

Early stages of polymer interdiffusion

E. Sivaniah,^{1,*} R. A. L. Jones,² and M. Sferazza³

¹*Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom*

²*Department of Physics and Astronomy, University of Sheffield, Hicks Building, Sheffield S3 7RH, United Kingdom*

³*Department of Physics, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom*

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We have examined the wavelength dependence of the diffusion coefficient in a multilayer deuterated polystyrene-hydrogenated polystyrene system. The measurements were performed using neutron reflectivity. The decay of the Bragg peak was also followed in great detail. The measured wavelength diffusion coefficient $D(k)$ was also not found spatially dependent on the distance of the diffusional couples to the substrate. On the basis of our results, it was possible to reconstruct the broadening interface of polymer bilayer sample geometry which had characteristics of a diffuse tail and a sharp core.

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Interfacial strength between polymer melts develops by a process of entanglement that occurs as single-chains interpenetrate across the interface. The limit of a single-chain crossing the interface occurs when the degree of entanglement at the junction is equivalent to that within the bulk phases and the interface has then effectively vanished. Beyond this time the transport behavior is well understood [1] and for pairs of polymers with comparable mobility properties this occurs by a process of mutual diffusion. However, the regime of greatest interest for understanding the development of interfacial strength corresponds to the broadening of an interface on length scales less than the overall chain dimensions, which we cannot expect to be controlled by simple center-of-mass diffusion. At these length scales, the thermodynamics of mixing must include the effects of steep concentration gradients and since interfacial broadening of the interface is achieved without whole chain motion, one must expect the diffusion coefficient to have a length scale dependence. In a previous paper [2], we have shown that this can be expressed in terms of a wave-vector dependent diffusion coefficient $D(k)$. In this Brief Report, we complete our understanding of the process by reexamining the theoretical wave dependence of $D(k)$ invoking also new results and examining the ramifications of wavelength dependent $D(k)$ on the interfacial profile. In doing so, we raise new questions as to the nature of the interfacial broadening phenomena below the reptation time.

Considering that interfacial broadening is fundamentally a collective, many chain effect it is interesting to relate it to an explicitly collective property. With our experiments, we were aiming to determine the collective diffusion coefficient using the decay of an artificial structure factor $S(k)$ imposed upon our system. To achieve this, we have prepared periodic multilayers of alternately deuterated and hydrogenated polymer layers (each of thickness l). In doing so, we replace the binary diffusion couple as employed by other authors [3–8] with a multiple couple. This has the effect of producing an artificial structure that is a perturbation from the equilibrium state of a fully homogeneous film. The multilayers are de-

scribed primarily by the time dependent structure factor component $S(k, t)$, where k is the composition wave vector corresponding to the fundamental period of the multilayer ($\lambda = 2l$). There will, of course, be higher order structure terms that are needed to describe the initial sharpness of what is essentially a square wave composition profile. However, these will be seen to decay very quickly upon initially annealing the system towards equilibrium. Making an assumption of transport described by Fick's law (which is validated by our results [2]), the multilayer profile will decay as a function of time t as

$$\phi(z, t) = \sum_{n=1} [A_n \cos(nkz) + B_n \sin(nkz)] e^{-t/\tau_k}, \quad (1)$$

with a characteristic time $\tau_k^{-1} = D(k)n^2k^2$, $k = 2\pi/\lambda$, and $D(k)$ is the wave-vector dependent diffusion coefficient (A_n and B_n are determined from the Fourier components of a square wave profile) [2]. Considered in a Fourier space, the components of the multilayer structure will decay as

$$\frac{\partial S(k, t)/S(k, 0)}{\partial t} = \exp[-2k^2 D(k)]. \quad (2)$$

Hence, it is possible to extract $D(k)$ from the gradient of the logarithmic decay in the characteristic structure peak (i.e., Bragg peak) of the multilayer. When observed with neutron reflectivity the multilayer profile is represented by unambiguous Bragg scattering peaks at distinct scattering momentum transfer q values. We can directly measure $D(k)$ by determining the decay rate of the maximum intensity $I(q)$ of the Bragg peak as the multilayer structure decays to its homogeneous state, since $I(q)$ is directly proportional to $S(k)$ [9]. For the present experiments, as well as for the previous one, we have used multilayers of polystyrene (PS) and deuterated polystyrene (DPS). The polymers were obtained by from Polymer Laboratories (U.K.) and had molecular weights of 629 000 and 641 000, respectively, with polydispersity less than 1.1. We used large-molecular-weight polymers (radius of gyration R_g is 220 Å) so that the natural length scale set by the polymer was as large as possible. A layer of DPS was spun cast onto a HF etched silicon disk, from a dilute toluene solution. Altering the solution concentration allowed us to adjust the polymer film thickness. Subsequent layers of alternating PS and DPS layers were then spun cast onto microscope glass and floated onto water be-

*Present address: Department of Polymer Chemistry, Kyoto University, Kyoto 606-8501, Japan.

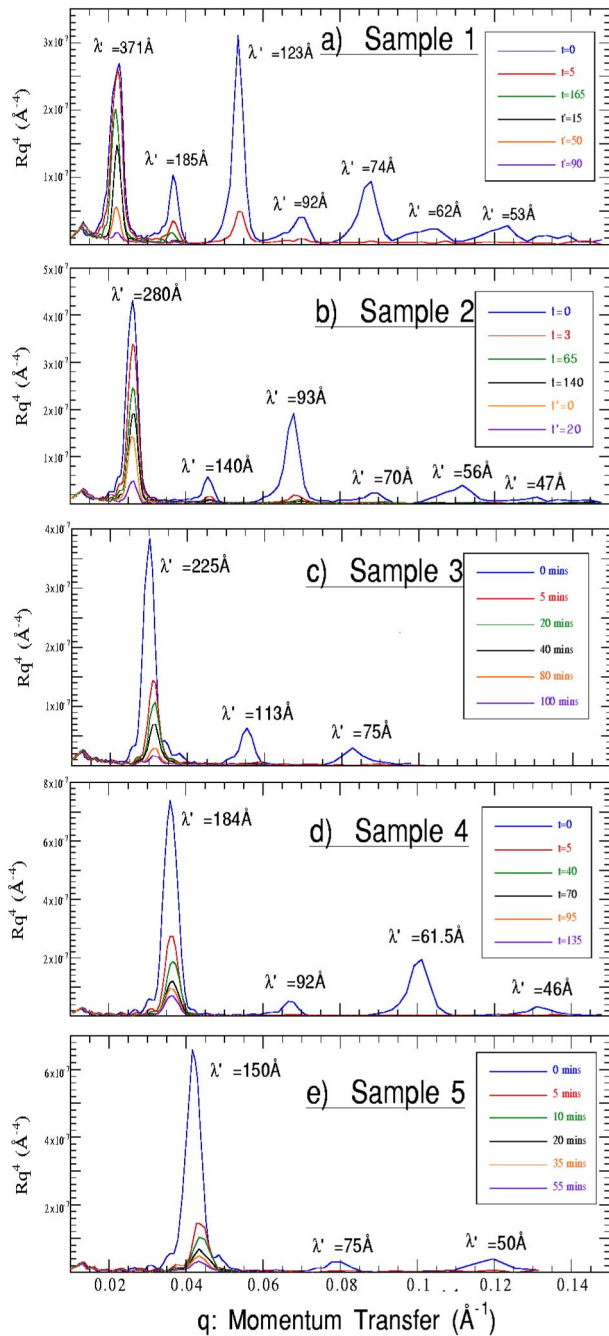


FIG. 1. Selected reflectivity anneal series data from the multilayers used shown in Rq^4 space. Sample 1 had a mean layer thickness l of 186 \AA , sample 2 of 137 \AA , sample 3 of 123 \AA , sample 4 of 94 \AA , and sample 5 of 80 \AA . The times (see insets) and data shown monotonically decrease together (the annealing temperatures used were 139°C and 133°C). Also shown are the wavelengths l corresponding to all detectable Bragg peaks.

fore being deposited onto the substrate. In total 16 layers (eight repeat units) of polymer were placed onto each sample. The thickness of each sample was measured by ellipsometry after every layer deposition and it was found that the layer thickness l only differed by 10 \AA . Different samples were prepared, with the mean layer thickness between $\sim 70\text{ \AA}$ and $\sim 180\text{ \AA}$. The neutron reflectometry experiments were carried out using the reflectometer CRISP at

the Rutherford Appleton Laboratory, U.K. Because of the rapidity of the diffusion process in these thin films the samples were annealed *in situ* using a Linkam microscope hot stage by iteratively measuring the reflectivity and annealing until the Bragg peak of interest had decayed to insignificant levels. Reflectivity data for different samples are shown in Fig. 1. The temperatures used in the new experiments were 133°C and 139°C , allowing us to investigate some of the early times. Since the first-order Bragg reflectivity peaks typically lie within a range of momentum transfer where the Born approximation is not valid, we cannot directly measure the diffusion coefficient from the decay of the Bragg peak data. We utilize a free-form fitting approach to our data using a maximum entropy method [10]. The fitting quality is excellent since the algorithm discretizes the sample profile, the thickness of which is known, and varies the composition of the resulting segments. Thus, if the decay of the concentration profiles is diffusive we can extract $D(k)$ from the slope with which the now idealized peak intensities decay. In a previous paper [2], we discussed a plausible explanation for the observed decrease in collective diffusion coefficient with a decreasing length scale. We revisited our data for a better understanding of the process that described very well our observation. The behavior can be ascribed to the dominant role of gradient energy effects at length scales below that of a bulk chain with a Gaussian conformation (R_g). The origin of the effect is then predominantly entropic; chains in multilayers whose wavelength are less than R_g have concentration gradients that are steep compared to the overall chain dimensions leading to a loss in conformational free energy and a larger net driving force for the relaxation of the corresponding composition fluctuations. This should promote a larger $D(k)$ at high k . However, because polymers are spatially extended objects by virtue of their connectivity, the chains have a nonlocal response to this driving force. This may be better pictured by considering both the driving force caused by the composition fluctuation (chemical potential) and the response of the chains (mobility) as fields. At low k , the driving force acts over wavelengths larger than the chain and the chain responds as a whole. In this case, the response is essentially the sum of the scalar monomeric friction coefficients. However, at high k ($k > 2\pi/R_g$), this driving force field is smaller than the chain dimension and individual portions of the chain can be considered to feel the force in opposite directions. As a result the net response of the chain is lower. These arguments were incorporated into a theoretical expression by Pincus [11], who derived the time scale for the relaxation of composition fluctuations as we have shown in our previous paper and in Fig. 2, where the experimental results and the theoretical prediction (dashed line) are reported [2]. There are reasonable corrections that can be applied to the theory to make it more amenable. The theoretical drop in $D(k)$ starts to decrease well before $k = 2\pi/R_g$, whereas it is more natural to expect the bulk diffusion coefficient to persist to this length scale [12]. Moreover, the conformation and orientation of the molecules in the thin films are likely to be significantly perturbed from a Gaussian description [13] in a way that the simple theoretical approach based on the random phase approximation may not be able to

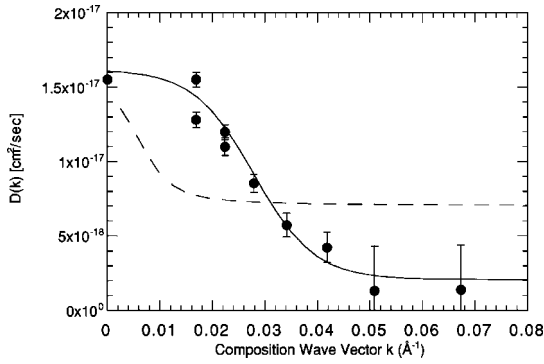


FIG. 2. Wave-vector dependence of $D(k)$. Also included are the Pincus prediction as in the previous paper (shown as a dashed line) and the tanh fit [Eq. (4)] (shown as a full line). See text for details.

represent. Relaxation of these potentially non-Gaussian and oriented conformations may in part account for the fast initial relaxation and the deviations of $D(k)$ from the theoretical prediction. Nonetheless, such features near the sharp interface are likely to be a real factor when considering the initial interfacial broadening phenomenon. Since we have extracted a good experimental picture of $D(k)$, it should be possible to reconstruct the specifics of the interfacial broadening process as it exists in a semiinfinite bilayer sample. This is simply the inverse Fourier transform of a sinc function that has been convoluted with an exponential envelope wherein $D(k)$ is described.

$$\phi(x,t) = \frac{1}{\pi} \int_{-\infty}^{+\infty} e^{-tD(k)k^2} \frac{\sin(k/l)}{k} e^{-ikx} \delta k. \quad (3)$$

A convenient functional form of $D(k)$ that describes our data can be expressed by a hyperbolic tangent function of the form

$$D(k) = D_{\infty} + 0.5D(0) \left(1 + \tanh \left[\frac{|k| - k_{\text{offset}}}{k_{\text{width}}} \right] \right). \quad (4)$$

The resulting fit parameters are $D(0) = 1.7 \times 10^{-17} \text{ cm}^2 \text{ sec}^{-1}$, $D_{\infty} = 2 \times 10^{-18} \text{ cm}^2 \text{ sec}^{-1}$, $k_{\text{offset}} = 0.0279 \text{ \AA}^{-1}$, and $k_{\text{width}} = 0.0115 \text{ \AA}^{-1}$, and the fit is shown in Fig. 2. k_{offset} and k_{width} are connected to the distance of the center of the tanh curve (where the value is halfway between the minimum and the maximum values) from the $k=0$ origin, and to the width of the tanh profile, respectively. Inserting Eq. (4) into Eq. (3), and solving numerically for a range of times, we can produce a series of simulated interfacial profiles for an interdiffusing semiinfinite bilayer. Figure 3 shows the simulated profiles (dashed lines) using times up to the τ_d (corresponding to an annealing temperature of $133 \text{ }^{\circ}\text{C}$). For comparison a simple erfc profile that arises for a k -independent diffusion coefficient [$D(k) = D(0)$] is also shown. What is immediately apparent is that the $D(k)$ interfacial profile contain a relatively sharp interfacial core (near $z = 1000$) with the tails appearing to diffuse into the bulk of the sample. As the interface becomes more diffuse the size of this core decays, almost disappearing at $t = \tau_d$. The sharpness of the interface is actually the summation of several orders of composition fluctuations. However, since our data has shown that the higher k contributions decay at a slower

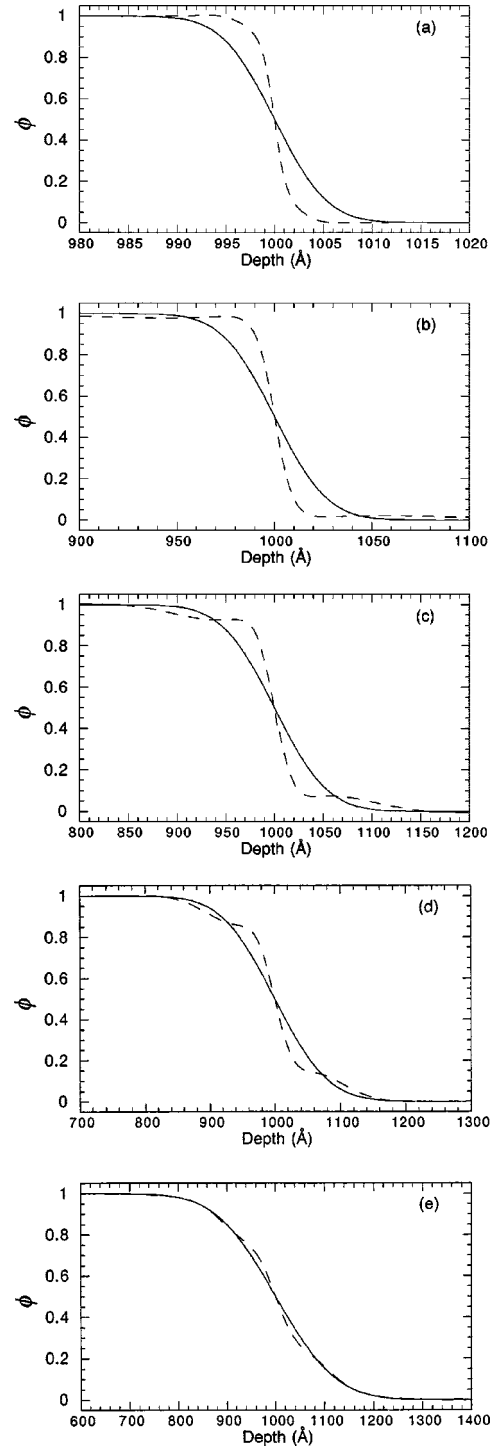


FIG. 3. Calculated interfacial profiles of a semi-infinite bilayer, using $D(k)$ in Eq. (4) (shown as dashed lines) and using $D(k) = D(0)$ (shown as full lines). A series is shown from late times to ca. τ_d . (a) 1.6 min, (b) 42 min, (c) 167 min, (d) 375 min, (e) 850 min.

rate, the core persists for a longer time. Eventually these will also decay and the surviving low- k Fourier components will all decay at approximately the same rate, $D(0)$. While we cannot claim a theoretical basis for the use of the tanh empirical $D(k)$ function, it does serve to replicate the phenom-

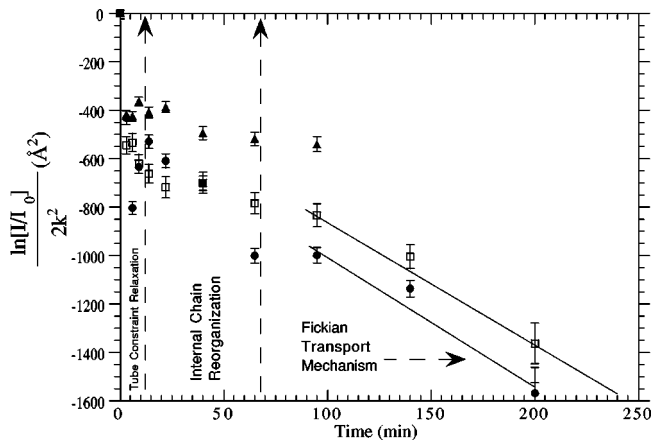


FIG. 4. Early stages of decay for all Bragg satellites of a sample; fundamental (circle), second order (square), third order (triangle). Times are shown for actual annealing temperature, 133 °C. τ_d for this temperature is 850 min [15]. Also shown schematically are the three regimes of interfacial broadening.

ena that is observed in the work of Reiter and Steiner [6], and Kunz and Stamm [7]. The goal of the research so far was to follow the final diffusive stages of the Bragg peak decay, the intermediate transport process if noteworthy. By annealing a sample at a lower temperature, we were able to follow the decay of the fundamental Bragg peak in greater detail as well as the decay of higher order Bragg peaks (as shown in Fig. 4). This highlights the existence of the intermediate stage in the transport process. The data also appears not to be monotonic. The observed oscillation in peak intensity suggesting that at this stage the artificial chemical potential imposed by the multilayer plays no part in determining chain motion but instead internal chain reorganization is occurring. This fact is underlined by the lack of synchronicity between the oscillations of the different Bragg satellites indicating that the effect is not caused by an external elastic force imposed on the sample through the method of preparation. An important result of our work is that most of the diffusive data collected was below the nominal reptation time τ_d for the molecular weight of polymer used. Our main conclusion from our studies is that the diffusion coefficient is dependent upon the degree to which the polymer chain is entropically constrained. This is expressed through the wave-vector dependence and therefore it is important to rule out other ef-

fects that might also cause a variation in $D(k)$. It has been reported recently that the diffusion coefficient can also be spatially dependent on the distance from an enthalpically attractive hard wall [14]. In our experiments, we effectively change the distance between the center of mass of the diffusional couple and the silicon substrate by varying the period of the multilayers, whilst maintaining the same number of multilayers. A larger period multilayer is effectively further away from the silicon substrate and will diffuse with a conventional diffusion coefficient $D(0)$. On the other hand, the center of mass of a smaller period multilayer is closer to the attractive wall so that more of the binary couples of these multilayers could feel the effects of the substrate leading to a diminished diffusion coefficient. Thus, a spatially dependent diffusion coefficient might also explain the variation in $D(k)$. In order to verify that this was not the case, two further multilayer samples were prepared. These samples were identical with respect to single-layer thickness (98 Å) and molecular weights. However, they also incorporated a relatively thick spacer layer of 50% deuterated polystyrene (2000 Å) that was placed either between the multilayer and the Si wafer or on top of the multilayer. In this way, we significantly varied the distance between the diffusional couples and the Si-polymer interface. These multilayers were annealed at 139 °C and the decay of the principle Bragg peak was followed in detail. From the data, we obtain diffusion coefficients of $(1.17 \pm 0.1) \times 10^{-17} \text{ cm}^2 \text{ sec}^{-1}$ and $(1.12 \pm 0.1) \times 10^{-17} \text{ cm}^2 \text{ sec}^{-1}$ for the samples where the spacer is placed between the multilayer, and the silicon, and on top of the multilayer, respectively. The rate of decay of the two samples is almost identical indicating that the wave-vector dependence of the diffusion coefficients that we obtained is not due to a spatially dependent D . As a result of our studies, we have identified three stages of chain motion. The first two of these are highly nonequilibrium and results mainly from the nature of the preparation of the thin films. The last of these stages, arguably the most interesting, indicates the existence of collective diffusional transport at times well below the reptation time and raises questions regarding the currently accepted picture of the early stages of interfacial broadening.

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