Evidence for Capillary Waves at Immiscible Polymer/Polymer Interfaces

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The width of the interface between two immiscible polymers, deuterated polystyrene and poly(methyl methacrylate), has been measured using neutron reflectivity as a function of the thickness of the deuterated polystyrene layer. A logarithmic dependence of interface width on film thickness is observed, characteristic of an interface broadened by thermal induced capillary waves, whose spectrum is cut off by dispersive interactions across the polymer layer. Reasonable agreement is obtained with the results of self-consistent field theory when suitably modified to account for capillary waves, resolving a long-standing discrepancy between theory and experiment. [S0031-9007(97)03096-2]

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The interface between two immiscible polymers is not atomically sharp, even for cases when the degree of immiscibility is quite strong. This is because the unfavorable enthalpy of mixing that occurs at a diffuse interface is offset by a gain in chain entropy. An analytic solution of the Edwards self-consistent field equations [1] due to Helfand and Tagami [2] predicts the width and the interfacial tension of an immiscible polymer interface. The volume fraction profile of one component through the interface, $\Phi_A(z)$, is predicted to take the hyperbolic tangent function form,

$$\Phi_A(z) = \frac{1}{2}\left[1 + \tanh\left(\frac{z}{w_I}\right)\right], \tag{1}$$

where the intrinsic interface width w_I is given in terms of the statistical segment length a and the Flory-Huggins interaction parameter χ as

$$w_I = \frac{a}{\sqrt{6\chi}}. \tag{2}$$

However, when the technique of neutron reflectivity was used to measure the interfacial width directly for the particularly well-characterized polymer pair of polystyrene (PS) and poly(methyl methacrylate) (PMMA), independent measurements by two groups [3,4] produced a result about 70% in excess of the predicted value.

An appealing and plausible explanation for the discrepancy is that what is observed in the neutron reflectivity experiment is not the bare, mean field interface as predicted by self-consistent field theory, but an interface roughened by thermally excited capillary waves [5,6]. The additional contribution to the interfacial width made by these capillary waves involves a logarithmic divergence, which, it is suggested, is cut off at short wave vectors by an upper length scale related to the in-plane coherence length of the reflected neutron beam. This explanation accounts well for the order of magnitude of the discrepancy between theory and experiment. However, recent computer simulation results [7] produce interfacial widths with a similar discrepancy from the simple theory, but whose lack of dependence on system size seems to rule out capillary waves as an explanation. Moreover, more recent measurements of interfacial width between PS and PMMA [8] have been interpreted as being consistent with the self-consistent field result without a capillary wave correction.

In this Letter we provide decisive evidence in favor of the capillary wave explanation of the observed apparent extra broadening of immiscible polymer-polymer interfaces. By measuring the interface between poly(methyl methacrylate) and rather thin films of deuterated polystyrene (d-PS), we enter a regime in which the short wave vector cutoff of the logarithmic divergence is provided not by the coherence length of the neutrons but by the effect of dispersion forces acting across the film. This results in the prediction of a logarithmic dependence of the interfacial width on film thickness. We have measured the interfacial widths between relatively thick (>4000 Å) PMMA layers and d-PS films of thickness ranging from ~50 to ~20 000 Å, and we find just such a logarithmic dependence on the d-PS film thickness, providing strong evidence for the capillary wave hypothesis.

An intuitive approach to the broadening of fluid interfaces due to thermal fluctuations was initiated by Buff, Lovett, and Stillinger [9,10]. Essentially, we imagine the interface as if it were a membrane in a state of tension characterized by the bare interfacial energy σ_0; it sustains a spectrum of capillary waves, each of whose average energy is determined by equipartition of energy. By integration over the spectrum of capillary waves, one finds the average mean square displacement of the interface $\langle \Delta\zeta^2 \rangle$ as

$$\langle \Delta\zeta^2 \rangle = \frac{k_B T}{4\pi\sigma_0} \ln\left(\frac{k_M^2 + k_v^2}{k_m^2 + k_v^2}\right). \tag{3}$$

Here k_M and k_m are, respectively, the largest and smallest wave vectors of capillary waves that can be sustained by the interface. The lower cutoff k_m is related to the total system size L or, alternatively, the length over which an experiment averages the interfacial width—for example, the in-plane coherence length of neutrons in a reflectivity experiment. The upper cutoff k_M must be related to the intrinsic width of the bare, mean field, interfacial profile w_1. The capillary waves will be modified if the interface is in an external potential such as gravity; writing the external potential as $v(z)$, one finds

$$k_v^2 = \frac{1}{\sigma_0}\left(\frac{\partial v(z)}{\partial z}\right). \tag{4}$$

Thus, for gravity, we find an additional cutoff characterized by a gravitational capillary length a_{grav}, given by

$$a_{\text{grav}}^2 = \frac{2\sigma_0}{g\Delta\rho}, \tag{5}$$

where $\Delta\rho$ is the difference in the mass density between the two phases.

For a polymer interface we can estimate the value of a_{grav} as being 2 mm, which compares with a neutron coherence length of the order of microns. Thus the gravitational cutoff will not be relevant for a determination of an interface width by neutron reflectivity. However, if one or both of the polymer phases is rather thin, then an additional potential comes into play—the dispersive or Van der Waals forces across the film. This leads to a dispersive capillary length a_{dis},

$$a_{\text{dis}}^2 = \frac{4\pi\sigma_0 l^4}{A}, \tag{6}$$

where l is the film thickness and A is the Hamaker constant for the interaction between the substrate and the air across the film [11]. This Hamaker constant may be estimated from refractive index and dielectric constant data using an approximation based on Lifshitz theory [12]; we obtain a value of 2×10^{20} J for PMMA interacting with air across a d-PS film, though it should be recognized that this estimate is not likely to be wholly reliable. For films in the thickness range 50 to 500 Å, the dispersive capillary length may then be estimated as falling between 300 Å and 3 μm. Thus, for films in this range of thicknesses, this dispersive capillary length, rather than the neutron coherence length, may be the origin of the lower wave-vector cutoff on the capillary waves. In these circumstances, we expect the average mean square displacement of the interface to take the form,

$$\langle \Delta\zeta^2 \rangle = \frac{k_B T}{4\pi\sigma_0} \ln \frac{(2\pi/\Delta_0)^2}{(2\pi/\lambda_{\text{coeh}})^2 + (2\pi/a_{\text{dis}})^2}, \tag{7}$$

where Δ_0^2 is the mean squared roughness of the intrinsic (unbroadened by capillary waves) interface, which is related to the interfacial width parameter w_I by $\Delta_0 = \frac{\sqrt{2}w_I}{\sqrt{\pi}}$, σ_0 is the interfacial tension, λ_{coeh} is the in-plane coherence length of neutrons, and a_{dis} is the dispersive capillary length given by (6). Thus we expect the capillary wave contribution to the measured interfacial width to vary logarithmically with the film thickness.

Bilayers of d-PS on PMMA were prepared by spin casting PMMA from the toluene solution onto the surface of a silicon wafer to produce a film between 4000 and 9000 Å thick. d-PS was spun from the toluene solution onto a glass slide and floated onto the PMMA substrate, producing layers of thickness ranging from ~50 to ~20 000 Å. Film thicknesses were measured using ellipsometry. After drying at 60 °C in a vacuum oven, the samples were then annealed at 120 °C for 6 h, which, neutron reflectivity experiments as a function of annealing time showed, is sufficient time for equilibrium to be reached. Various combinations of molecular weights were used: d-PS of molecular weight 244 000 with PMMA of molecular weight 365 000 (pair A), d-PS of molecular weight 387 000 with PMMA of molecular weight 365 000 (pair B), d-PS of molecular weight 641 000 with PMMA of molecular weight 365 000 (pair C), d-PS of molecular weight 400 000 with PMMA of molecular weight 365 000 (pair D), and d-PS of molecular weight 400 000 with PMMA of molecular weight 333 000 (pair E). All the polymers were obtained from Polymer Laboratories (UK), and were prepared by anionic polymerizations with M_w/M_N of 1.1 or less. We note that corrections to the interfacial width and interfacial tension due to finite molecular weight are expected to be of order $(\chi N)^{-1}$ [13]. This allows us to estimate that the upper limit on the discrepancy introduced by using these different molecular weight combinations is about one-half of one percent.

Neutron reflectivity measurements were carried out on the reflectometers SURF and CRISP at the Rutherford Appleton Laboratory. Figure 1 shows, as an example,

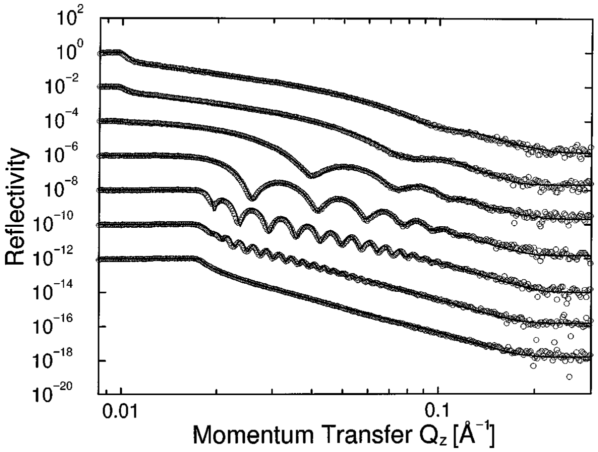

FIG. 1. Neutron reflectivity curves as a function of the neutron momentum transfer, Q_z, for bilayers consisting of films of deuterated polystyrene (molecular weight 244 000) with thicknesses varying from 60 Å (top curve) to 4800 Å (bottom curve), on thicker films of poly(methylmethacrylate) (molecular weight 365 000). The fits (solid lines) to the data are described in the text. The curves are shifted down by a factor of 100 with respect to each other for clarity.

reflectivity curves obtained for the samples of pair A, where the film thickness of the top *d*-PS layer has been varied, showing interference fringes characteristic of the *d*-PS layer thickness. The solid lines are fits obtained by a least-squares fit to a multilayer model with Gaussian roughness introduced at the surface and film interfaces. Apart from the interfacial width between *d*-PS and PMMA layers, all the parameters in this fit are measured independently; the silicon oxide layer thickness, PMMA layer thickness, and *d*-PS layer thickness by spectroscopic ellipsometry. The surface roughness of the *d*-PS layer is assumed to take a constant value of 7 Å, independent of the *d*-PS layer thickness, an assumption which is born out by reflectivity measurements of *d*-PS films of varying thicknesses on a silicon substrate. Standard errors in the interfacial width values are obtained from the fitting procedure and are typically 15%–25% of the actual values, depending on the q range and counting statistic of each data set.

Interfacial widths for all the polymer pairs studied are plotted as a function of the *d*-PS film thickness in Fig. 2. The width parameter Δ that is plotted is related to the hyperbolic tangent profile width $2w_I$ by $\Delta = 2w_I/\sqrt{2\pi}$, so the value of Δ of 20.3 Å corresponds to a hyperbolic tangent width $2w_I = 51$ Å, in satisfactory agreement with values obtained by other workers [3,4]. For thinner films, it is immediately apparent that there is a dependence of interfacial width on film thickness, which is at least approximately logarithmic. The logarithmic dependence persists up to a thickness of about 1000 Å, after which the data levels off. This is as we expect when the dispersive capillary length becomes larger than the neutron coherence length, and it allows us to estimate an in-plane coherence length of about 20 μm. This value is consistent with the results of a direct measurement of the coherence length on the CRISP reflectometer in a similar experimental configuration to that used by us on CRISP and SURF [14].

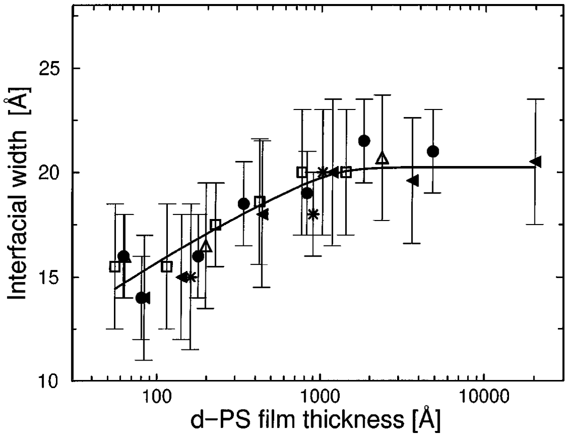

FIG. 2. The interfacial width parameter Δ for an interface between deuterated polystyrene (*d*-PS) and poly(methylmethacrylate) (PMMA), as a function of the *d*-PS film thickness, as measured by neutron reflectivity. The symbols (●) are for polymer pair A, (☐) are for polymer pair B, (◀) are for pair C, (△) are for polymer pair D, and (*) for polymer pair E, as described in the text. The solid line is a fit to Eq. (8).

To analyze this result more quantitatively, we assume that the contributions to the interfacial width, due to the intrinsic interface and due to capillary wave broadening, add in Gaussian quadrature; thus we write the observed interfacial width Δ as

$$\Delta^2 = \Delta_0^2 + \langle \Delta\zeta^2 \rangle, \tag{8}$$

where $\langle \Delta\zeta^2 \rangle$ is given by Eq. (7).

The solid line in Fig. 2 is a fit to Eq. (8) in which we vary the intrinsic interface width Δ_0 and the interfacial tension σ_0; λ_{coeh} is the in-plane coherence length of neutrons and has been fixed to 20 μm.

Very good agreement is achieved for parameter values $\Delta_0 = 9.3 \pm 1.4$ Å and $\sigma_0 = 2.7 \pm 0.3$ mJ m^{-2}. The error bars here are derived from the random error in the determination of the interface width; however, we should recognize that our value for the Hamaker constant A is extremely uncertain. Indeed, over the range of thicknesses used, retardation effects are likely to become important so the effective Hamaker constant will depend on thickness. Luckily, as A appears inside a logarithm, our results are rather insensitive to the value chosen; a 50% variation in the value of A results in a change in the best fit value of Δ_0 of about 10%, and has even less effect on the best fit value of σ_0. The value of the Flory-Huggins interaction parameter χ has been determined by small angle scattering from a block copolymer [15], and for our temperature takes the value $\chi = 0.037 \pm 0.002$. Using this and the average statistical segment length $a = 7$ Å, we can use Eq. (2) to evaluate Δ_0 as predicted by self-consistent field theory as 11.8 ± 0.6 Å. Similarly, the interfacial tension σ_0 may be calculated from the expression [2]

$$\sigma_0 = a\rho k_B T \sqrt{\frac{\chi}{6}}, \tag{9}$$

where ρ^{-1} is the volume of the monomer repeat unit, which takes the value 174 Å^3. Thus we find σ_0, as predicted from the self-consistent field theory, to be 1.7 ± 0.05 mJ m^{-2}.

Thus the comparison of our deduced bare interface width Δ_0 with theory is excellent, while our deduced interfacial energy is somewhat larger than predicted. We must, however, bear in mind the approximation implicit in the use of Eq. (8). For instance, we have assumed that the free surface of the *d*-PS film behaves like a rigid wall, whereas it will have its own spectrum of capillary waves that will be coupled to the waves at the interface. Since, however, the surface energy of *d*-PS is about an order of magnitude bigger than the *d*-PS/PMMA interfacial energy, the rigid wall assumption is a reasonable starting point.

The logarithmic dependence of interfacial width on film thickness is characteristic of a situation in which the spectrum of capillary waves is cut off by a long-range force such as the dispersion force. This is in interesting contrast to another recent study of interfacial widths between coexisting polymer phases, in which a square-root dependence of interfacial width on film thickness was observed [16]. In this case, the phases were rather close to the critical point, and the intrinsic interface width is a significant fraction of the total film width. In these circumstances, one expects an effective short-range force across the thin film which is due to the energy cost of truncating the equilibrium interface profile by the film boundary.

Our interpretation is in disagreement with another recent study of the PS/PMMA interface [8]. These authors conclude that capillary waves are not important for immiscible polymer interfaces on the basis that they measure a value of interfacial width $\Delta = 13$ Å (for relatively high molecular weight samples), in close enough agreement with the self-consistent field result, with no need for a capillary wave correction. However, these authors correct their raw measured interfacial width by subtracting, in quadrature, the measured roughness of the sample as made, before annealing. For an equilibrium measurement it is difficult to see why this procedure should be legitimate because, if the samples are annealed above the glass transition temperature long enough, the interface should come to an equilibrium which is independent of the starting state of the system. The uncorrected value measured was $\Delta = 17$ Å, significantly bigger than the self-consistent field result.

Our major conclusion, then, is that the interfacial width between two immiscible polymers has a logarithmic dependence on film thickness, indicating that capillary waves contribute substantially to the interfacial width as measured by neutron reflectivity, confirming earlier suggestions. When corrected for the effect of capillary waves, there is reasonable quantitative agreement between the predictions of self-consistent field theory and experimental measurements of interfacial widths between immiscible polymer pairs as a function of film thickness.

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$$A = \frac{3}{4} kT \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h\nu_e}{8\sqrt{2}} \times \frac{(n_2^2 - n_3^2)(n_2^2 - n_3^2)}{\sqrt{n_1^2 + n_3^2}\,\sqrt{n_2^2 + n_3^2}\left(\sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2}\right)},$$

where ε_i and n_i are the dielectric constant and refractive index of the medium i, respectively, and ν_e is the main electronic absorption frequency in the UV. For our case, medium 1 is air, medium 2 is PMMA, and medium 3 is the d-PS layer; J. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, San Diego, 1991), p. 184, 2nd ed.

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