

Early stages of dewetting of microscopically thin polymer films: A molecular dynamics study

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We present results from a molecular dynamics simulation of the dewetting process of microscopically thin polymer films cast on a solid surface. The chain length and time scales accessed in the present simulation would correspond to early stages of the dewetting process before hydrodynamic interactions become important. Even though the surface in contact with the film is purely repulsive, we find that there is a “nucleation time” for dry patches to appear due to the competition between the interfacial energy and the surface energy contributions. Kinetics of growth of dry patches during the early stages of the dewetting process is controlled by surface diffusion of polymers. © 1998 American Institute of Physics. [S0021-9606(98)51143-9]

I. INTRODUCTION

Thin uniform films of polymers on solid substrates have important applications in protective coating, adhesives, and microelectronics. A crucial consideration in applications of these thin films is their stability, that is, whether these films would remain flat and laterally uniform at a certain temperature of interest or they would break up into droplets and spontaneously dewet the substrate.¹ Confinement effects and interaction with the solid substrate radically change the conformation of chain molecules in a thin polymer film.² Dynamical aspects of the cooperative movement of the molecules near a confining surface influence the adhesion and wetting characteristics of the film. This, in turn, controls the stability of these thin films. A detailed knowledge of conformations and cooperative motion of polymer chains near a solid surface is essential for the development of artificial materials with specifically engineered properties. For this reason, the stability of these films has attracted much recent theoretical and experimental attention.^{3–9} In laboratory situations, thin polymer films of different thicknesses are often prepared by spin-coating polymer solutions of various concentrations onto a substrate which is not wettable. The sample is then heated above the glass transition temperature and the kinetics of droplet formation is studied in the experiment.

Theoretical description of this process¹ starts from a small fluctuation of the film thickness. Stability of the film is controlled by the balance between the disjoining pressure originating from molecular forces such as van der Waals forces and the Laplace pressure due to the thickness fluctuation. If the surface is nonwettable, unstable fluctuations develop into holes or dry patches similar to the spontaneous

amplification of fluctuations in the spinodal decomposition of a quenched binary liquid mixture.¹⁰ More complications for polymer films arise from the fact that entangled polymers do not flow like usual liquids, but slip on smooth surfaces.^{5,11} The slippage is characterized by a so-called extrapolation length, defined by the distance from the solid wall at which the velocity extrapolates to zero. A pressure gradient parallel to the film induces Poiseuille flow for films thicker than the extrapolation length (typically around 30 μm). In thinner films a plug flow is induced and the polymer moves more like a liquid with the viscous dissipation confined at the liquid/solid interface. The kinetics of dry-patch growth is different in these two cases: the characteristic size of the dry-patch (R) increases with time (t) as a power-law $R(t) \sim t^n$ with exponents $n = 2/3$ for a plug flow and $n = 1$ for a Poiseuille flow.

The theoretical description mentioned above refers to length scales larger than the monomeric length scales and time scale of the order of 10^3 s or more. A coarse-grained description is suitable for such a situation and the polymeric nature of the film enters through various phenomenological parameters. Although the theory mentioned above has been reasonably successful in explaining dewetting kinetics in polymer films, our understanding of microscopic aspects of the dewetting phenomena is still incomplete. Particularly, the effects of conformation of the individual polymer chains and the mobility of the polymers in a confined thin film⁵ on the early time kinetics of nucleation and growth of dry patches require further research. Recent experimental studies¹² indicate that dry patches do not evolve by spontaneous amplification of thermal fluctuations as in spinodal decomposition of quenched liquid mixtures, but instead they grow only if their linear size is larger than a critical radius. It is important to understand this phenomenon at an intermediate length scale in the presence of explicit polymer chain conforma-

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tions for gaining insight into the competition between the interfacial energy and the molecular energy. Molecular dynamics (MD) simulation of a model system of a thin polymer film containing reasonably large number of chains can provide such insight into the dewetting kinetics. Although no such MD calculation exists in the literature to our knowledge, a recent *Monte Carlo* simulation has been carried out by Milchev and Binder¹³ to study early stages of dewetting of thin polymer films adsorbed onto a solid substrate from a solution. However, Monte Carlo calculations may not be suitable for studying kinetics as the stochastic moves used in such studies do not correspond to the real movements of monomers. Dynamic Monte Carlo technique is still used for its simplicity and computational efficiency, but any prediction from Monte Carlo studies of kinetics should be checked by a more realistic model calculation. Moreover, Milchev and Binder study dewetting of a film adsorbed from solution onto a strongly attractive surface, while in most experimental situations polymer films are spun cast onto the substrate and are not formed by adsorption from a solution. In this paper we have carried out MD simulations of the dewetting process of thin polymeric films cast on a solid flat surface. This surface is totally nonwetttable once the dewetting process starts. Besides the fact that MD simulations provide more accurate description of a kinetic process than Monte Carlo simulations, our simulations are also more realistic as we use a melt-like density for the film, and an order of magnitude larger number of monomers than the previous Monte Carlo study. However, the time scale accessed in the present simulation corresponds to an early stage of the dewetting process.

II. MODEL AND NUMERICAL METHOD

The molecular dynamics method that we have implemented here is similar to the one previously used by Grest and co-workers¹⁴ for studying polymer melts and polymer brushes. In this MD scheme, a pair of monomers interact through a Lennard-Jones (LJ) potential V_{ij} given by

$$V_{ij} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r_c} \right)^{12} + \left(\frac{\sigma}{r_c} \right)^6 \right]; \quad r \leq r_c. \quad (1)$$

Here r_c is the cutoff distance beyond which the potential is taken to be zero, $r = |\mathbf{r}_i - \mathbf{r}_j|$, and \mathbf{r}_i , and \mathbf{r}_j are the locations of the i and j th particles, respectively. The parameter ϵ is the standard LJ energy parameter, and σ is the LJ length parameter which we have used as the unit of length throughout. The potential is a purely repulsive potential if the cutoff distance $r_c = 2^{1/6}\sigma$, but has an attractive part when $r_c = 2.5\sigma$. In addition, two successive monomers in a chain are subject to a finite-extension anharmonic spring-potential U_{ij} given by

$$U_{ij} = k \ln \left[1 - \left(\frac{r_{ij}}{R_0} \right)^2 \right], \quad (2)$$

where k is an energy parameter, r_{ij} is the distance between two successive monomers of the same chain, and R_0 is a length parameter which describes the extension range between two successive monomers. In this study we have chosen $k = 30$ and $R_0 = 1.5$ which makes chain crossing practi-

cally impossible.¹⁴ For this choice of the parameters the bond length (r_b) of the chains is about $r_b = 0.97\sigma$.

In order to simulate a constant temperature ensemble, the monomers are weakly coupled to a heat bath and the equations of motion read as

$$m\ddot{\mathbf{r}}_i = -\nabla U_i - \Gamma \dot{\mathbf{r}}_i + \mathbf{W}_i(t), \quad (3)$$

where Γ is the monomer friction coefficient and $\mathbf{W}_i(t)$ describes the random force of the heat bath acting on each monomer. $\mathbf{W}_i(t)$ is a Gaussian white noise with zero mean and satisfying fluctuation-dissipation relation

$$\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6k_B T \Gamma \delta_{ij} \delta(t - t'). \quad (4)$$

The equations of motion have been integrated by using an accurate scheme developed by van Gunsteren and Berendsen.¹⁵ In this scheme one uses a bivariate distribution of Gaussian random numbers to integrate the stochastic forces. A very fast Gaussian random number generator developed by one of us¹⁶ and a link-cell list help to make the integration quite efficient. Throughout this paper, we use the following reduced units for all physical quantities: ϵ for the unit of energy, ϵ/k_B for the unit of temperature, σ for the unit of length, and $\sigma(m/\epsilon)^{1/2}$ for the unit of time. In our simulations, $\Gamma = 0.5$, and the time step used is $\Delta t = 0.01$ (in reduced unit).

In the molecular dynamics simulation of dewetting the first step needed is the generation of an initial configuration of the film on a substrate. We start from a film of lateral (xy) area 64×64 and of thickness $D = 6$ (in units of σ). Periodic boundary conditions are implemented along both x and y directions. The film is initially confined between two solid walls at $z = 0$ (loosely called the “substrate surface” in this paper) and at $z = 6$. The total number of monomers in our system is $N_m = 19\,200$ and the chain lengths considered are $N = 16$ and $N = 32$. The monomer density of the polymer fluid is thus $\rho = 0.78$. Monomers at various locations z interact with the surface at $z = 0$ by the following LJ-like potential:¹⁷

$$V_0(z) = \frac{2\pi}{3} \rho_s \epsilon_0 \left\{ -\frac{1}{z^3} + \frac{2}{15} \frac{1}{z^9} \right\}, \quad (5)$$

where ϵ_0 is the energy parameter for this wall, and ρ_s is the particle density of the solid wall. We choose $\rho_s = 2$ which is higher than the density of the polymer fluid in the box. At $z = D$ we have another solid wall which has a pure repulsive potential given by

$$V_D(z) = \frac{4\pi}{45} \frac{\rho_s \epsilon_D}{(D - z)^9}. \quad (6)$$

This second wall is just used to confine the polymers inside the box.

Before the MD simulation starts, we first use a Monte Carlo scheme¹⁸ with a “pearl necklace model” with the same (fixed) bond length $r_b = 0.97$ to generate a reasonable initial configuration for the system. Using this Monte Carlo scheme we randomly place polymer chains into the system box, and then equilibrate the system at a fixed temperature $T = 2$ by using a kink-jump method. At this stage the cutoff distance used for the LJ potential is $r_c = 2^{1/6}$ (purely repul-

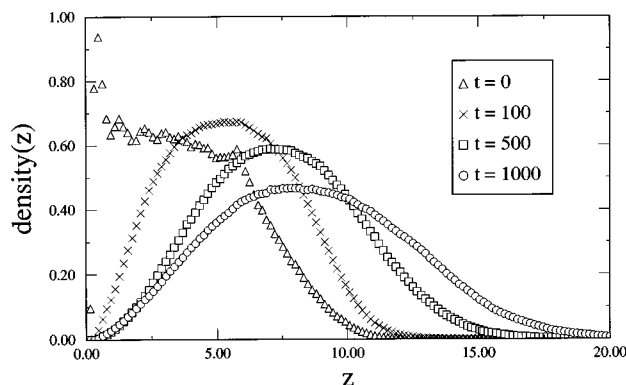


FIG. 1. Density profiles of the thin film (with $N=32$) during the dewetting process as a function of distance (z) from the substrate surface. The profile at $t=0$ is the initial shape of the film in contact with the nonwetable surface. The density as a function of z has been averaged over the lateral (xy) area of 64×64 .

sive) and the surface interaction parameters are chosen to be $\epsilon_0 = \epsilon_D = 0.1$. Since the model of polymer chains used in the Monte Carlo simulation is somewhat different from our molecular dynamics model of polymer chains, we carried out further equilibration with the MD method. After this equilibration, the monomer density near the surface at $z=0$ is somewhat enhanced (the density at the surface at $z=0$ is 0.93 which is about 20% higher than the film density of 0.78) due to the weak attractive interaction with the surface at $z=0$. However, this film configuration is not similar to that in an experimental situation in which the system has a semi-infinite open space and there is no confinement from the top of the film. To model this situation approximately, we next moved the upper wall into the position $z=64$ and run the MD simulation for another several hundred steps without changing any parameters. The wall at $z=64$ is far from the thin film and has practically no effect on the thin film. The relaxed film is about 10 units thick and thus has a lower overall density than the starting density of 0.78. The density profile of the film at this stage is shown in Fig. 1 for $N=32$ as at $t=0$. Since the monomers furthest away from the substrate surface relax the most when the surface at $z=6$ is moved away, the density peak at $z=0$ now stands much higher than the current overall film density.

After this initial configuration has been prepared, we start the MD calculation to study dewetting of this thin polymeric film. The cutoff of the LJ potential among the monomers is set to $r_c = 2.5$ so that the monomer-monomer interaction now has an attractive part as well. We have also increased the energy parameter of the wall at $z=0$ from $\epsilon_0 = 0.1$ to $\epsilon_0 = 0.5$ but changed the form of the surface interaction to be *purely repulsive* by discarding the z^{-3} term in the potential. This potential would then correspond to a non-wettable surface. Our results for dewetting are averaged over 20 different initial conditions of the films.

III. RESULTS

In Fig. 1 we show density profiles of the thin film with $N=32$ at various times during the dewetting process. As time progresses, the peak of the profile seen at $t=0$ near the

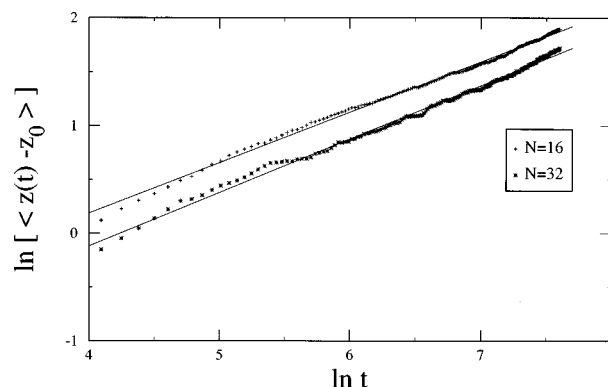


FIG. 2. Log-log plot of the average distance of monomers from the surface ($\langle z(t) \rangle - z_0$) vs time t . Here $z_0 \equiv z(t=0)$ and its value is 5.5 for both $N=16$ and $N=32$. The slope of each straight line yields an exponent of 0.5. Chains with $N=16$ move much faster from the surface compared to chains with $N=32$ as the diffusion constant for the larger chains is smaller.

substrate surface decreases and the profile becomes more extended. In order to characterize the motion of the monomers more quantitatively, we have measured the averaged distance of the monomers from the surface $\langle z(t) \rangle$ with time t for both $N=16$ and $N=32$. In each case the curves can be well represented by a form $\langle z(t) \rangle = z(t=0) + at^{1/2}$ as shown in Fig. 2 by plotting $[\langle z(t) \rangle - z(t=0)]$ vs t in a log-log plot. Although the power-law exponent is the same for both $N=16$ and $N=32$, the prefactor a is N dependent as chains with $N=16$ move much faster from the surface compared to chains with $N=32$ as the diffusion constant for the larger chains is smaller.

In Fig. 3 we show a series of snapshots for the dewetting process of thin films with chain length $N=32$. The results

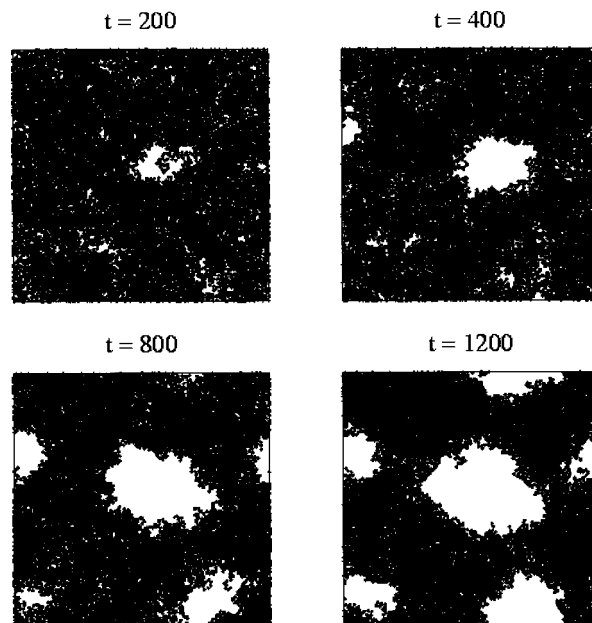


FIG. 3. Series of snapshots for the dewetting process of thin films with chain length $N=32$. These figures are views from the top of the thin films at various times during the evolution process. The local darkness in each snapshot indicates the coverage of the polymers projected onto the substrate surface at $z=0$; the white spots thus indicate the dry patches.

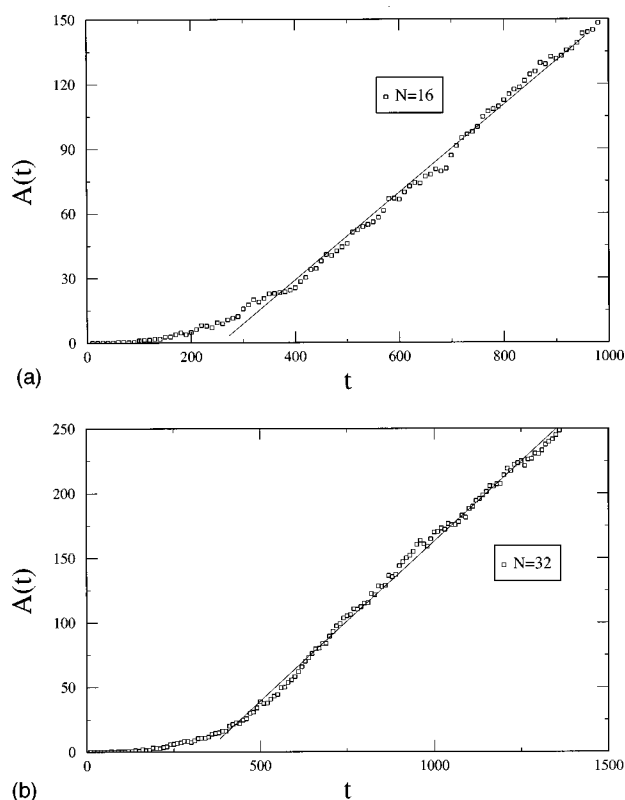


FIG. 4. (a) Total area $A(t)$ of the dry patches as a function of time t for $N=16$. Note that there is a waiting period before the dry patch area becomes appreciable. After this initial nucleation stage, the area $A(t)$ increases linearly with time [for times ($t \geq 400$)]. (b) Same as in Fig. 3 except $N=32$ here.

are similar for $N=16$. These figures are views from the top of the thin film at various times during the evolution process. The local darkness in each snapshot indicates the coverage of the polymers projected onto the substrate surface at $z=0$; the white spots thus indicate the dry patches. After a waiting period, some dry patches appear around $t=200$ during the dewetting process. However, many of these dry patches cannot be seen later. This indicates that dry patches grow only if their linear size is larger than a critical value. This growth process has some similarity with domain growth processes in a quenched off-critical liquid mixture,¹⁰ but, as we will see, the details of the growth process are different here due to the presence of the substrate surface.

To characterize the growth of the dry patches on the surface, we have measured the total area $A(t)$ of the dry patches as a function of time t . In Figs. 4(a) and 4(b) we present these results for $N=16$ and $N=32$, respectively. From these figures we find that there is a waiting period before the dry patch area becomes appreciable. Over this period small dry patches appear and disappear randomly. Although the surface is completely nonwetable, dry patches do not seem to grow by a spontaneous amplification of thermal fluctuations as expected in theoretical models.¹ The “nucleation time” of dry patches observed in the simulation can be understood in the following way. Although a *cylindrical* dry patch of radius R decreases van der Waals energy which is proportional to R^2 , such a patch would increase the interfa-

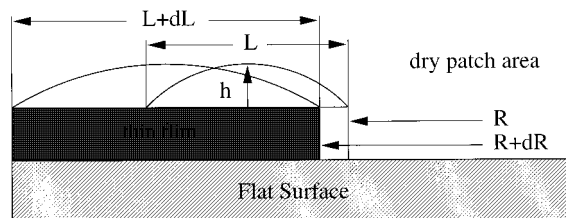


FIG. 5. Conformation of the lip and the dry patch when the thin polymer film is near the flat nonwetable surface. Via surface diffusion the polymer molecules at the front of the thin film recede to the top of the film and form a lip. Here dR is the increment in the linear size (radius) of the dry patch R , L is the size of the lip on top of the thin film, and h is the height of the thin film. Since the increment of the volume of the lip is proportional to $hLdL$, by mass conservation, one easily finds that $R \sim L^2$.

cial energy by an amount proportional to $R \times D$ where D is the thickness of the film.^{7,12,19} Thus, a dry patch would only grow if the size is larger than a critical radius, while patches with smaller radius would heal. We find that the nucleation time is larger for the larger chain length, but we have not been able to quantify this nucleation time by varying chain lengths, film thickness, and the strength of the surface interaction. After this initial nucleation stage, the area $A(t)$ increases linearly with time [for times ($t \geq 400$)] for both $N=16$ and $N=32$. This linear growth law for the *area* of the dry patches at early times follows from a surface diffusion mechanism. First we note that the bottom of the thin polymeric film is flattened against the surface.²⁰ For a thin film of this shape, a dry patch would grow by the following growth mechanism. Via surface diffusion the polymer molecules at the front of the thin film recede to the top of the film and form a “lip.” For a thin sample confined by the substrate, the receding mass of polymers is approximately proportional to the increment dR of the linear size (radius) of the dry patch (see Fig. 5). Thus, the size L of the lip increases with time by a surface diffusion process, but its height h does not change appreciably due to the flat shape of the film. Note that the increment of the volume of the lip is proportional to $hLdL$. Now, by mass conservation, this volume increment should be proportional to the increment dR of the radius of the dry patch. This yields a relation between the radius R of the dry patch and the size L of the lip on the film as: $R \sim L^2$. Since for growth of three-dimensional domains on a two-dimensional substrate $L(t) \sim t^{1/4}$, the linear size for the dry patches increases as $R(t) \sim t^{1/2}$. This would indicate that the *area* of the dry patches grows as $A(t) \sim t$ which we observe in the simulation for both $N=32$ and $N=16$. Since we have been able to study only two different values of chain lengths due to computer time limitations, a quantitative description of the amplitude of the growth law in terms of chain diffusion constants is not possible from this study. We note that Milchev and Binder have also explained the mechanism of dry patch growth in dewetting of adsorbed films in terms of a growth of three-dimensional lips which can exchange mass via two-dimensional surface diffusion.²¹ However, they have not been able to extract a consistent growth exponent from their numerical data. The good quality data obtained in our simulation allows us to quantify the early-time dewetting kinetics. It is interesting to point out that

Milchev and Binder have studied dewetting of a strongly adsorbed film while our films resemble spin-cast films on a solid substrate. The fact that the early time kinetics of dewetting turns out to be similar for these two different physical situations is interesting and points toward a possible universality.

IV. CONCLUSIONS

We have carried out molecular dynamics simulations to probe early stages of dewetting of thin polymer films cast on a solid surface. We have prepared a thin polymer film in contact with a nonwetable surface which has only a repulsive interaction with the monomers at the onset of the dewetting process. Even though the surface is purely repulsive, we find that there is a nucleation time for dry patches to appear due to the competition between the interfacial energy and the surface energy. This has been suggested¹² in some experiments; our studies provide theoretical support for this phenomenon. Dry patches grow only if their linear size is larger than some critical value; patches with size smaller than the critical value heal during the evolution process. Open questions remain, due to the limitations on available computer time, as how this nucleation time varies as a function of chain length, thickness of the film, and the strength of the surface interactions. Kinetics of growth of dry patches during the early stages of the dewetting process is controlled by surface diffusion of polymers yielding growth of three-dimensional domains on a two-dimensional substrate. This process of lip growth results in a growth law for the area of the dry spots as $A(t) \sim t$. This growth law is quite different from that expected from hydrodynamic studies.

The chain length and time scales accessed in the present simulation are quite different from the ones studied in laboratory experiments and in coarse-grained hydrodynamic models. Moreover, hydrodynamic interactions are screened²² in the present MD calculations due to a violation of global momentum conservation in the constant-temperature stochastic MD simulation method that we have used. For this reason, results of this MD simulation cannot be directly compared with experiments or with previous hydrodynamic theories. However, our results would be relevant for the early time kinetics of dewetting in a polymer film before hydrodynamic effects become important. We hope that the new growth law found in our work will lead to experimental studies of early time kinetics of dewetting in polymer films. Since the model used in the study is similar to the one previously employed by Kremer and Grest,¹⁴ their estimate of one unit of time ($= 3.1 \times 10^{-8}$ s for polystyrenes) should be quite reasonable. Thus the largest time accessed in the simulation (about 1500 units) would correspond to about 4.5×10^{-5} s. This largest time, however, is still smaller than can be accessed in an experiment to study *early stages* of dewetting. We note that all MD simulations tend to suffer from this drawback. However, the chain lengths used in this study are also much smaller than those used in experiments. Thus it is quite possible that the early time regime studied in this paper may be accessible in laboratory experiments (before hydrodynamic effects become important) for suitably

large chain lengths. We point out that in experimental studies of spinodal decomposition in polymer blends,²³ it has been found that hydrodynamic effects become important only in the late stages of coarsening while the early to intermediate time domain growth is controlled by a diffusive process. Since dewetting of polymer films has some similarity with spinodal decomposition (or nucleation and growth), it is not unreasonable to expect that the early diffusive stages of dewetting can be studied in laboratory experiments for a suitable system.

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- ²¹When the simulation is continued to much later times ($t > 1000$ for $N = 16$ and $t > 1500$, for $N = 32$) the whole thin film in our simulation is pushed far away from the surface and the confinement of the surface does not affect growth of dry patches any longer. We should note here that due to the absence of gravity in the simulation, the final "dewetted" drop would not sit on the surface with a large contact angle but will be pushed away from the surface altogether. Under this radially symmetric environment, the lips can grow three dimensionally. The receding mass of polymers is now approximately proportional to the increment dR and the square of the size L of lip, which leads to a growth law $A \sim t^{1/2}$ at late times. We observe this crossover to a slower growth law in the simulation when the average thickness of the film $\langle z(t) \rangle \geq 10$, but we do not think this has any experimental relevance as in a real, laboratory situation the film is never pushed back from the substrate surface completely.
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