be obtained more accurately than hitherto has been done, and the interval of annealing time $t'' - t'$ must be shorter than that presently employed. However we would like to compare the normalized difference plot with those calculated on the basis of a model, in which only the interface thickness has been changed.

Specific samples were prepared for the purpose, in the form of polymer bilayers on a flat round of silicon of 2" diameter. The lower layer of h-PS (Mw=233,000; thickness >3000Å) was spin coated on a silicon substrate from its solution in toluene and annealed for 48 hours at 160C. A layer of d-PS (Mw=203,000; thickness ~600Å) was then separately spin coated on a glass slide and subsequently floated off on to a pool of water. The floating d-PS film was then picked up from beneath by the silicon substrate with the coated h-PS to form a bilayer. The bilayer was then placed under vacuum for 12 hours at room temperature to remove any water molecules that may have been trapped between the layers.

The neutron reflectivity experiments were performed at the Intense Pulsed Neutron Source at Argonne National Laboratory. The experiment basically consisted of reflecting neutrons pulses between wavelengths 2-16 Å from the sample surface at very small angles of incidence (typically 1 degree) and measuring the number of reflected neutrons as a function of wavelength. The number of reflected neutrons normalized by the incident neutrons gives the reflectivity R , as a function of the neutron momentum k .

In Figure 1, experimental results are presented for the sample "as cast", and then annealed 22 and 53 minutes at 135C. Figure 1 shows also fits for the thickness of the layers d-PS/h-PS on Si, as well as the thickness of the interfaces. The fit to Figure 1(A) indicates a top layer d-PS of thickness 590Å on a "thick" lower layer. The thickness of the lower layer is certainly

Fig.1 $R(k)k^4$ as a function of k for a bilayered sample of d-PS ($M_w=233,000$) on top of h-PS ($M_w=203,000$) before heating [1(A)] and after heating for 22 minutes [1(B)] and 53 minutes [1(C)]. The solid points are the experimental data whereas the solid lines were calculated using a bilayered model with a symmetric interface between the upper and lower layer.

Fig. 2 Normalized difference curves as a function of k .
 The open circles are the experimental data
 obtained from the measurements 1(B) and
 1(C). The calculated reflectivity difference
 curves with 1(B) are shown by the solid line
 ($\sigma=200\text{\AA}$), the dashed line ($\sigma=250\text{\AA}$) and the
 dotted line ($\sigma=175\text{\AA}$) for fits to 1(C).

larger than $3000\text{\AA}$, which is the maximum distance which can be resolved for a beam of angular resolution of the order of 0.02° . The interface between the two polystyrene layers has initially a thickness $\sigma = 10\text{\AA}$. The fit 1(B) shows that the interface has broadened to $135\text{\AA}$, as a result of diffusion after the first annealing; after the second annealing the broadening is $200\text{\AA}$. The reflectivity in Figure 1(C) is almost featureless. In order to observe clearly how well the broadening is determined we replot in Figure (2) the experimental and calculated normalized difference of 1(C) with its previous frame 1(B). The hollow circles indicate the experimental difference points whereas the lines are normalized difference curves for three different values of σ ($=175, 200$ and $250\text{\AA}$) for fits to 1(C) with χ ($= 4.6, 4.4, 5.2$) respectively. Of the three σ values, $\sigma=200\text{\AA}$ has the minimum χ (the fit using this value of σ is shown in Figure 1(C)). The offset to the normalized difference from zero at large k in Figure 2 is caused by a small error in normalization of reflectivity for 1(B). We also see that if the offset is neglected, the integral of the normalized fluctuations is nearly zero, in accordance with equation (8) - that the total area under the normalized difference curve be zero.

From the value of $\sigma=200\text{\AA}$, is obtained a diffusion coefficient (cfr eq.(4)) $D=3.43 \times 10^{-16} \text{ cm}^2/\text{s}$ at $T=135^\circ\text{C}$. This value is already in reasonable agreement with that obtained for the same molecular weight at the same temperature from FRES measurements⁷: $D=4.35 \times 10^{-16} \text{ cm}^2/\text{s}$ and it is to be hoped that further improvements in the sophistication of the two techniques will yield results in yet better agreement and/or be able to focus on the causes of the discrepancy.

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