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Dewetting, partial wetting, and spreading of a two-dimensional monolayer on solid surface

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We study the behavior of a semi-infinite monolayer, which is placed initially on a half of an infinite in both directions, ideal crystalline surface, and then evolves in time due to random motion of the monolayer particles. Particles dynamics is modeled as the Kawasaki particle-vacancy exchange process in the presence of long-range attractive particle-particle interactions. In terms of an analytically solvable mean-field-type approximation we calculate the mean displacement $X(t)$ of the monolayer edge and discuss the conditions under which a monolayer spreads [$X(t)>0$], partially wets [$X(t)=0$], or dewets from the solid surface [$X(t)<0$]. [S1063-651X(98)50807-0]

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Dynamics and static properties of thin liquid films on solid surfaces have been studied for many years, resulting in a seemingly good understanding of the problem [1,2]. However, with the advent of new experimental techniques, that enable one to study properties of molecularly thin (MT) films, it has become clear that the developed theoretical concepts apply only to sufficiently thick films; for MT films significant departures from the standard behavior have been observed [3,4]. In particular, several remarkable features have been revealed by ellipsometric studies of the MT precursor films, i.e., films emitted by (sessile) liquid drops placed on solid substrates [4].

First, such films have been detected even in the case of nonwetting drops. This implies that physical conditions at which such a MT film appears may be different from the ones corresponding to the wetting/dewetting transition at *macroscopic* scales. Next, precursors do not spread at a constant rate; the mean displacement of the film's edge grows with time t only in proportion to $\sqrt{t}$. Last, ''fine structure'' of the MT precursors may be very different; in some cases the film's density shows a pronounced variation with the distance from the macroscopic drop, which reveals the surface-gas-like, rather than the liquidlike behavior. In other systems, the films are dense and compact. Even more striking, on the intermediate-energy substrates surprising ''terraced'' patterns appear, formed by several superimposed MT precursors each spreading at the $\sqrt{t}$ rate on top of lower layers.

Meanwhile, several attempts have been made to explain why do the MT precursor films spread at the $\sqrt{t}$ rate. Reference [5] proposed a ''stratified droplet'' model, in which a sessile drop is regarded as a succession of horizontal layers, each layer being a two-dimensional, incompressible Navier-Stokes liquid. This model suggests that the $\sqrt{t}$ law results from the competition between the liquid-solid attractions, which represent the driving force of spreading, and viscous-type frictional forces, which control particles dynamics on the solid surface. We note parenthetically that similar ideas have been used to describe dynamics of the reverse processes: dewetting of a monolayer [6] and squeezing of a MT lubricating film out of a gap between two solids [7], for which it has been also predicted that the radii of the dewetted areas grow at the $\sqrt{t}$ rate. Next, Ref. [8] described droplet spreading in terms of the Langevin dynamics of a nonvolatile fluid edge, modeled by horizontal solid-on-solid-model strings. Such an approach has reproduced the ''terraced'' profiles; the $\sqrt{t}$ law was found, however, only as a transient regime. Lastly, in a microscopic approach of Refs. [9] the MT film was considered as a lattice gas of interacting particles connected to a reservoir (droplet). Here, the $\sqrt{t}$ law was obtained for both precursors of the sessile drops and creeping films in the capillary rise geometries; it was claimed that such a behavior is controlled by migration of voids from the advancing edge of the film to the reservoir.

Despite reasonably good explanation of the dynamical behavior, provided by Refs. [5,8,9], several fundamental questions still remain largely unanswered. In particular, the dependence of the prefactor in the $\sqrt{t}$ law on the temperature, k_BT, and on the parameters of the interaction potentials has not been elucidated so far. As a matter of fact, the model of Ref. [5] discards the effects of the drop's surface tension and/or of the monolayer edge tension γ_e on spreading kinetics. In consequence, Ref. [5] predicts that ''terraced'' spreading appears as soon as any kind of attractive liquid-solid interactions (LSI) is present, which contradicts apparently to the experience [4]. Contrary to Ref. [5], the models of Refs. [8] and [9] take γ_e into account and show that the film may actually appear only if the strength of the LSI exceeds certain threshold value. However, a common subtle point of both Refs. [8] and [9] is that the prefactor in the $\sqrt{t}$ law is expressed in terms of several parameters, which are assumed to be independent of the dynamics; in Refs. [9], for instance, these are the particle density in the reservoir and γ_e. On the other hand, γ_e originates from attractive liquid-liquid interactions (LLI) and thus depends on the density profile in the film. The latter is itself dependent on the spreading rate, and hence, on γ_e. Therefore, the calculation of γ_e and, consequently, of the prefactor in the $\sqrt{t}$ law requires a solution of essentially a nonlinear dynamical problem in which attractive LLI are taken into account explicitly.

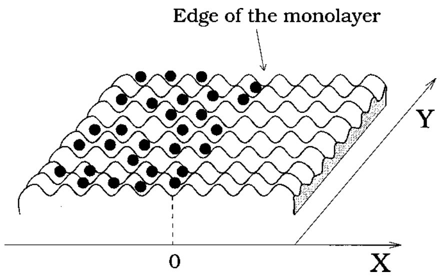

FIG. 1. Initial configuration of a monolayer on top of a solid surface. Wavy lines depict the potential energy landscape created by the solid atoms.

In this Rapid Communication we study analytically the behavior of a liquid monolayer, which occupies initially a bounded, macroscopically large area of the solid surface, and then evolves in time due to random motion of the monolayer particles. Particles' dynamics is modeled as the Kawasaki-type particle-vacancy exchange process in the presence of short-range repulsive (hard-core) and weak long-range attractive particle-particle interactions. Here we consider a simple case when the initially occupied region is the half-plane $-\infty < X \leqslant 0$, Fig. 1, and calculate the mean displacement $X(t)$ of the monolayer edge. We note that our results apply, as well, to the intermediate time behavior in several other two-phase geometries. Particularly, the initially dewetted region can be a hole of radius R, nucleated in a homogeneous monolayer, or the monolayer can occupy a circular region of radius R, which is a situation that appears at the late stages of sessile drops spreading [4]. For such geometries, our results describe the kinetics on time scales such that $X(t) \ll R$, in which regime the precise form of the phase-separating boundary is not important (see, e.g., Refs. [9]).

To determine the time evolution of $X(t)$, we develop a mean-field-like, self-consistent approach, in which the nonlinear coupling between the density distribution in the spreading film and the edge tension γ_e is taken into account explicitly. Within this approach we recover the result of Refs. [9], i.e., the law $X(t) = A\sqrt{D_0 t}$, in which D_0 is the bare diffusion coefficient describing dynamics of an isolated particle on the solid surface. Here, however, we define the prefactor A explicitly as a function of $k_B T$ and of the interaction parameters. We show that A can be positive or negative, which means that the monolayer can spread, partially wet or dewet from the solid surface, and determine the temperature $T_{w/dw}$ of the wetting-dewetting transition in the monolayer regime. Moreover, we find that spreading of the monolayer can proceed quite differently at different T, which agrees with the experimentally observed behavior [4]. When $T \geqslant T_b$, where T_b is also found explicitly, we have that $\gamma_e \equiv 0$, $A \sim \sqrt{\ln(t)}$ as $t \to \infty$, and the density in the monolayer varies strongly with the distance from the edge. We remark that this finding contradicts Refs. [9], which suggest that such a ''surface-gas''-like spreading may take place only in the absence of attractive LLI. For lower T, such that $T_{w/dw} \leqslant T < T_b$, we find that the density variation is less pronounced and both A and γ_e are positive and constant, which signifies that in this T range the monolayer spreads as a ''liquid.'' Last, for $T < T_{w/dw}$ the monolayer dewets from the surface.

The model to be studied here is defined as follows:

(i) The particles experience two types of interactions, the LLI and LSI. The LSI create effectively a lattice of potential wells (with the coordination number z and the interwell distance σ), such that the particles reside in the local minima of these wells. We assume that the LSI correspond to the limit of the so-called intermediate localized adsorption, which is appropriate for many adsorbates and persists over a wide T range [2]. In this limit the particles are neither completely fixed in the wells, nor completely mobile: The LSI wells are deep with respect to desorption (desorption barrier $U_d \gg k_B T$) so that only a monolayer can exist, but have much lower barrier U_1 against the movement across the surface. Further on, we suppose that the LLI are two-body, central, and additive; the LLI potential $U(r)$ is a hard-core at distance $r = \sigma$, which means that each well can be occupied by one particle at most, and is attractive for $r > \sigma$, $U(r) = -U_0(T)(\sigma/r)^n$, $n > 2$. The parameter $U_0(T) \ll U_d$, which is the case for many realistic situations [2] and which implies that the LLI incur only small local perturbations to the array of the LSI wells.

(ii) Occupation of the well with radius-vector $\mathbf{r}$ at time t is described by the variable $\eta(\mathbf{r};t)$, which can assume two values, 0 and 1; its realization average value, i.e., the local density, is denoted as $\rho(\mathbf{r};t) = \overline{\eta(\mathbf{r};t)}$. The initial configuration of the monolayer is depicted in Fig. 1, i.e., the monolayer particles are placed at random positions and at a fixed coverage $\rho < 1$ (number of occupied wells as a fraction of the total number of wells per unit area) in the wells of the half-plane $-\infty < X \leqslant 0$.

(iii) The particles motion is activated by chaotic vibrations of solid atoms and proceeds by rare events of hops between the local minima of adjacent wells. In absence of the LLI, one may estimate the diffusion coefficient for such a motion to be $D_0 \approx \omega\sigma^2/z$, where ω is the frequency of hops. Now, the LLI couple the dynamics of any given particle to the motions of all other particles: first, hard-core repulsion prevents multiple occupancy of any potential well; second, on escaping from the well with radius-vector $\mathbf{r}$, any given particle follows preferentially the local gradient of the LLI potential landscape $U(\mathbf{r};t)$,

$$U(\mathbf{r};t) = -U_0(T)\sigma^n \sum_{\mathbf{r}''} \frac{\eta(\mathbf{r}'';t)}{|r-\mathbf{r}''|^n}, \tag{1}$$

where the summation extends over the entire lattice, excluding $\mathbf{r}'' = \mathbf{r}$. To take the LLI into account, we stipulate that for any given particle leaving the well with radius-vector $\mathbf{r}$ at time moment t, the choice of the jump direction is random and governed by the position-and time-dependent probabilities [10],

$$p(\mathbf{r}|\mathbf{r}'_z) = Z^{-1} \exp\left(\frac{\beta}{2}\left[U(\mathbf{r};t) - U(\mathbf{r}'_z,t)\right]\right), \tag{2}$$

where $\mathbf{r}'_z$ is the radius-vector of one of z wells, adjacent to the well at $\mathbf{r}$, $\beta = 1/k_B T$, and Z denotes the normalization factor. When the jump direction is chosen, the particle attempts to hop into the target well. The hop is fulfilled if this well is unoccupied; otherwise, the particle attempting to hop is repelled back to the well at $\mathbf{r}$.

We proceed further on by assuming local equilibrium (see, e.g., Refs. [10]), which implies that occupations of different wells factorize and thus allows for the description in terms of local densities, $\rho(\mathbf{r};t)$. For these, we find

$$\frac{1}{\omega}\frac{\partial}{\partial t}\rho(\mathbf{r};t)=-\rho(\mathbf{r};t)\Sigma_{r_z'}\overline{p(\mathbf{r}|\mathbf{r}_z')}[1-\rho(\mathbf{r}_z';t)]+[1-\rho(\mathbf{r};t)]\Sigma_{r_z'}\overline{p(\mathbf{r}_z'|\mathbf{r})}\rho(\mathbf{r}_z';t), \quad (3)$$

in which $\overline{p(r|r_z')}$ are determined by Eqs. (2) and (1) with $\eta(r;t)$ replaced by $\rho(\mathbf{r};t)$. Equation (3) has to be solved subject to the initial condition that $\rho(\mathbf{r};t=0)=0$ for $X>0$ and $\rho(\mathbf{r};t=0)=\rho$ for $X\leqslant 0$.

Let us analyze now, on the basis of Eq. (3), the time evolution of the mean displacement $X(t)$ of the monolayer edge. To do this, we follow Refs. [9], supposing that for the long-ranged, but rapidly vanishing LLI a hop of any particle which is not directly at the edge does not change the energy in Eq. (1). This means, in virtue of Eq. (2), that for such particles all hopping directions are equally probable and their migration on the surface is constrained by the hard-core interactions only. The particles being at the edge, however, are effectively attracted by the ''bulk'' monolayer, which results in asymmetric hopping probabilities (see Refs. [9] for more details). We note that such an approximation is actually a translation onto the molecular level of standard descriptions of the liquid front dynamics as a competition between surface tension and internal pressure [1,2].

Further on, since we are interested in the behavior of the mean displacement of the edge, it is justified to neglect the fluctuations around $X(t)$ along the Y axis. Consequently, we suppose that the edge position does not depend on Y, Fig. 1, which makes the system effectively one-dimensional and the original two-dimensional geometry enters only through the 2D diffusion coefficient D_0 and 2D edge tension [see Eq. (9)].

Now, the one-dimensional model we have to study consists of a 1D hard-core lattice gas, which is put initially into a ''shock'' configuration and then evolves in time by particles attempting to hop to the nearest unoccupied sites. The ''shock'' configuration means that all particles are placed at random with a fixed mean density ρ at the sites $-\infty<X\leqslant 0$ of an infinite in both directions 1D lattice. All particles, except the rightmost one (RMP), which defines position of the edge, have equal probabilities ($=1/z$) for hopping to the left or to the right. The RMP, whose position is $X(t)$, is attracted by the gas particles and thus has asymmetric hopping probabilities, which obey Eq. (2) with $\eta(\mathbf{r};t)$ replaced by $\rho(\mathbf{r};t)$.

To determine $X(t)$ we now proceed as follows. Recollecting first the results of Refs. [9], we anticipate that at sufficiently large times the particle density past the RMP tends to some constant value. This implies, in virtue of Eqs. (1) and (2), that $p(X(t)|X(t)\pm\sigma)$ approach limiting values $p_{\pm}$, which are independent of $X(t)$ and t. Solving next the problem for arbitrary fixed $p_{\pm}$, we determine $X(t)$ and the density profile $\rho(\lambda;t)$, λ being the distance from the edge, $\lambda=X(t)-X$. Finally, inserting $\rho(\lambda;t)$ into Eqs. (1) and (2), we find the closure equation, which determines $p_{\pm}$ (and hence, A) self-consistently as functions of k_BT and of the LLI parameters.

The dynamics of a biased RMP in a 1D hard-core gas, placed in the just described ''shock'' configuration, has been studied in Ref. [11]. It was shown that $X(t)$ obeys

$$X(t)=A\sqrt{D_0 t}, \quad (4)$$

where the prefactor A is defined for $p_->p_+$ by

$$\frac{\sqrt{\pi}\,A}{2}\exp\left(\frac{A^2}{4}\right)\left[1+\Phi\left(\frac{A}{2}\right)\right]=\frac{\rho p_-}{p_--p_+}-1, \quad (5)$$

$\Phi(x)$ being the probability integral. In the special case $p_-=p_+$, A is no longer constant and grows with time as

$$A\propto\sqrt{2\ln\left(\frac{\rho^2\omega t}{\pi}\right)}, \quad \text{as } t\to\infty. \quad (6)$$

Next, it was found that the density profile $\rho(\lambda;t)$ past the RMP has a characteristic S-like shape; $\rho(\lambda;t)$ is almost *constant* (and different from ρ) in a region of size $\sim X(t)$,

$$\rho(\lambda;t)=\left(1-\frac{p_+}{p_-}\right)\left[1+\frac{A^2\lambda}{X(t)}+O\left(\frac{A^4\lambda^2}{X^2(t)}\right)\right], \quad (7)$$

while for greater λ, $\lambda\gg X(t)/A^2$, it approaches ρ exponentially fast. Such a form of $\rho(\lambda;t)$ stems from the fact that vacancies propagate into the gas-phase only diffusively and thus homogenize the density distribution past the RMP only at scales of order of $X(t)$. Note, however, that the total number of particles is conserved i.e., $\lim_{L\to\infty}L^{-1}\int_0^L d\lambda\,\rho(\lambda;t)=\rho$.

Turning now back to the 2D problem under study, we recall that $p_{\pm}$ are not arbitrary parameters, but their values are determined by the density distribution past the edge. Inserting Eq. (7) into the Eqs. (1) and (2), we find the self-consistent closure equation for p_+/p_-,

$$\frac{p_+}{p_-}=\exp(-\beta\sigma\gamma_e);\quad \gamma_e=\left(1-\frac{p_+}{p_-}\right)\frac{U_0(T)\delta}{2\sigma}, \quad (8)$$

$$\delta=\sigma^n\sum_{r'',\mathbf{r}''\neq\mathbf{r}_{\pm}}\left\{\frac{1}{|\mathbf{r}_--\mathbf{r}''|^n}-\frac{1}{|\mathbf{r}_+-\mathbf{r}''|^n}\right\}, \quad (9)$$

where $\mathbf{r}_{\pm}$ denote the 2D vectors $(X(t)\pm\sigma,Y)$.

Therefore, we find that the mean displacement of the monolayer edge obeys Eq. (4), in which A is related to $U_0(T)$, ρ, and β through Eqs. (5) and (8). Below we present some analytical estimates of $A(\varepsilon)$, where $\varepsilon=\beta U_0(T)\delta/2$ is a critical dimensionless parameter.

We find that depending on the value of the parameter ε four different regimes can be observed:

(1) When $\varepsilon\in[0;1]$ the only solution of Eq. (8) is $p_+/p_-=1$, which means that here $\gamma_e\equiv 0$ and the monolayer behaves as an ideal surface gas. In this regime $X(t)\sim\sqrt{t\ln(t)}$ and the density $\rho(\lambda;t)$ changes rapidly with the distance λ from the edge being equal to ρ for $\lambda\to\infty$ and to zero for $\lambda=0$.

(2) When $\varepsilon \in]1;\varepsilon_c[$, where $\varepsilon_c = -\ln(1-\rho)/\rho$, the prefactor A is positive and finite. Here, $X(t) \sim \sqrt{t}$ and the monolayer also wets the solid. The edge tension $\gamma_e > 0$ and vanishes as $\gamma_e \sim (T_b - T)$ when $T \to T_b$; T_b is thus the critical temperature of the surface gas-liquid transition, which is defined implicitly by equation $T_b = U_0(T_b)\delta/2k_B$, $(\varepsilon=1)$. In this regime A diverges when $\varepsilon \to +1$, $A \approx \sqrt{\ln[\rho/(\varepsilon-1)]}$, and vanishes when $\varepsilon \to \varepsilon_c$, $A \approx (1-\rho)(\varepsilon_c - \varepsilon)/[1-(1-\rho)\varepsilon_c]$. The density $\rho(\lambda;t)$ changes smoothly from the unperturbed value ρ to the value at the edge $\exp(-\beta\sigma\gamma_e)$, which is close to ρ.

(3) At $\varepsilon = \varepsilon_c$ the prefactor A is exactly equal to zero and the monolayer partially wets the substrate. Hence, we denote $\varepsilon = \varepsilon_c$ as the point of the wetting-dewetting transition for the monolayer. The corresponding critical temperature is determined by $T_{w/\mathrm{dw}} = U_0(T_{w/\mathrm{dw}})\delta/(2k_B\varepsilon_c)$ and depends on the coverage ρ. We note that $T_{w/dw}$ and T_b are simply related to each other. When $U_0(T)$ is independent of T (say, for London-type LLI) one has $T_{w/dw} = T_b/\varepsilon_c$. Actually, the inset in Fig. 2 displays the ρ dependence of the ratio $T_{w/dw}/T_b(=1/\varepsilon_c)$ for this case. For the Keesom-type interactions, when $U_0(T) \sim 1/T$, $T_{w/dw} = T_b/\sqrt{\varepsilon_c}$. We finally remark that the relation between ε and ε_c distinguishes whether it is favorable, at given physical conditions, to have a monolayer with coverage ρ on the solid surface or not. Consequently, knowing ε_c and the density distribution in a sessile drop with the respect to the height above the substrate, one can predict the number of superimposed layers in the ''terraced wetting'' regime.

(4) For $\varepsilon > \varepsilon_c$ the prefactor $A < 0$ and the monolayer dewets from the substrate. Here, a jammed region [where $\rho(\lambda;t) > \rho$, Eq. (7)] of size $\sim X(t)$ appears, which impedes the motion of the retracting edge; the ε dependence of A is thus very weak, being strongly limited by the diffusive squeezing out of ''voids'' at progressively larger and larger scales. In fact, for sufficiently large ε one may expect that the dewetting process will be accelerated by thickening of the monolayer, as is suggested in Ref. [6].

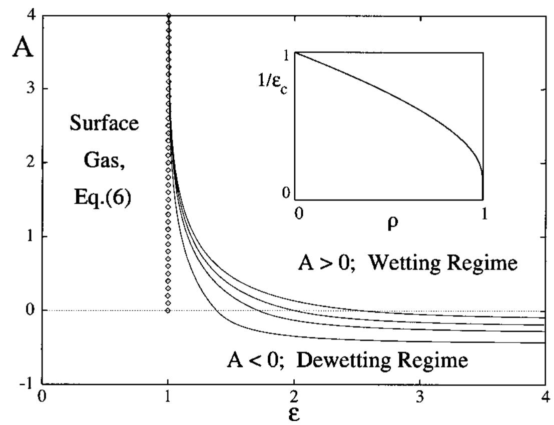

FIG. 2. Numerical solution of Eqs. (5) and (8). Solid lines from top to bottom show the dependence of A on dimensionless parameter ε for $\rho = 0.9$, 0.8, 0.7, and 0.5, respectively. The line $\epsilon = 1$ separates the ''surface gas'' and liquidlike phases. The inset displays the ρ dependence of ε_c, $[A(\varepsilon_c) = 0]$.

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