Spreading of Viscous Fluid Drops on a Solid Substrate Assisted by Thermal Fluctuations

Benny Davidovitch,[1] Esteban Moro,[2] and Howard A. Stone[1]

[1]*Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA*

[2]*Grupo Interdisciplinar de Sistemas Complejos (GISC) and Departamento de Matemáticas, Universidad Carlos III de Madrid, Avenida de la Universidad 30, E-28911, Leganés, Spain*

(Received 2 September 2005; published 9 December 2005)

We study the spreading of viscous drops on a solid substrate, taking into account the effects of thermal fluctuations in the fluid momentum. A nonlinear stochastic lubrication equation is derived and studied using numerical simulations and scaling analysis. We show that asymptotically spreading drops admit self-similar shapes, whose average radii can increase at rates much faster than these predicted by Tanner's law. We discuss the physical realizability of our results for thin molecular and complex fluid films, and predict that such phenomenon can in principal be observed in various flow geometries.

DOI: 10.1103/PhysRevLett.95.244505 PACS numbers: 47.20.Dr, 68.08.Bc, 68.15.+e

Water drops spreading on a table and oil drops lubricating a pan are two common examples of a phenomenon encountered frequently in the kitchen as well as in natural and industrial environments: Spreading of liquids on solid surfaces. Despite its prevalence and the basic hydrodynamic principles involved, it was not until the late 1970s that the asymptotic rate of spreading processes was found by Tanner [1] for surface-tension dominated flows. The spatial scale ℓ of a viscous drop spreading on a smooth plane increases asymptotically in time as $\ell \sim t^z$, where $z = 1/10,\ 1/7$ for radially symmetric two-dimensional and one-dimensional flow geometries, respectively. This asymptotic response has been found in many molecular and polymeric drops, whose decreasing thickness has been detected down to 10 nm [2]. As the field of nanofluidics is evolving towards formation of thinner liquid films, theoretical tools are needed to describe flow patterns in such geometries. However, the applicability of classical hydrodynamic theory for these systems is questionable. While the necessity to incorporate van der Waals (vdW) fluid-solid attraction was recognized long ago [3], other fundamental aspects have never been fully addressed. In particular: Does a three-dimensional hydrodynamic description hold for a film whose thickness is just a few molecular layers? What are the effects of thermal fluctuations on the deterministic hydrodynamics at such small scales?

To resolve these questions, extensive molecular dynamics (MD) or lattice-gas (LG) simulations of flow in liquid films are required to allow comparison and quantify deviations from a regular hydrodynamic theory [4]. While a full resolution of these questions is still not available within current computational possibilities, recent studies are indicative. For example, Abraham *et al.* [5] used the LG algorithm to study flow in a precursor film associated with a spreading drop and demonstrated significant deviations from the predictions of a hydrodynamic model [3]. Also, MD simulations of nanojets, whose initial radius was about 10 molecular diameters, were shown to be qualitatively consistent with simulations of a stochastic Navier-Stokes (NS) equation, where the viscous stress tensor was supplemented by a stochastic tensor whose temperature-dependent magnitude is determined from the fluctuation-dissipation theorem [6]. The emerging picture is that, at least in some cases, a hydrodynamic description can be used as a quantitative tool for the flow of nanofluids; however, modifications of the classical equations are required.

In this Letter we take one further step forward by exploring the influence of thermal fluctuations on the shape and rate of the spreading of nondimensional drops, while assuming a generalized NS equation holds, similar to [6]. We should note, however, that, in addition to thermal fluctuations, other modifications of the hydrodynamic equations that stem from density variations near the interfaces [7] might be necessary in this regime.

Consider the dynamics of the height $h(x, y, t)$ of an incompressible planar viscous fluid film on top of a smooth solid surface, located at $h = 0$ (Fig. 1). We consider viscous fluids, such that inertia can be neglected. The mass conserving dynamics of long wavelength fluctuations of the surface, $|\nabla h| \ll 1$, is described by the lubrication equation

$$\frac{\partial h}{\partial t} = \frac{1}{3\eta}\vec{\nabla} \cdot (h^3 \vec{\nabla} p), \tag{1}$$

where η is the viscosity and p is the pressure. The derivation of Eq. (1) from the NS equation is a standard exercise in fluid mechanics [8]. Spatial variations of the pressure associated with fluctuations of the liquid-vapor interface

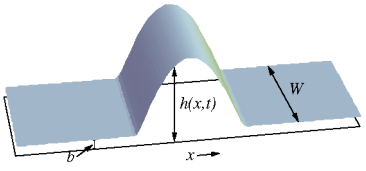

FIG. 1 (color online). Schematic representation of a one-dimensional spreading drop, confined in a channel of width W. The precursor layer of height b is also shown.

result from several sources: gravity, surface tension, and vdW attraction with the solid surface:

$$p = \rho g h - \gamma \nabla^2 h + A/h^3, \tag{2}$$

where ρ is the fluid density, g is the gravitational acceleration, γ is the liquid-vapor surface tension, and A is the Hamaker constant. Tanner's law corresponds to similarity solutions of Eq. (1)

$$h(\vec{x}, t) = |x|^{-\beta} f(|x|/t^z) \tag{3}$$

in the surface-tension-dominated regime $|\gamma \nabla^2 h| \gg |\rho g h|$, $|A/h^3|$ where the exponent $\beta = 1, 2$ is determined by requiring volume conservation $V = \int d^d \vec{x} h(\vec{x}, t)$, yielding $\beta = d$ for one-dimensional ($d = 1$) and two-dimensional ($d = 2$) flow geometries.

The central equation of this Letter is a stochastic generalization of Eq. (1):

$$\frac{\partial h}{\partial t} = \frac{1}{3\eta} \vec{\nabla} \cdot (h^3 \vec{\nabla} p) + \sqrt{\frac{2k_B T}{3\eta}} \vec{\nabla} \cdot [h^{3/2} \xi(\vec{x}, t)], \tag{4}$$

which captures effects of thermal fluctuations on the surface dynamics. Here, $\xi(\vec{x}, t)$ is a spatiotemporal Gaussian white noise. Equation (4) can be derived from the full 3D NS equation, similar to Eq. (1), by adding a stochastic stress, representing thermal fluctuations of the fluid momentum, to the viscous stress tensor [9]. We can avoid, however, such a tedious derivation by considering a linear version of Eq. (1), and use the fluctuation-dissipation theorem to find the correct magnitude of a Langevin term that gives rise to equipartition of the thermal energy carried by its eigenmodes $h_{\vec{q}}(\vec{x}, t) = H + \delta h_{\vec{q}}(t) \cos(\vec{q} \cdot \vec{x})$. Here $|\delta h_{\vec{q}}/H| \ll 1$, H is the average thickness of the film, and $\vec{q}$ is a planar wave vector. The linear eigenmodes of the stochastic surface dynamics are required to satisfy

$$\Gamma_{|q|} \frac{\partial \delta h_{\vec{q}}}{\partial t} + p_{\vec{q}} = \sqrt{2\Gamma_{|q|} k_B T} \xi_{\vec{q}}(t), \tag{5}$$

where $p_{\vec{q}} = (\rho g + \gamma |q|^2 - 3A/H^4) \delta h_{\vec{q}} \cos(\vec{q} \cdot \vec{x})$ is the pressure associated with a surface eigenmode, $\Gamma_{|q|} = 3\eta/|q|^2 H^3$ is its friction coefficient, and $\xi_{\vec{q}}(t)$ is the spatial Fourier transform of $\xi(\vec{x}, t)$. Notice that the long wavelength approximation underlying Eq. (1) implies $|q|H \ll 1$. Dividing both sides of Eq. (5) by $\Gamma_{|q|}$ and taking the inverse Fourier transform we obtain

$$\frac{\partial \delta h}{\partial t} = \frac{1}{3\eta} \vec{\nabla} \cdot (H^3 \vec{\nabla} p) + \sqrt{\frac{2k_B T H^3}{3\eta}} \vec{\nabla} \cdot \xi(\vec{x}, t). \tag{6}$$

The linear Eq. (6) describes near-equilibrium thermal fluctuations of a surface, $|\delta h| \ll H$. The spreading dynamics of a drop that does not satisfy this condition must be described by a nonlinear equation. To this end, notice that Eq. (1) can be recovered from the deterministic part of Eq. (6) by making the transformation H, $\delta h \to h$ and requiring the resulting equation to conserve fluid mass. By following exactly the same steps, the nonlinear Langevin Eq. (4) can be derived from Eq. (6).

A word of caution is in order. For any extrapolation of the fluctuation-dissipation theorem to nonlinear, far from equilibrium dynamics, a local equilibrium assumption must be made [10]. Namely, the description of the surface dynamics with Eq. (4) assumes that the magnitude of thermal fluctuations of the liquid-vapor interface at $\vec{x}$ is determined by the local value of the surface height $h(\vec{x}, t)$. This assumption is justified only for thermal fluctuations whose wavelength $\lambda \ll \lambda^*(\vec{x}, t) = h/|\nabla h|$. The relaxation dynamics of fluctuations whose wavelength $\lambda > \lambda^*(\vec{x}, t)$ is strongly coupled to interface fluctuations, and thus their magnitude cannot be assumed to be given by the near-equilibrium result (4). Including these modes in the stochastic analysis involves advanced methods [10], and is not pursued here. Since we expect $\lambda^*(\vec{x}, t) \to \infty$ as $t \to \infty$, our local equilibrium assumption becomes asymptotically correct. In addition, the number of linear eigenmodes with $\lambda > \lambda^*$ scales as $(\lambda^*/L)^{d-1}$, where L is the lateral size of the drop. Therefore, we expect Eq. (4) to provide a better description of the intermediate time dynamics in two-dimensional than in one-dimensional geometries.

In studying Eq. (4), our basic motivation was to understand the possible effects thermal fluctuations may have on the asymptotic rates of spreading, e.g., by modifying Tanner's law. With this view, we focused our analysis on two characteristic flow geometries: (i) one-dimensional drops confined in a channel of width W (Fig. 1), and (ii) two-dimensional radially symmetric drops. In the first case, Eq. (4) assumes the form

$$\frac{\partial h}{\partial t} = -\frac{\gamma}{3\eta} \frac{\partial}{\partial x} \left(h^3 \frac{\partial^3 h}{\partial x^3} \right) + \sqrt{\frac{2k_B T}{3\eta W}} \frac{\partial}{\partial x} [h^{3/2} \xi(x, t)]. \tag{7}$$

In the second case, Eq. (4) becomes

$$\frac{\partial h}{\partial t} = -\frac{\gamma}{3\eta} \frac{1}{r} \frac{\partial}{\partial r} \left[r h^3 \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial h}{\partial r} \right) \right] + \sqrt{\frac{2k_B T}{3\pi\eta}} \frac{1}{r} \frac{\partial}{\partial r} [h^{3/2} r^{1/2} \xi(r, t)]. \tag{8}$$

We simulated the volume-conserving spreading of a drop according to (7) by using finite-difference-based computational techniques as in [11], which guarantee non-negativity of the field $h(x, t)$ for the deterministic part of (7). In our simulations, the noise term is included in the right-hand side (RHS) of a spatial-temporal discrete version of Eq. (7), which is advanced in time through an implicit method. Non-negativity of $h(x, t)$ is implemented by a short-range repulsive potential between the liquid and the solid substrate, which should be included in the pressure in Eq. (4). We avoid the explicit use of such a potential by allowing numerical noise realizations only if they preserve the non-negativity of $h(x, t)$. Such a procedure induces correlations in the otherwise white noise field, which are unavoidable if the repulsive potential is not introduced

explicitly. In our simulations we use a nondimensional version of Eq. (7):

$$\frac{\partial \tilde{h}}{\partial \tilde{t}} = -\frac{\partial}{\partial \tilde{x}}\left(\tilde{h}^3 \frac{\partial^3 \tilde{h}}{\partial \tilde{x}^3}\right) + \sqrt{2\sigma}\frac{\partial}{\partial \tilde{x}}[\tilde{h}^{3/2}\xi(\tilde{x},\tilde{t})], \quad (9)$$

where $\tilde{h} = h/h_0$, $\tilde{x} = x/h_0$, $\tilde{t} = t/t_0$ where h_0 is the maximal height of the initial drop, $t_0 = 3\eta h_0/\gamma$, and $\sigma = k_B T/\gamma W h_0$. Our initial condition is a one-dimensional droplet with circular cross section, and a substrate wet by a precursor film of height b to ensure complete wetting (see Fig. 1). Physically, b is a scale below which short range forces (e.g., vdW interaction with a solid substrate for molecular fluids, or colloid diameter for colloidal suspensions) govern the surface dynamics.

Typical drop shapes obtained by averaging $\tilde{h}(\tilde{x},\tilde{t})$ over many realizations of Eq. (9) with several values of σ are presented in Fig. 2, and compared to the dynamics of a spreading drop governed by the deterministic Eq. (1). Figure 2 clearly indicates the effect of thermal fluctuations in enhancing the rate of spreading drops.

To gain some quantitative understanding of this effect, we measured the average rate by which characteristic lateral scales $\tilde{\ell}$ of the drop evolve for various magnitudes of the stochastic force, and compared them to Tanner's law in this geometry: $\tilde{\ell}_{\rm det} \sim \tilde{t}^{1/7}$. To estimate $\tilde{\ell}$ we have used the averaged second moment of the height profile,

$$\tilde{\ell} = \left\langle \left[\frac{1}{V}\int d\tilde{x}(\tilde{x}-\tilde{X})^2 \tilde{h}(\tilde{x},\tilde{t}) \right]^{1/2} \right\rangle, \quad (10)$$

where $\tilde{X} = [\int d\tilde{x}\,\tilde{x}\,\tilde{h}(\tilde{x},\tilde{t})]/V$ is the instantaneous droplet center position, $V = \int d\tilde{x}\,\tilde{h}(\tilde{x},\tilde{t})$ is the constant volume of the droplet, and $\langle\cdots\rangle$ represents an average over realizations of the noise $\xi(\tilde{x},\tilde{t})$. The results of this analysis are shown in Fig. 3(a), from which we extract a modified asymptotic spreading rate in volume-preserving one-dimensional flow geometry: $\tilde{\ell}_{\rm stoch} \sim \tilde{t}^{1/4}$. Obviously, the larger σ is the earlier is the deviation from Tanner's to the fluctuations-dominated asymptotic rate of spreading.

The appearance of a new power law for spreading suggests that the dynamics of the spreading drop is self-similar. The self-similarity is demonstrated through the excellent data collapse shown in Figs. 3(b) and 3(c). Indeed, the power law $\tilde{\ell}_{\rm stoch} \sim \tilde{t}^{1/4}$ follows by assuming a self-similar solution (in the statistical sense) of the form (3) to Eq. (9) [12]. Conservation of drop volume in one-dimensional geometry implies $\beta = 1$ in the self-similar form (3). Substituting this in Eq. (9) gives rise to two possible scalings. The first, obtained by assuming that the surface-tension term is dominant on the RHS of (9), is Tanner's law $\tilde{\ell}_{\rm det} \sim \tilde{t}^{1/7}$. By contrast, if the stochastic force is dominant, we consider a self-similar dynamics of the average $\langle\tilde{h}\rangle = f(|\tilde{x}|/\tilde{t}^{z})/|\tilde{x}|$. On the RHS of Eq. (9) we substitute the average stochastic force $\langle\xi\rangle = 1/\sqrt{\tilde{t}|\tilde{x}|}$ over a time interval $\tilde{t}$ and space interval $|\tilde{x}|$. Thus we obtain $\tilde{\ell}_{\rm stoch} \sim \tilde{t}^{1/4}$, in agreement with the simulations. Assuming the scaling relations $\tilde{h} \sim |\tilde{x}|^{-1}$ and $\tilde{t} \sim |\tilde{x}|^4$ we evaluate the surface-tension term in Eq. (9) as $|\tilde{x}|^{-8}$ and the average of the stochastic force as $\sqrt{2\sigma}|\tilde{x}|^{-5}$. Requiring dominance of the stochastic term and returning to dimensional variables, we obtain that the stochastic scaling behavior is expected for

$$|x| \gg x^*, \qquad h \ll h_0^2/x^*, \quad (11)$$

where $x^* = h_0^{7/6} W^{1/6}/\ell_T^{1/3}$ and $\ell_T = \sqrt{k_B T/\gamma}$. Thus, a necessary condition for observation of stochastic scaling behavior is $h_0 \gg W \gg \ell_T$. Typical values of ℓ_T are a few angstroms for molecular fluids (far from the critical point), or the colloid size a for colloidal suspensions [13]. Applying a similar analysis for the radially symmetric spreading, Eq. (8), shows that self-similarity dominated by the stochastic force gives an enhanced rate of spreading $\tilde{\ell}_{\rm stoch} \sim \tilde{t}^{1/6}$, compared to Tanner's law $\tilde{\ell}_{\rm det} \sim \tilde{t}^{1/10}$. The average stochastic force is dominant over surface tension if

$$r \gg h_0^{4/3}/\ell_T^{1/3}, \qquad h \ll h_0^{2/3}\ell_T^{1/3}, \quad (12)$$

and thus requires $h_0 \gg \ell_T$.

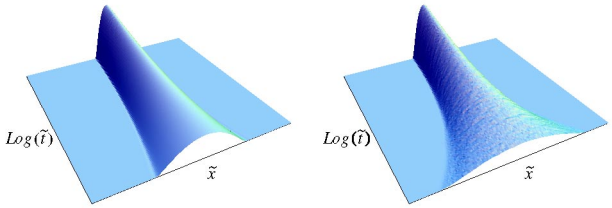

FIG. 2 (color online). Average shape of the droplet $\langle\tilde{h}(\tilde{x},\tilde{t})\rangle$ over 50 realizations as a function of time for zero temperature (left) and $\sigma = 10^{-2}$ (right). The right picture clearly shows the enhanced spreading of the droplet in the presence of thermal fluctuations. The numerical parameters used in this simulation are $\Delta\tilde{t} = 0.01$, $\Delta\tilde{x} = 0.05$, and $\tilde{b} = 0.01$.

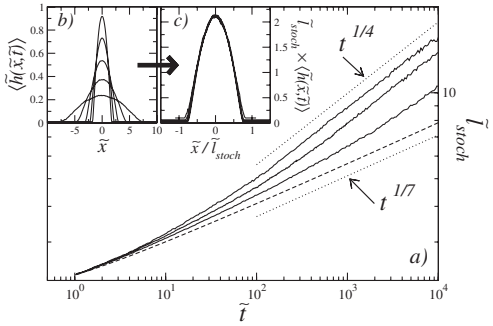

FIG. 3. Results of volume-conserving dynamics in one-dimensional geometry. (a) Lateral scale of the droplet (10) as a function of time. Solid lines represent averages over 50 realizations of (9) with $\sigma = 10^{-2}$, 5×10^{-3}, 10^{-3} (from top to bottom), while the dashed line is the noiseless ($\sigma = 0$) dynamics. Dotted lines correspond to the power laws $\tilde{t}^{1/4}$ and $\tilde{t}^{1/7}$. (b) Averaged profile of the droplet for times $\tilde{t} = 10^{3n/4}$, $n = 0, 1, 2, 3, 4$. (c) Rescaled droplet profiles.

For molecular fluids, the enhanced rates associated with stochastic scaling behavior can be observed if the stochastic force in Eq. (9) is dominant not only with respect to the surface-tension term as is expressed in (11) and (12), but also with respect to the vdW force that can be strong for thin films [14]. In the nondimensional units of Eq. (9) this force is $\frac{A}{\gamma h_0^2}\frac{\partial}{\partial \tilde{x}}(\tilde{h}^{-1}\frac{\partial \tilde{h}}{\partial \tilde{x}})$. For the one-dimensional geometry we use the scaling relations $\tilde{h} \sim |\tilde{x}|^{-1}$ and $\tilde{t} \sim |\tilde{x}|^4$ to compare between the average stochastic and vdW forces and obtain the additional condition for the stochastic scaling regime

$$x \ll h_0^{3/2}\ell_T^{1/3}/\ell_{\mathrm{vdW}}^{2/3}W^{1/6}, \tag{13}$$

where $\ell_{\mathrm{vdW}} = \sqrt{A/\gamma}$. An overlap between the intervals in Eqs. (11) and (13) is achieved if $h_0 \gg W(\ell_{\mathrm{vdW}}/\ell_T)^2$. Typical values of A are $100k_BT$ [14] and thus $\ell_{\mathrm{vdW}} > \ell_T$, and this overlap can be obtained for $h_0 \gg W \gg \ell_T$. Similar analysis for two-dimensional geometry yields the result $r \ll (h_0^{11}\ell_T^2/\ell_{\mathrm{vdW}}^4)^{1/9}$. Consistency of this condition with Eq. (12) is possible only if $h_0 \ll \ell_T^5/\ell_{\mathrm{vdW}}^4$, which seems unfeasible for typical fluids. We conclude that volume-preserving fluctuation dominated spreading can be observed for molecular fluids in one-dimensional flows if the initial height of the drop is large enough.

By contrast, the weak vdW attraction of complex fluids with a solid substrate is not expected to affect spreading, and thus we require the lateral scale (x for one- and r for two-dimensional geometries) $\ll h_0^2/a$ and $h \gg a$. An overlap with Eqs. (11) and (12) is achieved if $h_0 \gg (a^6W/\ell_T^2)^{1/5}$, $a^{3/2}/\ell_T^{1/2}$ for one- and two-dimensional geometries, respectively. Both conditions are easily realized if the initial drop is large enough.

Another spreading dynamics in which a stochastic scaling behavior might be observed is a ''leaking'' process, in which the height of the film at $x = 0$ is fixed to a constant value h_0 by a continuous supply of fluid. A self-similar dynamics in this case has the form (3) with $\beta = 0$. Following similar analysis, we obtain for one-dimensional geometry the scaling behaviors: $\tilde{\ell}_{\mathrm{det}} \sim \tilde{t}^{1/4}$, $\tilde{\ell}_{\mathrm{stoch}} \sim \tilde{t}^{1/3}$, while for two-dimensional geometry both $\tilde{\ell}_{\mathrm{det}}$ and $\tilde{\ell}_{\mathrm{stoch}} \sim \tilde{t}^{1/4}$. For the one-dimensional geometry we obtain an increased asymptotic rate of spreading due to thermal fluctuations. To check the realizability of the stochastic scaling regime, we compare the average stochastic force with surface-tension and vdW terms, using the scaling relations $\tilde{h} \sim$ const and $\tilde{t} \sim \tilde{x}^3$. For molecular fluids where vdW forces are important, the stochastic scaling behavior is expected in the regime $h_0^{3/2}W^{1/2}/\ell_T \ll x \ll h_0^{5/2}\ell_T/W^{1/2}\ell_{\mathrm{vdW}}^2$, which is again possible provided $h_0 \ll W(\ell_{\mathrm{vdW}}/\ell_T)^2$. Stochastic scaling behavior of a complex fluid drop under this condition is achieved if $h_0 \gg a$ and $x \gg h_0^{3/2}W^{1/2}/\ell_T$.

To conclude, we derived a Langevin lubrication Eq. (4), and showed that it gives rise to asymptotic behavior which is significantly different from Tanner's law of spreading. By comparing the average stochastic force with classical forces such as surface tension and van der Waals, we showed that fluctuation-assisted spreading is expected asymptotically in various flow geometries of molecular and complex fluids. Complex fluids are attractive candidates for studying the enhanced spreading rate phenomenon predicted in this Letter, since confocal microscopy techniques enable direct observation of interfacial thermal fluctuations in systems such as colloidal suspensions [13]. We believe that this result will motivate further studies of the role of thermal fluctuations in small dimensional systems.

We thank M. Brenner, R. Cuerno, and M. Kardar for useful discussions. This work was supported by Harvard MRSEC (DMR-0213085) (B. D. and H. A. S.) and by Ministerio de Ciencia y Tecnología (Spain) through Projects No. FIS2004-01001 and No. BFM2002-04474-C02 and the Real Colegio Complutense at Harvard University (E. M.).

Note added.—The same stochastic lubrication Eq. (4) was derived independently in a recent study of dewetting phenomena [15].

[1] L. Tanner, J. Phys. D **12**, 1473 (1979).
[2] P. Kavehpour, B. Ovryn, and G. H. McKinley, Phys. Rev. Lett. **91**, 196104 (2003).
[3] P. G. DeGennes, Rev. Mod. Phys. **57**, 827 (1985).
[4] J. Koplik, J. R. Banavar, and J. F. Willemsen, Phys. Fluids A **1**, 781 (1989); J. B. Freund, Phys. Fluids **15**, L33 (2003); G. He and N. G. Hadjiconstantinou, J. Fluid Mech. **497**, 123 (2003); D. R. Heine, G. S. Grest, and E. B. Webb, Phys. Rev. Lett. **95**, 107801 (2005).
[5] D. B. Abraham, R. Cuerno, and E. Moro, Phys. Rev. Lett. **88**, 206101 (2002).
[6] M. Moseler and U. Landman, Science **289**, 1165 (2000).
[7] L. M. Pismen and Y. Pomeau, Phys. Rev. E **62**, 2480 (2000).
[8] G. K. Batchelor, *An Introduction to Fluid Dynamics* (Cambridge University Press, Cambridge, England, 2000).
[9] E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics II* (Butterworth-Heinemann, Washington, DC, 1980).
[10] A. M. S. Tremblay, M. Arai, and E. D. Siggia, Phys. Rev. A **23**, 1451 (1981).
[11] See J. A. Diez, L. Kondic, and A. Bertozzi, Phys. Rev. E **63**, 011208 (2001), and references therein.
[12] A.-L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, England, 1995).
[13] D. G. A. L. Aarts, M. Schmidt, and H. N. W. Lekkerkerker, Science **304**, 847 (2004).
[14] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, New York, 1992).
[15] G. Grün, K. Mecke, and M. Rauscher (to be published); K. Mecke and M. Rauscher, J. Phys. Condens. Matter **17**, S3515 (2005).