Efffect of substrate corrugation on the spreading of polymer droplets

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We have performed molecular dynamics simulations of chain molecules of length 16 adsorbed on corrugated van der Waals substrates. We find that substrate corrugation qualitatively changes the motion of individual atoms during spreading. Both the corrugation strength and the degree of commensurateness affect the dynamics of spreading.

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The spreading of nonvolatile polymer droplets has been the subject of much recent experimental [1–4] and computational [5–8] study. Theoretical work has treated droplets as continuous objects([9], and references herein), with the exception of the theory of de Gennes and Cazabat [10], which treats the spreading of a layered droplet of simple liquid. This theory predicts that particles in droplets of simple liquid move downward only near the edge of the droplet, in an annulus of thickness ξ.

The two existing computational studies of flow within a spreading droplet do not reach the same conclusions about the prediction of the layered-drop model. Our previous study [7] showed some evidence that, during spreading, chains move downwards uniformly throughout the droplet. The study of d'Ortona *et al.* [8], however, finds that particles move downwards predominantly in an annular region near the outer edge of the droplet, suggesting that the prediction of the layered simple-liquid theory may be extended to polymer droplets.

There are two main differences between these studies. First, d'Ortona *et al.* use larger droplets in [8] (radii of largest droplets roughly twice as large as those of [7]), and can therefore resolve a larger ξ. Secondly, the substrate on which the droplets spread differs in the two studies. d'Ortona, *et al.* used a microscopically realistic substrate, consisting of massive atoms in a solid phase interacting with the atoms of the droplet via a Lennard-Jones (LJ) potential of variable depth and an added attractive tail to represent the aggregate effect of atoms outside the finite range of the LJ potential. Such a substrate might be useful for the investigation of heat dissipation during spreading. Wagner's substrate was simply the potential due to a semi-infinite volume of continuously distributed LJ material, as was the substrate used in [6]. Droplets on such a substrate experience a force always perpendicular to the substrate (in the z direction, say), which may be thought of as a microscopic implementation of free-slip boundary conditions in a continuum model. There are other methodological differences between the studies (e.g., method of numerical integration, implementation of non-LJ bonding forces), but there seems to be no reason to consider them relevant.

This article focuses on the effect of varying the substrate potential from that of a smooth attractive substrate to that of a substrate corrugated in a way intended to mimic the effect of forces due to the roughness of a surface composed of atoms. More precisely, we use a truncated LJ potential with a modulated attractive tail,

$$V(x,y,z) = 4\pi\epsilon_w \left(\frac{\sigma_w}{\sigma}\right)^3 \left\{ \frac{1}{45}\left[\left(\frac{\sigma_w}{z}\right)^9 - \left(\frac{\sigma_w}{z_C}\right)^9\right] - \frac{1}{6}\left[\left(\frac{\sigma_w}{z}\right)^3 - \left(\frac{\sigma_w}{z_C}\right)^3\right] f(x,y) \right\} \quad (1)$$

for $z \le z_C$, and $V(x,y,z) = 0$ for $z > z_C = 2\sigma$, with

$$f(x,y) = 1 + C\left\{ \cos(Kx) + \cos\left[K\left(\frac{x}{2} + \frac{y\sqrt{3}}{2}\right)\right] + \cos\left[K\left(-\frac{x}{2} + \frac{y\sqrt{3}}{2}\right)\right]\right\}. \quad (2)$$

By varying the parameter C, we vary our underlying potential from the smooth substrate of our previous study (when $C = 0$) to a surface with a regular triangular array of peaks and valleys. The parameter K adjusts the spacing of the surface features, and can be varied to investigate the importance of commensurateness of the substrate with the spacing of atoms in the droplet.

In obtaining our results, we use standard molecular dynamics (MD) techniques. We use a linked-list based program to implement the truncated LJ potential acting between atoms in the fluid [11,12],

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r_C}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r_C}\right)^6\right] \quad (3)$$

for $r \le r_C$ and $V(r) = 0$ for $r > r_C = 2\sigma$. Rigid bonds between neighboring atoms in each chain are imposed with the method of Ryckaert *et al.* [13]. There are no bond-bending forces. We use the "Verlet method" to integrate the equations of motion, with a time step of $h = \tau/141$, where $\tau = \sqrt{(m\sigma^2/\epsilon)}$, the unit of time derived from (3). Our results were obtained in simulations where constant mean kinetic energy was maintained by periodically rescaling velocities to a temperature of $T^* = T/\epsilon = 0.8$, with qualitatively similar results obtaining in the microcanonical ensemble. The initial conditions for our spreading runs were obtained by the

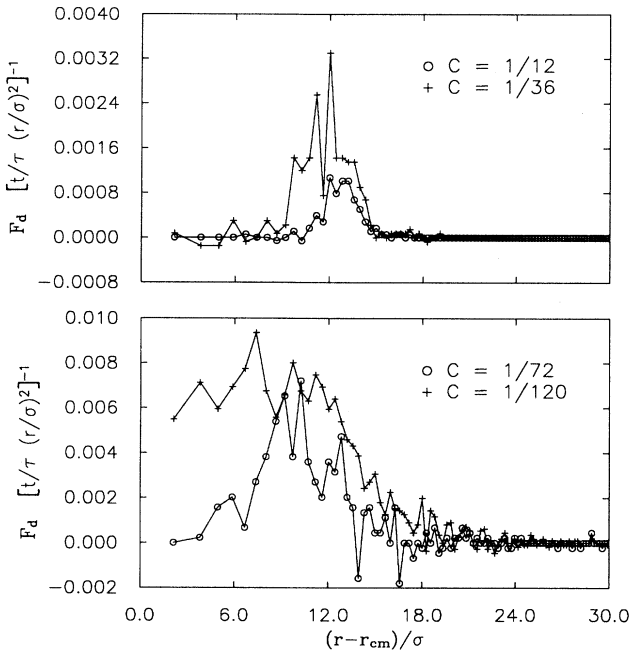

FIG. 1. Downward mass flux density F_d (number of atoms per dimensionless unit time per dimensionless unit area) for various corrugation amplitudes. The number of particles crossing a surface at $z = 1.5$, roughly the dividing surface between the first and second layers during an interval $\Delta t^* = 71$, was averaged between $t^* = 354$ and $t^* = 708$, that is, during the initial phase of expansion. Results are averages of several (two to six) runs from distinct initial conditions. For all simulations, droplets of 100 chains spread on a substrate characterized by $\epsilon_w/\epsilon = \epsilon_w^* = 4.8$, $\sigma_w = \sigma$, $K = K_c = 4\pi\sqrt{3}/1.12\sigma$, and $T^* = 0.8$.

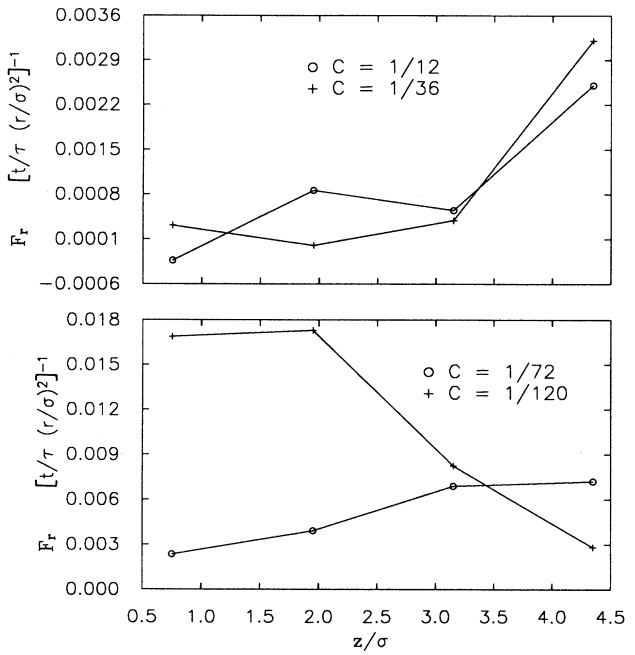

FIG. 2. Radial mass flux density F_r for various corrugation amplitudes. The number of particles crossing a cylindrical surface with radius $r = 6\sigma$ was averaged as in Fig. 1, and binned according to the thickness of the atomic layers. The leftmost datum of each curve may be used in conjunction with the data of Fig. 1 to verify that the first atomic layer is approximately incompressible near the droplet center.

following procedure. Many (100 or 600) chains in an arbitrary initial configuration interact via the LJ potential and an additional weak attractive force centered at the center of the simulation volume with velocity rescaling. The resulting spherical droplets are equilibrated at constant energy and then brought into contact with a weakly attractive rough substrate. Times referred to here are relative to the discontinuous change imposed on ϵ and C at $t = 0$. This is a different convention for the origin than was used in [8].

Our chief results are shown in Fig. 1, which depicts downward mass flux for droplets spreading on substrates whose corrugation is commensurate with the interatomic spacing of atoms in a chain ($K = 4\pi\sqrt{3}/1.12\sigma$). With larger C, the downward mass flux becomes concentrated in a region near the edge of the spreading droplet; in other words, ξ is a decreasing function of C. This suggests that the difference between the results of [8] and [7] may be explained at least partly by the different roughness of the substrates used in the two studies. To realize why a roughened substrate allows downwards motion only near the edge of the droplet, consider that an atom pinned in a potential well cannot easily move aside to make room for downwardly mobile atoms above it, particularly if its

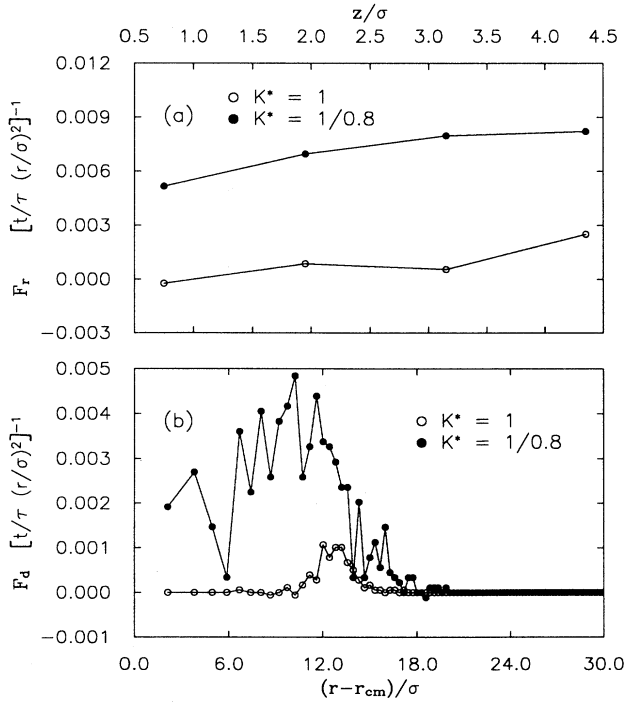

FIG. 3. Radial (a) and downward (b) mass flux densities for commensurate and incommensurate substrates. $C = 1/12$ for all runs. The captions use $K^* = K/K_c$.

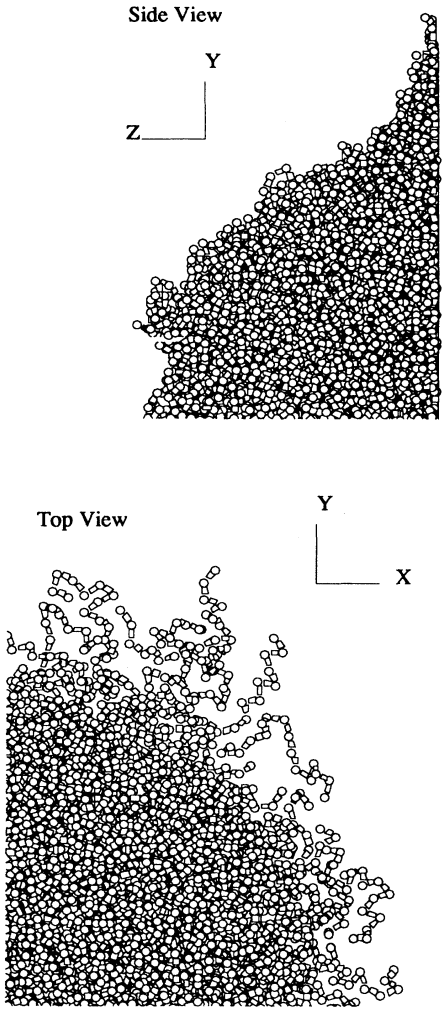

FIG. 4. One quadrant of a top view and one half of a side view of a 600-chain droplet on a smooth substrate with $\epsilon_w^* = 3.6$ and $T^* = 0.8$. The behavior of the precursor layer is quite sensitive to temperature. At $T^* = 0.68$, the precursor layer forms very slowly, while at $T^* = 0.8$ there is some quasi-two-dimensional evaporation; i.e., chains confined to the surface become dissociated from the droplet.

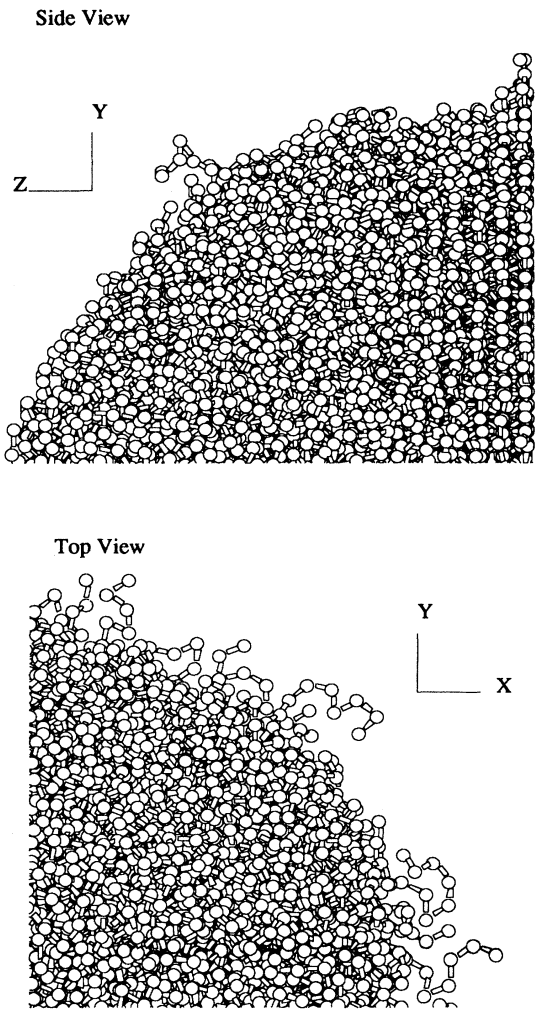

FIG. 5. One quadrant of a top view and one half of a side view of a 600-chain droplet on a corrugated substrate with $C = 1/12$, $\epsilon_w^* = 4.8$, $K = K_c$, and $T^* = 0.8$. The regularity of the substrate potential is reflected in the limited precursor layer of the droplet on the corrugated substrate.

neighbors are similarly confined. Consequently, atoms have an opportunity to descend into the first layer only near the edge of the droplet, where outward expansion is possible. Macroscopically, the pinning of the lowest layer of atoms can be interpreted as a microscopic implementation of a no-slip boundary condition. The experiment of Dussan and Davis [14] suggests that the no-slip boundary condition is macroscopically appropriate for droplet spreading.

Along with the downward mass flux, it is possible to calculate the radial mass flux. This quantity, plotted in Fig. 2, confirms that the mobility of the first layer of atoms falls off sharply with increasing C. Since the droplet still spreads, the outward mass flux is now confined to the parts of the droplet far from the pinning substrate, as may be seen in Fig. 2(a). In fact, the radial mass flux and the downward mass flux show that the portion of the first layer in the center of our spreading droplets is approximately incompressible; $\Delta\rho/\rho \leq 3\%$. The radial and downward mass fluxes taken together suggest that the motion of individual atoms varies from a uniform downward drift with outward flow occurring primarily in the lowest layers in the case of a smooth substrate to an outward drift above the stationary lowest layers near the droplet center with downward motion occurring only where vacancies can form in the lowest layer, close to the edge of the droplets in the case of commensurate corrugation.

The preceding results are quite sensitive to commensurateness of the atomic spacing in the droplet with the periodic potential of the substrate. Figure 3 shows the effect of varying K from $4\pi\sqrt{3}/a$, for which value the potential minima are separated by $a = 1.12\sigma$, the interatomic spacing of neighboring atoms in a chain, to

$4\pi\sqrt{3}/0.8a$. With the incommensurate substrate spacing, single chains of atoms tend to adopt configurations with some atoms in both the first and second layers. The potential barrier between such configurations is much smaller than the potential barrier between two of the essentially two-dimensional configurations typical for a substrate commensurate with the spacing of atoms in chains. Consequently, chains have much higher mobility on an incommensurate substrate. The behavior of isolated chains cannot be taken as a full explanation of the collective phenomena shown in Fig. 3, but the macroscopic manifestations of imposing external stresses on layers of atoms have appeared frequently in MD studies of other systems [15].

A final point we would like to address is whether it is possible to associate lowest-layer pinning by the substrate with the macroscopic form of the droplet. The droplets used to obtain the preceding results were rather small (1600 atoms in 100 16-atom chains). Less extensive simulations run with larger droplets showed some qualitative differences in the shape of the droplet (Figs. 4 and 5). These simulations suggest that a corrugated, commensurate substrate inhibits the formation of a precursor layer. Of course, a precursor layer may form with a corrugated substrate, as shown in [8] and confirmed by our simulations of smaller droplets, but its extent and rate of formation appear to depend on the smoothness of the substrate.

To conclude, we have performed a series of molecular dynamics simulations which show that droplets spread differently on smooth and corrugated substrates. The downward mass flux agrees with the qualitative prediction of the theory of de Gennes and Cazabat [10] on a strongly enough corrugated substrate, while it disagrees on a smooth substrate. While the droplets simulated here are much smaller than those accessible to experiment, a laboratory investigation of the effect of varying the spacing of substrate atoms, perhaps anisotropically, might be interesting.

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