Surface Self-Diffusion of an Organic Glass

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Surface self-diffusion has been measured for an organic glass for the first time. The flattening of 1000 nm surface gratings of liquid indomethacin occurs by viscous flow at 12 K or more above the glass transition temperature and by surface diffusion at lower temperatures. Surface diffusion is at least 10^6 times faster than bulk diffusion, indicating a highly mobile surface. Our data suggest that surface diffusion is the leading mechanism of surface evolution for organic glasses at micrometer to nanometer length scales.

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Surface mobility influences many processes in condensed matter: crystal growth, catalysis, sintering, and more. A fundamental measure of surface mobility is the in-plane surface diffusion coefficient D_s. While D_s has been measured extensively for metals and semiconductors [1,2], there have been no data reported for organic solids (crystalline or amorphous). Understanding surface diffusion in organic solids is relevant for several areas of current research: for example, developing soft materials for biomedical and electronic applications, understanding fast crystal growth at surfaces [3,4] and formation of highly stable glasses by vapor deposition [5], and resolving an ongoing debate over the surface mobility of polymer glasses [6–8]. We present here the first measurement of surface self-diffusion coefficients for an organic glass. We show that surface diffusion is at least 1×10^6 times faster than bulk diffusion, indicating the existence of a highly mobile surface.

Powerful methods such as ion and electron microscopies have been developed to study surface diffusion of metals and semiconductors, but many do not apply to organic solids owing to their lower chemical stability and conductivity. Techniques specifically developed for studying mobility of crystal surfaces [9] are unsuited for amorphous solids. In this study we used the method of surface grating decay [10] to measure surface diffusion on a model organic glass. Driven by surface tension, an initially corrugated surface flattens over time by various mechanisms, among which surface diffusion is the leading mechanism at sufficiently short length scales. We prepared sinusoidal surface gratings on glasses of indomethacin [1-(*p*-chlorobenzoyl)-5-methoxy-2-methyl-indole-3-acetic acid (IMC)] by embossing with master gratings. Master gratings were purchased from Edmund Scientific (1000 and 2000 nm), separated from Blu-ray disks (300 nm), or prepared by photo-polymerizing an optical adhesive on a metal grating (330–550 nm). Master gratings were coated with gold to prevent transfer of contaminants. To print a surface grating, a master was placed over an IMC liquid at 45 K above its glass transition temperature T_g (315 K) for 1 min. On cooling, the master was detached, yielding an IMC glass with a corrugated surface. The grating was nearly sinusoidal as shown by weak high-order harmonics in the Fourier spectrum.

The smoothing of IMC surface gratings was followed at a constant temperature in dry N_2 with an atomic force microscope (AFM; Veeco Multimode IV) or an optical microscope (Nikon Optiphot 2). Tapping-mode AFM scans were perpendicular to the grating grooves. The height profile along each scan line was Fourier transformed to obtain the grating's amplitude; the results were averaged for each image. The optical microscope was used to record a grating's diffraction pattern in transmission through a Bertrand lens. The incident light was 530 nm obtained by filtering white light with a 20 nm band-pass filter. The square root of the first-order diffraction intensity was taken to be proportional to the grating amplitude. Grating diffraction was also monitored in vacuum with a 532 nm laser to assess whether the decay rate changed from dry nitrogen to vacuum.

Figure 1 shows typical data of grating decay collected with AFM and optical diffraction. AFM was the primary method and used wherever possible; optical diffraction was used to allow measurement of faster decays. For samples measured with both techniques (295–320 K), similar decay kinetics was observed. Moreover, using 1000 nm gratings, we confirmed that the square root of diffraction intensity increased linearly with grating amplitude (as determined by AFM). Together these methods covered 5 orders of magnitude in decay rate. Figure 2(a) shows the grating decay constant K vs temperature for 1000 nm IMC gratings. At $T > T_g$, the grating amplitude h decreased exponentially: $h = h_0 \exp(-Kt)$, where K is the decay constant; below T_g, the decay was slightly nonexponential and well described by a stretched exponential: $h = h_0 \exp[-(Kt)^\beta]$, where β is slightly smaller than 1. We attribute the stretched-exponential kinetics to glass relaxation during measurement and regard the observed K as the average decay rate over the measurement time.

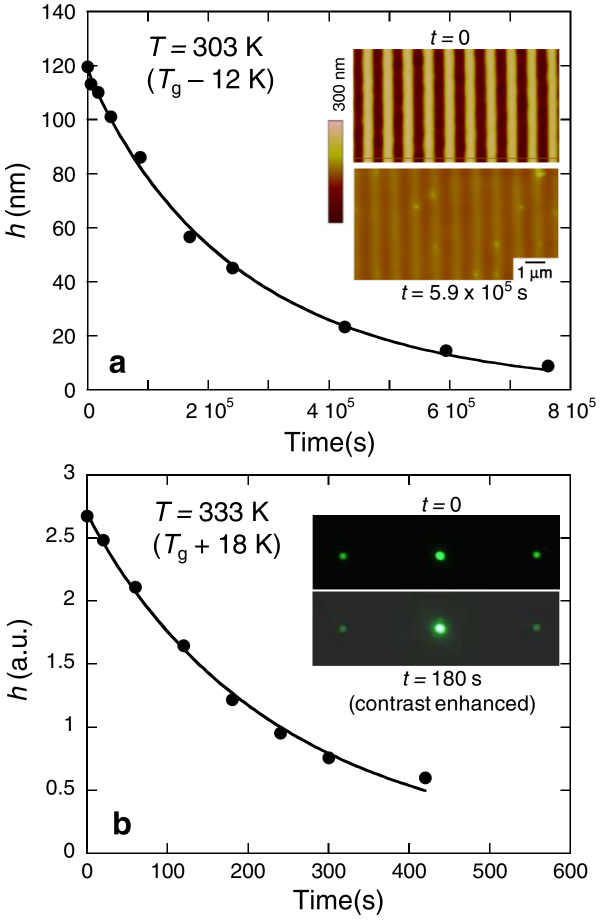

FIG. 1 (color online). Decay kinetics of 1000 nm IMC gratings. (a) Grating amplitude h vs time at 303 K measured with AFM. Inset: AFM images at 0 and 5.9×10^5 s. (b) h vs time at 333 K measured with diffraction. Inset: Diffraction patterns at 0 and 180 s. The side spots are from first-order diffraction. Contrast is enhanced in the 180 s pattern to make the diffraction spots more visible.

Mullins has shown that the decay constant for a sinusoidal grating of wavelength λ is given by [10]

$$K = Fq + Aq^2 + Dq^3 + Bq^4, \qquad (1)$$

where

$$q = 2\pi/\lambda, \qquad F = \frac{\gamma}{2\eta}, \qquad A = \frac{p_0 \gamma \Omega^2}{(2\pi m)^{1/2}(kT)^{3/2}},$$

$$D = A' + C = \frac{\rho_0 D_G \gamma \Omega^2}{kT} + \frac{D_v \gamma \Omega}{kT}, \qquad B = \frac{D_s \gamma \Omega^2 v}{kT}.$$

Here, γ is the surface free energy, η the viscosity, p_0 the equilibrium vapor pressure, Ω the molecular volume, m the molecular mass, ρ_0 the equilibrium vapor density, D_G the diffusion coefficient of evaporated molecules in the inert atmosphere, D_v the bulk diffusion coefficient, D_s the surface diffusion coefficient, and v the number of molecules per unit area of surface. The terms in Eq. (1) correspond to surface smoothing by viscous flow (F), evaporation-condensation (A and A'), bulk diffusion (C), and surface diffusion (B). In this model, surface diffusion refers to lateral diffusion in the top layer of molecules. Malshe *et al.* have shown by simulation that D_s determined by using Mullins' model agrees with that calculated from mean-squared displacements of particles in the top layer [11].

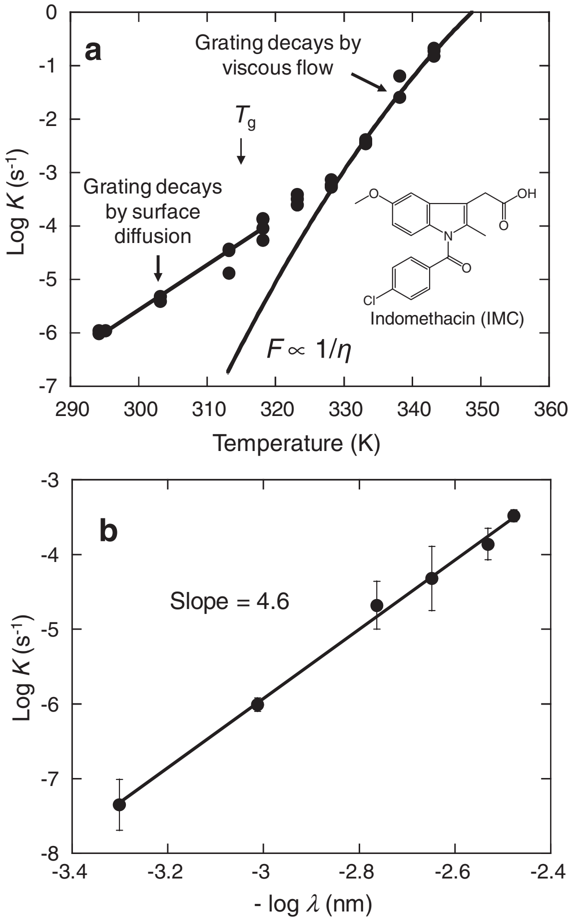

FIG. 2. (a) Decay constants K of 1000 nm gratings of IMC liquids and glasses. (b) K vs grating wavelength at 295 K.

For our system, the evaporation-condensation terms make negligible contributions to the observed decay constant K of 1000 nm gratings owing to the low vapor pressure of IMC. This conclusion is reached by calculating these terms from known properties: $\gamma = 50$ mN/m [12], $\Omega \approx 3 \times 10^{-28}$ m^3, $D_G = 0.1$ cm^2/s for organic molecules diffusing in ambient atmosphere [13], and p_0 is known from vacuum desorption rates of liquid IMC [14]. We find that the A and A' terms are at least 100 times smaller than the observed K. This conclusion is consistent with our observation that IMC gratings decayed at comparable rates in vacuum and in dry N_2. Similarly, using the bulk diffusion coefficients D_v of liquid IMC measured by secondary-ion mass spectrometry [15], we find that the bulk diffusion term (C) is at least 1000 times smaller than the observed K.

To evaluate the viscous-flow term (F), we obtain the viscosity of liquid IMC from a direct measurement [16] and calculate it from the structural relaxation time τ [17,18], the shear modulus G [19], and the Maxwell equation $\eta = \tau G$. This term reproduces remarkably well the observed decay rates at higher temperatures [curve F, Fig. 2(a)]. Curve F was obtained by using η calculated with τ from Ref. [17] and G from Ref. [19] without any adjustable parameter. The results calculated with η from other sources [16,18,19] are vertically shifted from curve F by +0.6 and +1.0 decade. Considering typical errors in the measurement of γ and η, the agreement is reasonable between calculated and observed decay constants. This agreement indicates that, at higher temperatures, viscous flow is responsible for the flattening of 1000 nm gratings of IMC. This mechanism of surface smoothing has been observed for other liquids [20,21].

Although the viscous-flow term (F) accounts for the grating decay rates at higher temperatures, it fails to do so at temperatures below $T_g + 12$ K [Fig. 2(a)]. It is significant that the failure occurs well *above* T_g, indicating that the effect is not caused by the liquid's glass transition. This leaves surface diffusion (B) the only mechanism in Mullins' model responsible for the grating decay observed below ca. 320 K. We confirmed this conclusion independently with gratings of different wavelengths. According to Eq. (1), the decay constant K is proportional to λ^{-4} if surface diffusion is the principal decay mechanism. This relation was indeed observed for an IMC glass at 295 K ($T_g - 20$ K) by using gratings with λ from 300 to 2000 nm [Fig. 2(b)]. The observed relation $K \propto \lambda^{-4.6}$ matches the expected relation within experimental error.

Figure 3 shows the surface diffusion coefficients D_s of an IMC glass calculated by assigning surface diffusion as the mechanism of surface smoothing at $\lambda = 1000$ nm below 320 K. In this calculation, we assume that the IMC glass surface has an areal density of $\nu = 2 \times 10^{18}$ molecules/m^2. Figure 3 also shows the bulk diffusion coefficients D_v of liquid IMC [15]. At the same temperature, D_s is substantially larger than D_v, with $D_s/D_v \approx 10^6$ at T_g, indicating that diffusion is much faster at the surface than in the bulk. D_s and D_v were fitted to the equation $D = D_0 \exp(-Q/RT)$ to obtain the activation energy Q. The activation energy for surface diffusion is approximately half that for bulk diffusion: $Q_s/Q_v = 0.5$.

Whereas Mullins' model considers several mechanisms of surface evolution, studies of organic glasses (including polymers) have generally regarded viscoelastic relaxation as the mechanism [7,8,22]. That view would interpret our data in Fig. 2(a) as reflecting near-surface viscosities (or moduli) that are similar to their bulk values at high temperatures but substantially lower than their bulk values at low temperatures. It would also attribute the K vs λ relation in Fig. 2(b) to different surface viscosities appropriate for gratings of different wavelengths. In contrast, Mullins' model can explain the same data with a single set of surface diffusion coefficients (Fig. 3). Our study argues that surface diffusion, not viscoelastic relaxation, is the mechanism of surface evolution for organic glasses at length scales and temperatures similar to those used here. Identifying the correct mass-transport mechanism is relevant for a fundamental understanding of surface mobility.

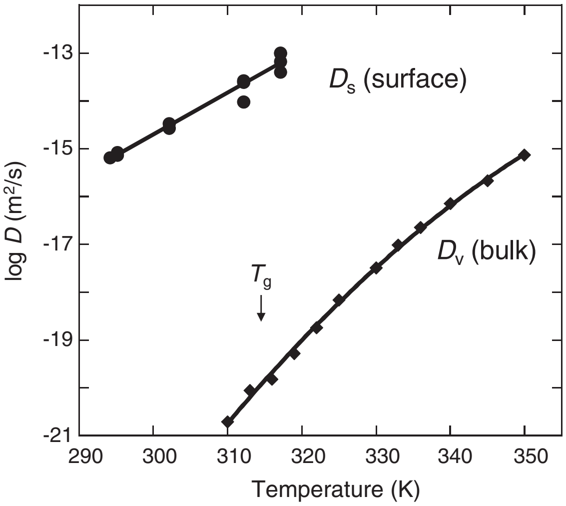

FIG. 3. Surface and bulk diffusion coefficients of IMC liquid and glasses.

If interpreted with Mullins' model, our data provide further information on how rapidly diffusivity must decrease from the surface molecules to the molecules underneath. Mullins defines surface molecules as those exposed to free space and bulk molecules as the rest and shows that surface and bulk diffusion contribute differently to the rate of grating decay [Bq^4 and Dq^3, respectively; Eq. (1)]. If surface diffusion is responsible for grating decay, $Dq^3 < Bq^4$ and $D_v/D_s < \Omega \nu q \approx aq$, where a is the molecular diameter and D_v is the diffusivity of molecules immediately beneath the surface layer. Because $Dq^3 < Bq^4$ for 1000 nm gratings at 295 K [Fig. 2(b)], D_v/D_s must be <0.006; that is, diffusivity must decrease substantially from the surface molecular layer to the layers below. If Mullins' model is valid, it would be reasonable to regard the mobile surface layer for an IMC glass at 295 K as one or a few monolayers thick. This picture is consistent with other estimates of the range of surface mobility [5,8,11,23–25]. Mullins' method of separating contributions from surface and bulk molecules to surface smoothing is analogous to the use of q dependence to assign mass-transfer mechanisms for step fluctuations on crystal faces [9]; in this case, the contributions from surface and bulk diffusion to the rate of step fluctuation are proportional to q^3 and q^2, respectively.

Surface diffusion of small-molecule organic glasses may be relevant for understanding the surface mobility of polymer glasses. Despite recent studies [6–8,22], there has been no consensus on the nature of surface mobility of polymer glasses. Small-molecule organic glasses are free from chain-entanglement effects, which can influence the mobility at polymer surfaces [22,26]. In surface-smoothing experiments, small-molecule glasses are patterned without storing elastic energy in distorted molecular conformations, making subsequent surface evolution much more easily interpreted. Such experiments rigorously establish the limiting behavior of low-molecular-weight polymers.

To our knowledge, this study is the first to measure surface self-diffusion for an organic solid (crystalline or amorphous). It is of interest to compare surface diffusion in this and other materials. The Q_s/Q_v ratio for the IMC glass (0.5) agrees remarkably well with a recent theoretical prediction [27] but exceeds typical values for crystalline metals [9]. As a fraction of the enthalpy of vaporization, the activation energy for surface diffusion is larger for amorphous IMC (70%) than for typical metals (20%–60%) [2]. For amorphous IMC, the surface-smoothing mechanism at $\lambda = 1000$ nm transitions from viscous flow to surface diffusion well above T_g [Fig. 2(a)], whereas oxide liquids do not exhibit such transitions even at $\lambda = 400$ nm [21]. This difference is remarkable since mass transport by surface diffusion is expected to be more important at shorter length scales. These contrasting behaviors could reflect fundamental differences between surface diffusions in molecular and network glasses.

The surface diffusion coefficients of IMC glasses are relevant for understanding recently discovered surface phenomena [3–5]. First, organic glasses can grow crystals much faster (by a factor as large as 10^3) at the surface than in the bulk [3,4]. The fast surface diffusion suggests a connection between the phenomenon and surface mobility. For an IMC glass at 313 K, the surface crystal growth front advances 1 nm or one molecular layer per second [3,4]; during this time, an average molecule in the bulk diffuses $(2D_v t)^{0.5} = 0.1$ nm and a surface molecule could diffuse $(2D_s t)^{0.5} = 100$ nm. This comparison suggests that bulk diffusion is not fast enough to sustain the rate of surface crystal growth but surface diffusion is. In the second phenomenon, exceptionally low-energy glasses are formed by depositing the vapor of organic molecules to a substrate held at 0.85 T_g at a low rate [5]. This phenomenon has been attributed to fast surface mobility, which allows rapid equilibration of newly deposited molecules before they are buried by later arriving molecules. The fast surface diffusion of IMC glasses supports this view. For an IMC glass, D_s is estimated to be 10^{-18} m^2/s at $0.85T_g$ by extrapolation. At a typical deposition rate for forming stable glasses (0.2 nm/s), the average surface molecule can undergo substantial rearrangement, diffusing 2 nm or 2 molecular diameters, before being covered by a new layer of molecules.

We have measured for the first time surface self-diffusion of an organic solid. We find that surface diffusion in this system is at least 10^6 times faster than bulk diffusion, indicating a highly mobile surface. Our study suggests that surface diffusion, not viscoelastic relaxation, is the mechanism of surface evolution for organic glasses at micrometer to nanometer length scales. Our finding explains recently discovered surface phenomena of organic glasses and is relevant for understanding surface mobility of different classes of materials, especially polymer glasses.

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