Microscopic Model of Upward Creep of an Ultrathin Wetting Film

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We propose a microscopic, analytically solvable model describing the growth of a thin wetting film climbing on a solid wall (or a fiber) from the bath of liquid. We find analytically that both the length and the mass of the film grow with time t as $\sqrt{t}$, in accord with experimental observations, and specify the physical mechanism responsible for such behavior.

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Spreading of liquid droplets on surfaces and fibers plays a crucial role in numerous technologies including painting, coating, dyeing, gluing, and many others [1,2]. In all cases, efficient practical applications require precise knowledge of the conditions and laws of spreading. The behavior of the *macroscopic* properties characterizing spreading drops, e.g., the radius of the macroscopic liquid edge, the height, the profile, and contact angle, are presently well understood; these are described by universal Tanner laws [1–8]. In contrast, current understanding of remarkable universal spreading laws on a *microscopic,* molecular level, evidenced by recent experiments [9], still remains tentative and controversial [10].

The salient features at the microscopic scale is that a spreading drop is announced by a thin liquid film (precursor [11]) which precedes the macroscopic liquid edge. The film's thickness may vary from several (molecular size) to a few hundreds of angstroms. Refined ellipsometric measurements, carried out on different substrates and with various kinds of simple liquids, polymeric and surfactant melts, have scrutinized the growth of this film and reached a rather surprising conclusion: The length h_t of film obeys a universal law $h_t \propto \sqrt{t}$ [9,12], t being time, regardless of the nature of the species involved. The same holds also for the capillary rise geometry, in which a vertical wall is put into a contact with a bath of liquid. Here a film of microscopic thickness (or sometimes several monolayers) extracts from the macroscopic meniscus and creeps upwards along the wall. In this case, the length of the film follows the $\sqrt{t}$ law within an extended time domain [13], until it gets truncated at very high altitudes due to gravity. Additionally, spreading of macroscopic metallic beads on a horizontal vibrating corrugated surface also yielded the $\sqrt{t}$ law [14]. Therefore, as far as only time dependence is concerned, the $\sqrt{t}$ law turns out to be independent of the nature of the substrate and of the liquid, as well as of the geometry, intermolecular interactions, and size of molecules, which can be even macroscopic as in the case with beads: The prefactors in this law, of course, do depend on the system's parameters.

Theoretical studies of this phenomenon have been largely numerical [10,15–17], with the exception of a few analytical approaches. Continuum hydrodynamic theory elaborated in [6] attributed the origin of the $\sqrt{t}$ law to gradients of the disjoining pressure [1]. This theory is, however, justified [6] only until the thickness of the film remains at least in *mesoscopic* range, and thus does not explain the growth of molecularly thin films. In [13], this approach was empirically generalized to the microscopic scale, adopting a macroscopic description of [6], but assuming a different origin of frictional forces. A different approach has been proposed in [18], which viewed the liquid drop as an incompressible and completely layered structure, transport of molecules being allowed only in a "permeation ribbon" near the edges of successive layers. This picture yields the correct behavior of the advancing monolayers at long times, when one expects the difference between the radii of neighboring layers to be large. However, it does not account for the short-time regime. Besides, the validity of a macroscopic hydrodynamic description of dissipative forces, employed in [18], requires a more detailed microscopic justification [1]. An alternative description [19] employed the solid-on-solid model (SOSM) approximation and derived the spreading of a precursor film from the Langevin dynamics of a driven liquid-vapor interface. In [19], which ignored the molecular structure of the wetting film, the precursor was found, however, to advance at a constant speed, in disagreement with experimental observations.

In this paper we present first a microscopic model describing growth of the molecularly thin films, focusing on the capillary rise geometry, in which the solid immersed into the bath of liquid is either a flat plane or a cylidrical fiber. In our model we consider the liquid bath as a reservoir of particles and view the wetting film as a two-dimensional hard-sphere fluid, enclosed by the SOSM-type interface, which stabilizes fluid and mimics the presence of attractive forces between the fluid molecules. The fluid particles move under the action of random thermal forces and attractive van der Waals forces exerted by the solid. Besides, particles at the tip of the film [the boundary particles (BP), Fig. 1], which are in contact with the interface, experience an action of the "restoring" force exerted by the interface. In this approach we establish

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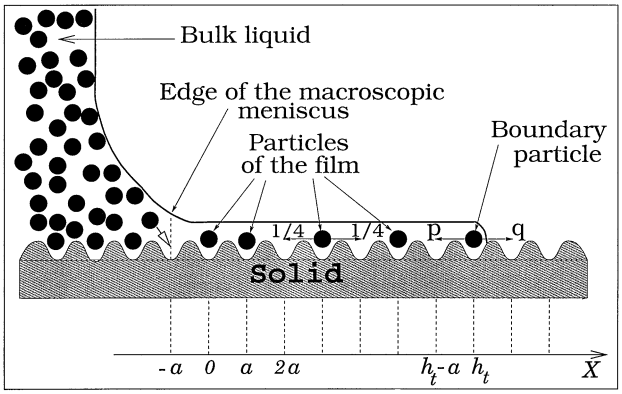

FIG. 1. Upward creep of a thin liquid film on a solid wall.

analytically the $\sqrt{t}$ law for growth of the film and find the dependence of the prefactor on pertinent parameters. We also determine the *microscopic* spreading parameter, which controls growth. Our results suggest the "vacancy-controlled" mechanism of the film growth; we show that the physical origin of the $\sqrt{t}$ law is due to the diffusive transport of vacancies from the tip of the film to the edge of the macroscopic meniscus (EMM), Fig. 1, where they are filled by fluid particles.

More specifically, we define our model as follows.

(a) We consider the liquid bath as a reservoir of particles, which maintains a constant particle concentration C_0 at the EMM. We estimate C_0 as follows: Suppose that one has a vacancy directly at the EMM and denote as $E_\downarrow$ the energy gained by moving a particle from the volume of the macroscopic meniscus onto this vacancy. The value of $E_\downarrow$ is determined by two factors—the energy gained due to the motion in the direction of the van der Waals forces and the energy lost due to the breaking of bonds with several fluid molecules, since for the particles in the volume of the meniscus the number of neighbors is greater than that for particles directly on the solid. Assuming $\beta E_\downarrow \gg 1$, where $\beta = 1/kT$, and employing standard Langmuir-type detailed balance arguments we have

$$C_0 \approx 1 - \exp(-\beta E_\downarrow). \tag{1}$$

(b) Consider next particles' dynamics on the solid surface which can be either planar (solid wall) or cylindrical (fiber). We view the motion of particles as an activated random hopping, constrained by hard-core interactions, between the local minima (with typical separation a) of a waferlike array of potential wells (wavy line in Fig. 1). Such wells occur due to the mutual interactions of the particles in the film (as for the motion in bulk liquids) and also because these move in the domain of short-range forces exerted by the atoms of the solid. Without going into details of these interactions, we suppose that for the transition to one of neighboring potential wells a fluid particle has to overcome a potential barrier. This barrier does not create a preferential hopping direction, but results in a finite time interval τ between the consecutive hops, defined through the Arrhenius formula. To specify the wells' positions, we introduce a pair of perpendicular axes (X, Y), X being a vertical coordinate, which measures the altitude of a given well above the EMM, while Y defines the horizontal position of this well along the EMM.

We assume that all particles (except the BP) have symmetric transition rates: a probability of hop in any of four directions is $\frac{1}{4}$. Then, the diffusion coefficient is $D = a^2/4\tau$. Hard-core interactions constrain particles' hopping motion; no two particles can simultaneously occupy the same well. Thus a hop is not fulfilled if the particle attempts to hop onto an occupied well.

(c) Now we define dynamics of the BP, which among all particles at a given Y are at the maximal altitude h_t. For the BP the hops down to the EMM and along the Y axis are constrained by hard-core interactions, while upward hops are unconstrained since wells above $X = h_t$ are always vacant. The most important point is that for the BP the choice of hopping direction is asymmetric along the X axis; we stipulate that upward hops occur with smaller probability (p) than downward hops (q), $p < q$.

Such an asymmetry may be roughly illustrated in terms of standard the SOSM approximation [19]. Here, the cost of interfacial energy F for having a film of length h_t (Fig. 1) is $F = Jh_t$, where the prefactor J is related to the surface tension of the liquid-vapor interface. Consequently, the interface exerts a constant pressure on the film or, in other words, the BP experiences an action of a constant "restoring" force $f = -\partial F/\partial h_t = -J$, which favors its hops downwards to the EMM.

Here we will, however, phrase it differently. The microscopic origin of the asymmetric hopping rates stems from the particle-particle interactions in the film. Typical interactions in real systems are characterized by a harsh repulsion of a hard-core type at short scales and attraction at longer distances. Now, upward and downward hops of the BP do not change the number of particles at a given Y but result in stretching or shrinking of the film. Thus the change in the length of the film comprising a fixed number of particles results in the change of energy. Stretching of the film (an upward hop of the BP) will lead to an increase of energy. Conversely, shrinking of the film decreases, on average, the interparticle distances and thus results in a decrease of energy. In other words, the presence of particle-particle attraction results in correlations between the local transition rates and spatial distribution of particles; these tend to move towards the spatial regions in which the particle concentration is high. Since the concentration is maximal at the EMM and decreases with an increase of altitude, the particles in the film experience, on average, an action of a force which is directed to the EMM. In our model this circumstance will be taken into account by introducing an integral (over all particles of the film) force which acts on the BP only, which is equivalent to the presence of a SOSM-type

interface with some effective surface energy $W_{\leftarrow}$. In view of previous discussion, we will define $W_{\leftarrow}$, which is the difference of energies lost and gained due to the upward and downward hops of the BP, as the work required to transport a vacancy from the tip of the film to the EMM. Using detailed balance arguments we obtain

$$p/q = \exp(-\beta W_{\leftarrow}). \tag{2}$$

Note that $W_{\leftarrow}$, by definition, equals the difference of the potential energy of vacancy placed at the EMM and the potential energy of vacancy at the tip of the film, and hence is independent of the length and mass of film.

Next, we turn to the mathematical description of the film's growth defined by (a) to (c). We introduce $C(X, Y, t)$ the time-dependent occupation variable of the well with coordinates (X, Y). We note that the origins of the X and Y dependences of $C(X, Y, t)$ are quite different. Along the X axis we have a fixed boundary condition at $X = -a$ and well-defined "restoring" force acting on the BP. Consequently, we may expect a regular shape of $C(X, Y, t)$ along the X axis. In contrast, there is no regular Y dependence; despite the uniform boundary at the EMM, the particle dynamics may cause fluctuations along the Y axis. Here we ignore these fluctuations [20] and suppose that the particle concentration varies along the X axis only, $C(X, Y, t) = C(X, t)$. Then, $C(X, t)$ is a variable describing occupation of the site X in a stochastic process in which hard-core particles perform hopping motion, with the time interval τ between the consecutive hops, on a one-dimensional lattice of spacing a. All particles, except the BP, have probabilities $\frac{1}{4}$ for hops from X to $X \pm a$, and probability $\frac{1}{2}$ to stay at X (arising from the hops along the Y axis). The BP, being at X, may jump to $X + a$ with probability p and to $X - a$ with probability q ($p + q = \frac{1}{2}$), provided that this site is vacant; and may remain at X with probability $\frac{1}{2}$. Finally, a source at $X = -a$ maintains a fixed occupation of this site. This process is a generalization of a "directed walk in a lattice gas" model, studied analytically and numerically in [21] and here we will extend the previously elaborated continuous space and time description to the process under study.

We start with the dynamics of the BP. Its mean displacement h_t obeys the following exact equation:

$$\tau \frac{dh_t}{dt} = ap - aq(1 - C_1), \tag{3}$$

where $C_1 = C(X = h_t - a, t)$, i.e., the mean occupation of the site adjacent to the position of the BP. Equation (3) shows that hops away from the EMM occur at rate ap/τ and are unconstrained, while hops in the direction to the EMM have a rate aq/τ and are constrained by factor $1 - C_1$, i.e., the probability that site $X = h_t - a$ is vacant.

Consider now the evolution of $C(X, t)$ on sites X of the interval $[0, h_t - 2a]$. The particles, which may be present at this interval, all have equal probabilities of hops up and down and all are indistinguishable. In consequence, a forbidden attempt of any particle to hop onto an occupied well is equivalent to the event when both particles interchange their positions, which means that hard-core exclusion is not important on this interval. Thus, as a reasonable approximation we suppose that $C(X, t)$ obeys (for $t \gg \tau$) the diffusion equation

$$\frac{\partial C(X,t)}{\partial t} = D \frac{\partial^2 C(X,t)}{\partial X^2}, \quad D = \frac{a^2}{4\tau}. \tag{4}$$

Finally, the dynamics of $C(X, t)$ at $X = h_t - a$, for which effects of the hard-core exclusion do matter because of the asymmetry induced by the BP, is governed by

$$\frac{dC_1}{dt} = -\frac{a}{4\tau} \frac{\partial C(X,t)}{\partial X}\bigg|_{X=h_t-a} - \frac{C_1}{a}\frac{dh_t}{dt}, \tag{5}$$

where the gradient term accounts for the exchange of particles between the sites $h_t - 2a$ and $h_t - a$. The second term describes the "birth" of vacancies at $X = h_t - a$ due to the motion of the BP away from the EMM. The factor C_1 arises due to the fact that occupation of the site $X = h_t - a$ is changed (in the moving frame) only if this site was occupied before the BP's hop.

Now we have a complete, coupled system of Eqs. (3)–(5) describing particles' dynamics and evolution of h_t. We express $C(X, t)$ in terms of a scaled variable $\omega = (X + a)/h_t$. Then Eq. (4) takes the form

$$\frac{d^2 C(\omega)}{d\omega^2} + A_m \omega \frac{dC(\omega)}{d\omega} = 0, \quad A_m = \frac{1}{2D}\frac{dh_t^2}{dt}. \tag{6}$$

Hence, A_m is the key parameter which determines the growth of the film. To find it we first solve Eq. (6) subject to boundaries $C(\omega = 0) = C_0$ and $C(\omega = 1) = C_1$:

$$C(\omega) = C_0 + (C_1 - C_0)\frac{\mathrm{erf}(\omega\sqrt{A_m/2})}{\mathrm{erf}(\sqrt{A_m/2})}, \tag{7}$$

where $\mathrm{erf}(x)$ denotes the error function. Then, inserting Eq. (7) into Eq. (5) and employing Eqs. (3) and (6) we find

$$\sqrt{\frac{\pi A_m}{2}} \exp\left(\frac{A_m}{2}\right) \mathrm{erf}\left(\sqrt{\frac{A_m}{2}}\right) = \frac{p - q + qC_0}{q - p}. \tag{8}$$

From Eq. (8) we infer that A_m is a well-defined constant (except for the case $p = q$ which will be studied separately). Hence, Eq. (6) yields

$$h_t = \sqrt{2A_m DT}, \tag{9}$$

i.e., the experimentally observed behavior [9,13].

Now, we estimate from Eq. (8) the form of A_m in the asymptotic limits when A_m is small or large. We find that when either $\beta W_{\leftarrow} \gg 1$ or $\beta s \ll 1$, where

$$s = E_{\downarrow} - W_{\leftarrow}, \tag{10}$$

the parameter A_m is small and follows

$$A_m \approx \frac{1 - \exp(-\beta s)}{\exp(\beta W_{\leftarrow}) - 1}. \tag{11}$$

Let us note that growth of the film ($A_m > 0$) occurs as long as s is positive. Therefore, by analogy with the spreading parameter S [1,2] which controls the wetting transition at macroscopic scales, we call s the *microscopic* spreading parameter. This parameter equals the difference of the energy gained by filling a vacancy at the EMM by a fluid particle and the work required to transport this vacancy from the tip of film to the EMM.

Now, when $\beta W_{\leftarrow} \ll 1$ and βs is sufficiently large, A_m may be large. In this limit it reads

$$A_m \approx -2\ln(\beta W_{\leftarrow}) + \ln(2[1 - \exp(-\beta s)]^2/\pi). \quad (12)$$

Behavior as described by Eq. (12) may occur for liquids which are volatile in two dimensions [9], since it is appropriate to situations with low surface tension ($\beta W_{\leftarrow} \ll 1$) and strong attraction to the solid surface ($\beta E_{\downarrow} \gg 1$).

Next, we may estimate the mass of the film. Integrating $C(X, t)$ from $-a$ to $h_t - a$ and using Eq. (7) we find

$$M_t = h_t \exp(A_m/2)[1 - \exp(-\beta W_{\leftarrow})], \quad (13)$$

which shows that M_t also grows in proportion to $\sqrt{t}$, in accord with experimental observations [9,22].

In conclusion, we have presented a microscopic model describing the growth of a thin wetting film climbing along a solid wall from bath of liquid. In terms of this model we have established analytically the $\sqrt{t}$ law for the growth of the film's length and mass, i.e., experimentally observed behaviors, and also determined the *microscopic* spreading parameter. We have shown that, in accord with observations made in numerical simulations [17], the physical mechanism responsible for such a growth is associated with the diffusive transport of vacancies from the tip of the film to the edge of the macroscopic meniscus, where they get filled with fluid particles.

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