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Symmetric and asymmetric instability of buried polymer interfaces

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We demonstrate using neutron reflectometry that the internal interfaces in a trilayer system of two identical thick polystyrene layers sandwiching a much thinner (deuterated) poly(methyl methacrylate) layer 15 nm thick (viscosity matched with the polystyrene layers) increase in roughness at the same rate. When the lower polystyrene layer is replaced with a layer of the same polymer of much greater molecular mass, two different growths of the interfaces are observed. From the growth of the interface for this asymmetric case in the solid regime using the theoretical prediction of the spinodal instability including slippage at the interface, a value of the Hamaker constant of the system has been extracted in agreement with the calculated value. For the symmetric case the rise time of the instability is much faster.

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The stability of thin polymer films has been the subject of intense investigations for the last few decades [1,2]. Considerable research activity, both theoretically and experimentally, has been devoted to the understanding of the physics behind the wettability of surfaces, not only for the fundamental aspects of phase behavior in confined geometry, but also for the importance that thin polymer films have in many applications [3,4]. Understanding the parameters influencing the stability is a crucial step for optimizing thin films that are used in many applications, from coatings [5,6], adhesives [7,8], and organic transistors [9,10] to mention just a few.

The instability of a thin film may proceed via the classical nucleation process, governed by the competition of the capillary forces. The result is the balance of the three interfacial tensions (liquid-substrate, air-liquid, and substrate-air) and the viscous forces that are connected to the hydrodynamics of the liquid and to friction and slippage at the interface [11]. Many studies have been devoted to the dynamics of this dewetting to understand the role of the interface on the process [12–16]. Another crucial mechanism for very thin polymer films is instead connected to the instability of thermal fluctuations at the interface destabilized by van der Waals forces: spinodal dewetting. This process has been extensively studied both theoretically and experimentally following the pioneering theoretical work of Brochard-Wyart *et al.* [17,18] and the experimental work of Reiter [19]. The dewetting at the late stage is characterized by a final dewetted structure that exhibits a characteristic dewetting length scale. Less work has, in general, been devoted to spinodal dewetting at polymer-polymer interfaces. For example, the dewetting of a thin poly(methyl methacrylate) (PMMA) layer on a polystyrene (PS) layer has been studied using (both specular and off-specular) neutron reflectometry [20,21]. Here, the early stage of the instability of the polymer-polymer interface was analyzed; the roughness of the interface grows with time, while the upper polymer surface, with a surface tension approximately one order of magnitude greater than the interfacial tension, will grow much more slowly with time. The off-specular scattering allowed characterization of the fastest growing length scale, and a comparison with the theory of spinodal dewetting was illustrated. The instability of the interface was also studied using a system with a thin PS layer on a silicon substrate with a thick PMMA layer on top [22,23]. Spinodal dewetting was observed both with neutron reflectometry and with scanning force microscopy after removing (only) the upper PMMA layer with solvent, which was good for PMMA but poor for PS. The examples mentioned above consider cases where just one interface is destabilized.

In this Brief Report we illustrate, using neutron reflectometry, two cases: one where both interfaces are unstable on the same time scale, a condition that is necessary for a direct observation of the peristaltic mode of dewetting [18], and one where the instabilities of the interfaces grow at different rates.

Time-of-flight (ToF) neutron reflectometry experiments were performed using the reflectometer EROS on the Orphée reactor at the Laboratoire Léon Brillouin, and the reflectometer D17 at the ILL reactor facility, Grenoble. Neutron reflectometry (NR) is an ideal technique to probe buried polymer interfaces [24]. The neutron scattering length density varies as a function of distance perpendicular to the surface (i.e., depth), with a resolution of better than 1 nm, and is measured as a function of the reduced momentum transfer, $q_z = (4\pi/\lambda)\sin\theta$ (where θ is the incident angle and λ the neutron wavelength). To distinguish interfaces between different polymer layers, one component is usually deuterated. Neutron reflection has been used in the past to identify and probe the growth of capillary waves at the interface between a deuterated layer and a hydrogenated film [25–27]. With selective deuteration, contrast between the layers is increased and details of the interfaces can be extracted.

In a time-of-flight reflectometer a range of wavelengths (for example, between 3 and 25 Å on EROS) irradiates the sample at the same time and the reflectivity measured for a q_z range determined by the incident angle θ and λ. With our samples

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two or three fixed angles were used to cover a large q_z range (0.01–0.25 Å^{-1}).

The sample geometry used was composed of three layers: a thin deuterated poly(methyl methacrylate) layer (dPMMA) of thickness 15 nm between two (normal undeuterated) PS layers of 145 nm thickness. The thicknesses were measured separately with ellipsometry. The samples were prepared by spin coating the PS layer of molecular weight $M_w = 573$ kg/mol onto a silicon substrate of 5 cm diameter and 0.5 cm thick of [110] crystallographic orientation. The silicon substrate had a thin (2 nm) native oxide layer. The thin dPMMA layer of $M_w = 53$ kg/mol was spin cast onto a glass slide and, by the technique of floating, was deposited onto the PS substrate layer. The same technique was employed to deposit a thick 145 nm PS capping layer. The system prepared was then annealed at 50 °C under vacuum for a few hours to allow the evaporation of solvent and water.

Two systems are described here. The first is a symmetric one, in which the molecular masses of the PS and PMMA were chosen such that the three layers have similar viscosities. We also prepared a system where the molecular weight of the substrate layer is around 2880 kg/mol. This system, which we denote asymmetric, has a markedly increased viscosity compared to the first PS layer, which on the experimental time scales described here can be considered an elastic solid. The samples were then annealed for increasing lengths of time at 160 °C, well above the glass transition of both polymers. Examples of the NR data obtained are shown in Fig. 1.

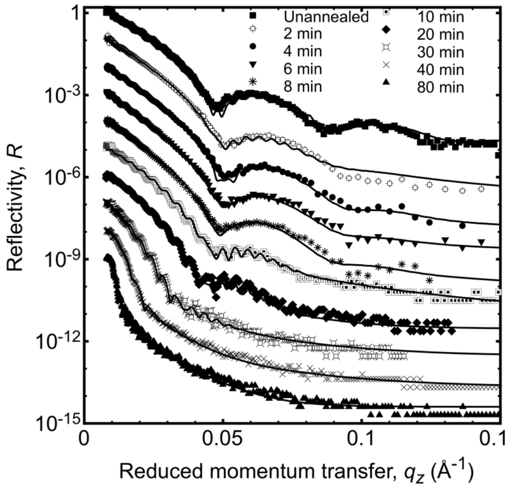

FIG. 1. NR data and fits (solid lines) for the asymmetric trilayer of dPMMA film between two thick PS films. The reflectivity profiles as a function of the annealing time are shown. The solid lines are fits to the data. The annealing times are reported in the figures, and the reflectivity data are staggered by factors of 10 for clarity.

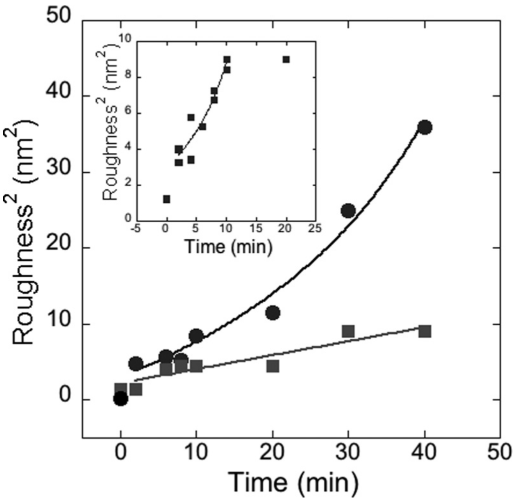

FIG. 2. Square of the roughness of the different d-PMMA/PS interfaces as a function of the annealing time for an asymmetric trilayer (substrate PS film is much more viscous than that at the surface). In the inset the roughness increases for both interfaces for the symmetrical case are also shown (upper/lower interface viscosity matched). The lines are fits to the data as described in the text (the roughnesses at $t = 0$ were not included in the fit). Solid squares refer to the lower interfaces and solid circles to the upper interfaces.

The reflectivity data of Fig. 1 show some features connected to the thickness of the layers: the lower frequency oscillation are related to the thickness of the dPMMA layer and higher frequency fringes connected to the thickness of the PS layer. As the annealing time is increased, the fringes associated with the dPMMA layer decrease in intensity until at later times they disappear, which indicates the dewetting of the dPMMA layer. To follow the process in detail, the NR data were fitted using a trilayer model, consisting of three polymer layers with Gaussian roughness at the interfaces. The main (determining) fitting parameters were the interfacial roughnesses associated with the upper and lower interfaces of the middle (dPMMA) layer. In the main plot of Fig. 2, the square of the top and bottom interfacial roughness of the thin dPMMA layer for the asymmetric system is shown as a function of annealing time. In the asymmetric case, the lower polymer-polymer interface increases much more slowly due to the high viscosity of the bottom polymer layer, while the top roughness increases fast, reaching 6 nm after 50 min. The symmetric case is shown in the inset of Fig. 2: both upper and lower PS/PMMA interfaces increase similarly as a function of time up to 10 min where the total rupture of the film is observed, with a roughness of 3 nm.

The growth of the interfacial roughness was fitted considering the growth in capillary roughness at the interfaces (as we have performed in our previous work). The growth in rms roughness σ as a function of time t is given by $\sigma^2(t) = \langle[\zeta(t) - e]^2\rangle$, with e the thickness of the thin film and ζ representing dispersive perturbations [20,28]. By integrating the roughness above over all wave vectors, the following relation for the interfacial roughness is obtained:

$$\sigma^2(t) = K_1 + \frac{K_2 e^{t/\tau}\,\mathrm{erf}(\sqrt{t/\tau})}{\sqrt{t/\tau}}, \tag{1}$$

where K_1 and K_2 are constants, and τ is the characteristic time of the process [20,28]. Using this expression, a characteristic time for the growth of each interface has been extracted from the fit (see Fig. 2). For the asymmetric system, interestingly the top PS/PMMA roughness increases with a characteristic time of τ of around 18 min, while the bottom roughness, being between a much higher viscosity layer and a lower viscosity thin film, increases much more slowly, of the order of 2×10^5 min. The symmetric interfaces present instead a characteristic time τ of around 4–5 min, after which the system is dewetted.

In general, it is important to define the nature of the substrate. For a liquid film of viscosity η_F on a solid substrate of viscosity η_S, the crossover from a liquid to a solid substrate regime should occur when $\eta_S > (\eta_F/\theta_E,)$ where θ_E is the Neumann equilibrium contact angle [18]. This contact angle, estimated by the values of interfacial tension between PS and PMMA and the surface tensions of the two polymers, is of the order of 1 rad (1.28 rad has been calculated for $T = 150\,^{\circ}\mathrm{C}$ [29]). An estimation of the viscosity η of the polymers can be obtained from the Vogel-Fulcher-Tammann equation, $\eta(T) = \eta_0 e^{-C_1(T-T_0)/(C_2+T-T_0)}$ [30–32], where η_0 is the zero shear rate viscosity, i.e., the value of the viscosity at a reference temperature T_0, C_1 and C_2 are constants that depend on the reference temperature chosen, and T is the temperature. (The zero shear rate viscosity was estimated for our molecular weight by considering the values from literature and corrected for molecular weight using $\eta \propto \mathrm{M_w}^{3.4}$.) Considering the values of the constant of reference for PS [30,33] and PMMA [34], the viscosity obtained for the polymer phases at 160 °C are the following: PS of 572 kg/mol has $\eta = 2.7 \times 10^7$ Pa s, and PMMA of 53 kg/mol has $\eta = 2.1 \times 10^7$ Pa s, while the viscosity of the PS layer with 2880 kg/mol has a viscosity of 5.5×10^9 Pa s. We see that while the symmetric system has the viscosities matched between the PS and PMMA layer, for the asymmetric case we have that the bottom layer has more a solid type of behavior. The Hamaker constant for the PS/PMMA/PS system can be calculated easily considering the simple Lifshitz approximation, which is dependent only on the dielectric constants and refractive indices of the components, and the temperature [35,36]. For a system constituting two semi-infinite layers, 1 and 2 (the PS films), and separated by a medium 3 (the thin PMMA layer), a value for the Hamaker constant of 3×10^{-21} J is obtained. The Hamaker constant is positive, indicating the possibility of dewetting via dispersive forces.

In the asymmetric system we have a thin polymer layer deposited on a very high viscous substrate, with another liquid layer on top. This case could be simplified by considering that it corresponds to a thin liquid film (the dPMMA layer) on a solid substrate below another liquid (the other thick PS layer). The effect of having another capping layer on top of the thin dewetting dPMMA film instead of a gas, for example, has actually two major effects: on the one hand the value of the Hamaker constant of the system, and on the other the value of γ, the interfacial tension instead of the surface tension of a free polymer layer. With this approximation (considering the solid regime), the characteristic growth time τ_m of the fast-growing fluctuation (λ_m), assuming no slippage at polymer/polymer interface, is directly proportional to the viscosity of the dPMMA layer (η_{PMMA}) and is given by

$$\tau_m = \frac{3(6\pi)^2 \gamma\, \eta_{\mathrm{PMMA}} d^5}{2A^2}, \tag{2}$$

where d is the PMMA thickness, γ is the interfacial tension, η_{PMMA} is the viscosity of the thin layer, and A is the Hamaker constant of the system. Considering the experimental characteristic time of 18 min, the value of the PMMA viscosity, the interfacial tension for PS/PMMA of 1.6×10^{-3} J/m^2 from the literature, and the thickness of 15 nm for the PMMA layer, Eq. (2) can be used then to estimate the Hamaker constant. A value of 2×10^{-18} J is obtained, three orders of magnitude larger than the calculated value using the Lifshitz approximation (3×10^{-21} J). However, slippage can be important and needs to be taken into account. Previous studies have illustrated the importance of the slippage at both the solid-polymer interface and polymer-polymer interface. It is possible to define a slippage length b, given by the ratio between the viscosity and the friction coefficient k, $b = \eta/k$. The slippage for a polymer-polymer interface can be of the order of tens of microns, as discussed elsewhere [37,38]. A simple estimation for our system is of the order of 11 μm [20,28]. Assuming slippage, Eq. (2) can be written as

$$\tau_m = \frac{3(6\pi)^2 \gamma\, \eta_{\mathrm{PMMA}} d^6}{2(d+3b)A^2}. \tag{3}$$

Using this expression, a value of the Hamaker constant of 7.4×10^{-20} J is obtained, of the order of the estimated value, considering the crude approximations. We have assumed that the bottom substrate is solid, and during the process the bottom interface grows very slowly. The different growths may also suggest that the interfaces are not correlated. While for the asymmetric case we observe two time constants, for the symmetric case, the characteristic time is even faster and the system is essentially dewetted after 5 min. The top and bottom interface grows to a roughness of 3 nm (as shown in Fig. 2) for each interface after 5 min. For a 15 nm film, and given that there are two growing interfaces, this is close to the onset of the rupture of the film. The faster dewetting for the symmetric trilayer may be an indirect indication of the peristaltic mode of dewetting giving rise to a more efficient material flow.

In conclusion, we have used neutron reflectometry to study the dewetting of symmetric and asymmetric interfaces. We have observed a slow broadening of the interface connected to the growth at long times of capillary wave modes, which involve large-scale hydrodynamic flows, leading to the dewetting. By following the growth of the interface as a function of time for different annealing times, the characteristic rise time of the instability was extracted. Using the relation of the characteristic growth of the interface from the spinodal dewetting theory in the solid regime case, including slippage at the interface, a good prediction agreement is obtained for the growth of the interface.

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