Variational theory of preroughening

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Saito’s variational mean-field theory of roughening [Y. Saito, Z. Phys B 32, 75 (1978)] is generalized to include preroughening. The starting point is a sine-Gordon Hamiltonian with a cosine parameter changing sign at a temperature $T_{PR}$. This theory accounts for a number of known features of preroughening from solid-on-solid lattice models, including logarithmic divergence of the average interface width as a function of the system size and continuous crystal growth at $T_{PR}$. When $T_{PR}$ reduces to one quarter of the roughening temperature or less, preroughening becomes first order. We also consider adsorption over an attractive substrate. Using our variational theory, we calculate adsorption isotherms. They show a reentrant layering pattern, which connects well with observations for noble gases adsorbed on graphite. [S0163-1829(98)05543-X]

I. INTRODUCTION

Since the introduction of the preroughening (PR) transition of crystal surfaces by Den Nijs and Rommelse, a number of theoretical approaches, and of numerical studies of solid-on-solid lattice models as well as of step models, have clarified the behavior at this unusual phase transition. Here we list a number of well-established results. The average surface height jumps from roughly integer in the smooth, or ordered flat phase, below PR, to roughly half-odd integer values in the disordered flat (DOF) phase, above PR. The average square height difference diverges logarithmically approaching the (isolated) PR transition temperature $T_{PR}$. The surface-specific heat has a nonuniversal singularity at PR. 

Clearcut experimental evidence of a surface PR transition on e.g., metal surfaces, has apparently not yet been identified, possibly due to slow kinetics or to associated phase-separation phenomena between DOF phases with neighboring heights. However, reentrant layering has been observed in adsorption isotherms for several rare gases on graphite, and has been attributed to PR. Preroughening is also found in realistic Lennard-Jones surface simulations, where it appears to mark the onset of surface melting.

Surprisingly enough, there is as yet no mean-field treatment of PR for comparison with this wealth of theoretical, experimental, and simulation evidence. In the present paper, Saito’s treatment of the roughening transition, which employs a variational, mean-field approach to study surface equilibrium, supplemented by a Langevin equation for growth and dynamics, is extended to PR. The extension is obtained simply by allowing, phenomenologically, the cosine parameter of the sine-Gordon trial Hamiltonian to become negative at a temperature $T_{PR}$ (the PR temperature) below $T_R$. In this way, we are able to reproduce, qualitatively in all cases, exactly in some cases, the known phenomenology related to PR and to the DOF phase.

This paper is organized as follows. After an initial review in Sec. II of known results which will be needed later, we present in Sec. III our model and the variational derivation of its static properties, and in Sec. IV a numerical exemplification of the equilibrium phase diagram in a variety of conditions. Then, in Sec. V, we consider growth, by analyzing the dynamical response to a chemical-potential driving force. In Sec. VI, we consider adsorption on a substrate, and derive adsorption isotherms, which are in their turn exemplified numerically in Sec. VII. Finally, we present a short discussion and concluding remarks in Sec. VIII.

II. BRIEF REVIEW

Crystal surfaces are often described within the solid-on-solid (SOS) approximation, characterized by a single two-dimensional lattice height variable $h_i$, separating the interior of the crystal and the outside vacuum. The simplest nontrivial surface model of this kind is the discrete Gaussian (DG) model

$$\mathcal{H}_{DG}=\frac{J}{2} \sum_{i,\delta} (h_i-h_{i+\delta})^2,$$

with integer heights, $h_i=0, \pm 1, \pm 2, \ldots$, and where the sum is restricted to nearest-neighbor pairs of lattice sites (to be specific, from now on we consider a square lattice). In Eq. (2.1), $J>0$ is the surface stiffness, and the heights are expressed in units of the vertical lattice spacing. The DG model is well known to undergo a roughening transition of the Kosterlitz-Thouless type at $T_R=4\pi/\sqrt{J}$ (hereafter, all temperatures in units of $J/k_B$).

A closely related model is the sine-Gordon model
with continuous heights and $y_2 > 0$. This model is in the same universality class as the DG model, but is easier to handle analytically, being a field theory. A number of well-known results have been obtained from renormalization-group treatments of Hamiltonian (2.2).\(^{16}\) Summarizing, the roughening transition is of infinite order, i.e., the surface free energy shows an essential singularity at $T_R$ of the kind $f \sim \exp[-A(T - T_R)^{-1/2}]$; below $T_R$ the surface is flat, meaning that the average surface height $\bar{h} = \langle (1/N) \sum h_i \rangle$ is well defined, and the average square height difference approaches a number at large distance. Precisely, one finds

$$\langle (h_i - \bar{h})^2 \rangle \sim 2\langle (h_i - \bar{h})^2 \rangle + B \exp\left(-\frac{|r_i - r_j|}{\xi}\right),$$

(2.3)

with a correlation length $\xi$ diverging, as the roughening temperature is approached from below, as $\xi \sim \exp(C(T_R - T)^{-1/2})$.

Two decades ago, when renormalization-group methods were in their infancy, Saito devised a variational theory of the roughening transition which, even if partly failing to reproduce the precise behavior at $T_R$, nonetheless had the advantage of capturing the main features of the roughening phenomenon, being in addition transparent and straightforward.\(^{12,13}\) In this approximation, the transition temperature is exact, and the infinite-order character of the transition is accounted for. More detailed, the form of the free-energy singularity is slightly wrong, since one finds $-\ln f_{\text{sing}} \sim \ln \xi \sim (T_R - T)^{-1}$, instead of $(T_R - T)^{-1/2}$, for $T \approx T_R$. In dynamics, Saito’s theory correctly describes the jump from activated to continuous surface growth, reproducing the results of the more rigorous theory.\(^{17,18}\)

Given its simplicity and effectiveness, it is desirable to generalize this kind of variational theory so as to embody the additional possibility of preroughening. The usual way to introduce PR in a SOS Hamiltonian is to add some interaction between the surface steps. When parallel steps (i.e., steps of same sign) repel each other more than antiparallel steps, PR will generally occur at some temperature $T_{PR} < T_R$. Between $T_{PR}$ and $T_R$, the surface is in a DOF state, characterized by a mesh of up-down correlated steps, leading to a half-coverage of the topmost surface layer, that is to a half-odd-integer average surface height. One particular case of antiparallel-step attraction, leading to PR, is realized on some surfaces which have a tendency toward missing-row surface reconstructions. When realized, as for example in Au(110), these reconstructions consist of a statically ordered array of up-down steps, already leading to half-coverage at $T=0$. In this case, the PR transition and the deconstruction transition coincide.

**III. MODEL AND ITS VARIATIONAL TREATMENT**

Phenomenologically, preroughening can be mimicked by means of a sine-Gordon Hamiltonian, where the cosine parameter sign can change.\(^{10}\) For example, it suffices to modify the sine-Gordon model slightly as follows:

$$\mathcal{H}_0 = \frac{J}{2} \sum_{i,\delta} (h_i - h_{i+\delta})^2 + y_2 \sum_i [1 - \cos(2\pi h_i)],$$

(2.2)

$$\mathcal{H} = \frac{J}{2} \sum_{i,\delta} (h_i - h_{i+\delta})^2 + y_2 \sum_i [1 - \cos(2\pi h_i)]$$

$$+ y_4 \sum_i [1 - \cos(4\pi h_i)],$$

(3.1)

by keeping $y_2 > 0$ constant, and by allowing $y_4$ to change sign at a temperature $T_{PR}$. To be specific, let us assume a linear $T$ dependence

$$y_4(T) = C(T_{PR} - T),$$

(3.2)

with $C > 0$. Equations (3.1) and (3.2) can be considered as a coarse-grained approximation to the true microscopic Hamiltonian, in that $C$, $T_{PR}$, and $y_4$ parametrize for a specific SOS lattice model exhibiting the same thermodynamic properties. An explicit mapping between a restricted SOS model with parallel-step repulsion and a sine-Gordon-type free energy with $y_4$ changing sign at some temperature $T_{PR}$ has been recently produced using a plaquette mean-field theory.\(^{19}\)

The mechanism inducing PR in the Hamiltonian (3.1) is simply explained. When $y_4 > 0$ and the temperature is not too high, the $\cos(4\pi h)$ term pins the surface height indifferently at either integer or half-integer values. However, as $y_4$ becomes negative, i.e., upon crossing $T_{PR}$, the average surface height jumps from integer to half-integer, thus provoking PR of the surface.

Variationally, we can now approximate the exact, unknown free energy of $\mathcal{H}$ by means of that generated by a simpler, soluble Hamiltonian:

$$\mathcal{H}_0 = \frac{J}{2} \sum_i (h_i - h_{i+\delta})^2 + J \xi^{-2} \sum_i (h_i - \bar{h})^2,$$

(3.3)

with continuous heights. Here the average height $\bar{h}$ and the correlation length $\xi$ are variational parameters (both are assumed to be dimensionless, measuring numbers of vertical and horizontal lattice spacings, respectively). As in other mean-field theories, the variational principle is provided by the Bogolubov thermodynamic inequality\(^{20}\)

$$F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0,$$

(3.4)

where $F_0$ is the free energy relative to $\mathcal{H}_0$ and $\langle \cdots \rangle_0$ is an average over the ensemble specified by $\mathcal{H}_0$. At each temperature, choosing such $\bar{h}$ and $\xi$ that minimize $F^* = F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$ will give the optimal free energy per site as

$$f_{\text{best}}(T) = \frac{1}{N} \min_{\bar{h}, \xi} F^*(T; \bar{h}, \xi).$$

(3.5)

At the same time, we shall identify the stable surface phase according to the following “dictionary”: $\xi^{-2} = 0$, rough phase; half-integer $\bar{h}$ and $\xi^{-2} > 0$, DOF phase; integer $\bar{h}$ and $\xi^{-2} > 0$, ordered flat phase.

Details of the calculation, which is straightforward, can be found in Appendix A. In the rough phase, the variational free energy reads:
\[
\beta f^*(\xi^{-2}) = \frac{\beta F^*(\xi^{-2})}{N} = \frac{-\pi}{8} \ln \frac{\pi}{\beta J} + \frac{\pi}{8} [\ln(\pi^2) - 1] + \beta(y_2 + y_4).
\]

with \(\beta J = 1/T\). Equation (3.6) gives the optimal free energy whenever \(\Delta f^*(\xi^{-2}) = f^*(\xi^{-2}) - f^*(0)\) is minimum at \(\xi^{-2} = 0\) (i.e., strictly positive). It is shown in detail in Appendix A that

\[
\beta \Delta f^* = \frac{\pi}{8} \ln(1 + (\pi \xi)^{-2})
\]

\[-\beta y_2 \cos(2\pi \tilde{h}) [1 + (\pi \xi)^2]^{-\left(\pi/4\beta J\right)}
\]

\[-\beta y_4 \cos(4\pi \tilde{h}) [1 + (\pi \xi)^2]^{-\left(\pi/\beta J\right)},
\]

\( \text{with} \)

\[
\sin(2\pi \tilde{h}) = 0 \]

\( \text{as necessary conditions in order that} \Delta f^* \text{be extremal.} \)

We have two classes of solutions for \(\tilde{h}\) from Eq. (3.8): integers \([\cos(2\pi \tilde{h}) = 1]\) and half-integers \([\cos(2\pi \tilde{h}) = -1]\). Given Eq. (3.2), the ordered flat phase (integer \(\tilde{h}\)) is more stable than the DOF phase (half-integer \(\tilde{h}\)) when \(T < T_{PR}\), and the opposite for \(T > T_{PR}\). Hence, PR occurs precisely at \(T_{PR}\). Moreover, \(y_2 \cos(2\pi \tilde{h}) = y_2, \cos(4\pi \tilde{h}) = 1\), and Eqs. (3.7) and (3.9) simplify to

\[
\beta \Delta f^* = \frac{\pi}{8} \ln(1 + (\pi \xi)^{-2}) - \beta y_2 [1 + (\pi \xi)^2]^{-\left(\pi/4\beta J\right)}
\]

\[-\beta y_4 [1 + (\pi \xi)^2]^{-\left(\pi/\beta J\right)},
\]

\[
J \xi^{-2} = 2\pi^2 y_2 \cos(2\pi \tilde{h}) [1 + (\pi \xi)^2]^{-\left(\pi/4\beta J\right)}
\]

\[+ 8\pi^2 y_4 \cos(4\pi \tilde{h}) [1 + (\pi \xi)^2]^{-\left(\pi/\beta J\right)}.\]

Equation (3.11) is still too complex to solve analytically. However, we can at least analyze what happens near \(T_R\) and \(T_{PR}\), where, as can be readily shown, there are divergent \(\xi\) solutions to Eq. (3.11).

When \(\xi \gg 1\), Eq. (3.11) becomes

\[
2 \left|\frac{y_2}{J}\right| (\pi \xi)^{2\left[1 - (T/T_R)\right]} + 8 \left|\frac{y_4}{J}\right| (\pi \xi)^{2\left[1 - 4(T/T_R)\right]} \ll 1,
\]

where \(T_R = 4/\pi\). If \(T \leq T_R\), then \((\pi \xi)^{2\left[1 - (T/T_R)\right]} \ll 1\) can be ignored, and we obtain

\[
\xi = \frac{1}{\pi} \exp \left[\frac{1}{2} \ln \left(\frac{1}{1 - \frac{T}{T_R}}\right)\right],
\]

which diverges to \(+\infty\) as \(T \to T_R\), provided \(J(2|y_2(T_R)|) > 1\), or \(C < C^*(T_{PR})\), where

\[
C^*(T) = \frac{J}{2(T_R - T)}.
\]

When \(y_2\) is a positive constant, Eq. (3.13) describes the behavior near the roughening transition. Hence \(T_R\) is recognized as the roughening transition temperature. As already noted, \(\xi\) in Eq. (3.13) diverges with the wrong power of \(1\) instead of \(\frac{1}{2}\). When \(C > C^*(T_{PR})\), there is no divergent solution to Eq. (3.11) for \(T \leq T_R\), and \(\xi\) remains finite at \(T_R\), which therefore is no longer the roughening temperature. As we shall see below, the true roughening is first order and takes place at \(T_R^+ > T_R\).

Now consider \(T \geq T_{PR}\), when \(T_R^+/4 < T_{PR} < T_R\). In this case, a divergent \(\xi\) must be such that

\[
\frac{2C(\xi^{-2} - 1) - 1}{J} \sim |T - T_{PR}|^{-\nu},
\]

leading in turn to

\[
\xi = \frac{1}{\pi} \left(\frac{2C(T - T_{PR})}{J}\right)^{-\left[1/2(1 - T_{PR}/T_R)\right]} \sim |T - T_{PR}|^{-\nu},
\]

with

\[
\nu = \frac{T_R}{2(T_R - T_{PR})}.
\]

Hence, \(\xi\) diverges as a power law at the PR transition. Note, in particular, the absence of \(y_4\), and \(\xi\), which diverges to \(+\infty\) as \(T \to T_R\), and \(\xi\) is irrelevant to the critical behavior of the extended sine-Gordon model, at least so long as \(T_R^+ > T_R/4\).

According to Eq. (3.16), the best \(\mathcal{H}_0\) at \(T_{PR}\) is a Gaussian model, i.e., the same as for the regular rough phase. Thus, for a finite surface of lateral size \(N\) at \(T = T_{PR}\) we have \((\delta h)^2 \sim (4\pi \xi K_c)\ln N\), with a roughness parameter \(K_c = \pi \nu'(4\nu - 2)\) (Ref. 1) equal to

\[
K_c = \frac{\pi}{4} \frac{T_R}{T_{PR}}.
\]

We note that the absolute surface roughness exactly at \(PR\), as measured by the prefactor of \(\ln N\), namely, \(1/4\pi K_c\), is just a fraction \(T_{PR}/T_R\) of that at roughening, and will thus be proportionally lower, the lower \(T_{PR}\) is with respect to \(T_R\).

Given Eq. (3.17), the specific-heat exponent is obtained from the hyperscaling relation:

\[
\alpha = 2 - 2\nu = \frac{T_R - 2T_{PR}}{T_R - T_{PR}}.
\]

\(\alpha\) is negative for \(T_{PR}/2 < T_{PR} < T_R\), varying from \(-\infty\) as \(T_{PR} \to T_R^-\), to \(+\frac{1}{3}\) as \(T_{PR} \to (T_R/4)^+.\) Nonuniversal critical
exponents have indeed been predicted for PR. Equations (3.17) and (3.19) indicate an approximate connection between them and the transition temperatures.

Another important quantity is the PR order parameter, defined (in the smooth phase) as

\[ P = \left| \frac{1}{N} \sum_i \left( -1 \right)^{h_i} \right| \].  

After noting that \((-1)^{h_i} = e^{\pi i h_i}\), we can use Eq. (A21) to obtain

\[ P = \left| \left[ 1 + (\pi \xi)^2 \right]^{-(\pi/16 \beta j)} \right|. \]

In particular, for \( T = T_{PR} \) we have \( P = (T_{PR} - T)^{\beta_P} \), with

\[ \beta_P = \frac{T_{PR}}{4(T_R - T_{PR})}. \]

This result is consistent with Gaussian criticality at PR, which would in fact predict the same \( \beta_P \), i.e., \((\pi/4)/(4K_c - \pi)^2\).

When \( T = T_{PR} = T_R/4 \), Eq. (3.11) becomes

\[ J \xi(T_{PR})^{-2} = \frac{8\pi^2 y_4}{1 + \pi^2 \xi(T_{PR})^2}, \]

which gives a finite \( \xi \) solution, \( \xi(T_{PR}) = 1/\pi \left[ (8y_4/J) - 1 \right]^{-1/2} \), when \( y_4 > J/8 \). Otherwise, the only solution to Eq. (3.22) for \( y_4 < J/8 \) is \( \xi(T_{PR}) = \infty \).

When \( T_{PR} < T_R/4 \), there is no \( \xi \) divergence from Eq. (3.11) near \( T_{PR} \). In fact, \( \xi \) shows a cusplike singularity at \( T_{PR} \), and PR becomes first-order (Sec. IV). \( \xi(T_{PR}) \) can still diverge exponentially as \( T_{PR} \to (T_R/4)^+ \):

\[ \xi(T_{PR}) \approx \frac{1}{\sigma} \exp \left\{ \frac{1}{4} \frac{\ln \left( \frac{J}{8y_4} \right)}{1 - 4T_{PR}/T_R} \right\}, \]

but only if \( y_4 < J/8 \). Otherwise, \( \xi(T_{PR}) \) remains finite as \( T_{PR} \to (T_R/4)^+ \).

Finally, when \( y_4 = 0 \) and \( T = T_{PR} \), the correlation length behaves like Eq. (3.16), which is now valid for any \( T_{PR} < T_R \). This means that the change from critical to first-order behavior at \( T_{PR} = T_R/4 \) only occurs when \( y_4 > 0 \).

We now evaluate \( \langle (h_m - \bar{h})^2 \rangle_0 \) for \( h_m = (1/N) \sum_i h_i \), in order to check how sharply is \( \bar{h} \) defined at equilibrium. Using a similar device to Eq. (A10), we obtain:

\[ \langle (h_m - \bar{h})^2 \rangle_0 = \frac{1}{N^2} \sum_{i,j} \langle (h_i - \bar{h})(h_j - \bar{h}) \rangle_0 = \frac{\xi^2}{2NBJ}, \]

which is to be considered as a good definition whenever \( \xi \) is finite, i.e., away from criticality.

Once \( \xi(T) \) is given, the average surface width follows directly from the general relationship [after Eqs. (A20) and (A27)]

\[ \langle \delta h^2 \rangle = \frac{1}{N} \left| \sum_i (h_i - \bar{h})^2 \right|_0 = \frac{1}{8\pi BJ} \ln [1 + (\pi \xi)^2]. \]

Using the above results, we can derive the behavior of \( \langle \delta h^2 \rangle \) near criticality. For \( T \approx T_R \) and \( C < C^*(T_{PR}) \), we have

\[ \langle \delta h^2 \rangle \approx \frac{T}{2\pi} \frac{\ln \left( \frac{J}{2(y_2(T)} \right)}{T - T_R} \]

(power-law singularity at roughening), whereas

\[ \langle \delta h^2 \rangle \approx -\frac{T}{2\pi} \frac{\ln \left( \frac{2C[T - T_{PR}]}{J} \right)}{T - T_{PR}} \]

near \( T_{PR} \), when \( T_{R}/4 < T_{PR} < T_R \) (logarithmic singularity at PR).

Finally, we analyze the free-energy singularity at the two transitions, as follows from Eq. (3.10) and from the above \( \xi \) solutions. When \( T > T_R \) and \( \xi^{-2} < 1 \), one has

\[ \beta \Delta f^* = \frac{1}{8\pi} \xi^{-2}, \]

and \( \xi^{-2} = 0 \) is a local minimum of \( \Delta f^* \), but not necessarily the lowest. On the other hand, when \( T < T_R \), \( \xi^{-2} = 0 \) provides a local maximum for \( \Delta f^* \) (i.e., zero). When \( T \approx T_R \) and \( \xi^{-2} < 1 \), it follows that

\[ \Delta f_{best} = -\frac{J}{2} \left[ -\frac{J}{2(y_2(T)} \right] \]

as long as \( C < C^*(T_{PR}) \). \( \Delta f_{best} \) then shows an essential singularity at \( T_R \), but of the wrong type, as already commented. Near \( T_{PR} \), \( \xi \) only diverges for \( T_{PR} > T_R/4 \), in which case we have

\[ \Delta f_{best} = -\frac{J}{2} \left[ -\frac{2C[T - T_{PR}]^\omega}{J} \right], \]

with

\[ \omega = 2\nu = \frac{T_R}{T_R - T_{PR}}. \]

We remark that the specific heat, proportional to \( \partial^2 \Delta f_{best}/\partial T^2 \), behaves like \( [T - T_{PR}]^{\omega - 2} \) near PR; hence \( \alpha = 2 - \omega \), a result consistent with hyperscaling [Eq. (3.19)].

All of the above indicates that PR only exists as a continuous transition when \( T_{PR} > T_R/4 \). We now move to the numerical analysis and see whether the solutions found really provide in each case the absolute minimum free energy.

IV. NUMERICAL RESULTS: FREE SURFACE

In order to make these results more tangible, we now present a numerical exemplification. In Fig. 1, we plot \( \xi(T) \) for \( T_{PR} = 0.5 \), \( C = 0.5J \), and \( y_4 = 0.1J \) (other values of \( y_4 \) were not found to affect substantially the \( \xi \) profile in Fig. 1). Note that \( C < C^*(0.5) \). Looking at Fig. 1, we see that the correlation length distinctly diverges at PR as a power law [cf. Eq. (3.16)], signalling a second-order phase transition (with \( \alpha = 0.535 \)). When approaching \( T_R \) from below, \( \xi \) di-
In Fig. 2, we plot \( \xi(T) \) for \( T_{PR} = 0.25, C = 0.5J \), and \( y_4 = 0.1J \). With these parameters, \( C > C^*(0.25) \), and the correlation length remains finite at \( T_R \), which in this case is not the roughening temperature. There is instead a first-order roughening transition at \( T_R^b = 1.2785 > T_R \). The PR transition is critical for \( y_4 = 0, \) but first order for \( y_4 = 0.1J \) (in the inset, the free energy \( \beta \Delta f_{\text{best}} \) for \( y_4 = 0.1J \) shows a cusplike singularity at \( T_{PR} \)).
somewhat surprising, considering the nominal mean-field nature of our theory. In fact, our trial Hamiltonian (3.3) embodies nontrivial correlations between the heights, and this explains why the present theory is so informative.

V. GROWTH: LANGEVIN DYNAMICS

In this section, we analyze the near-equilibrium dynamics of the extended sine-Gordon model [Eq. (3.1)]. We consider the Langevin growth equation

\[
\frac{dh_i}{dt} = -\frac{\beta \delta H}{\tau} h_i + \xi_i, \quad (5.1)
\]

where a term \(-\Delta \mu \Sigma_i h_i\) (with \(\Delta \mu > 0\)) has been absorbed into \(H\) to induce crystal growth. In Eq. (5.1), \(\tau\) is the relaxation time, and \(\{\xi_i(t)\}\) is a Gaussian white noise:

\[
\langle \xi_i(t) \rangle = 0, \quad \langle \xi_i(t) \xi_j(t') \rangle = \frac{2}{\tau} \delta_{ij} \delta(t-t'), \quad (5.2)
\]

where the averages are over a Gaussian distribution \(P[\{\xi_i(t)\}] \propto \exp \left[-\frac{\beta}{4} \int \delta \Sigma_i \langle \xi_i(t) \rangle^2 \right]\).

A first, limited, result is the exact solution of the Langevin equation for the mean surface height \(h_m = \langle 1/N \rangle \Sigma_i h_i\), when \(T = T_{PR}\) and \(y_4 = 0\). In this case, Eq. (5.1) becomes

\[
\frac{dh_m}{dt} = \frac{\beta \Delta \mu}{\tau} + \zeta_m, \quad (5.3)
\]

with \(\zeta_m = \langle 1/N \rangle \Sigma_i \xi_i\), \(\langle \xi_m(t) \rangle = 0\), and \(\langle \xi_m(t) \xi_m(t') \rangle = (2/\tau) \delta(t-t')\). Integrating Eq. (5.3) and then averaging, we obtain

\[
\langle [h_m(t) - h_m(0)]^2 \rangle = \left(\frac{\beta \Delta \mu}{\tau} \right)^2 + \frac{2}{N \tau} \tau. \quad (5.4)
\]

At equilibrium, \(\Delta \mu = 0\), we find that the interface as a whole diffuses like a Brownian particle, with a diffusion coefficient \(1/\tau\) which is vanishingly small in the infinite-size limit.

Next, we move to the general case. As usual, Eq. (5.1) can be studied through the associated Fokker-Planck equation

\[
\frac{\partial P[\{h_i(t)\}]}{\partial t} = \frac{\beta}{\tau} \sum_i \frac{\delta \delta h_i}{\partial h_i} \left( \frac{\delta H}{\partial h_i} \frac{\partial P}{\partial h_i} + \frac{1}{\beta} \frac{\partial P}{\partial h_i} \right). \quad (5.5)
\]

for the height density function \(P[\{h_i(t)\}] = \langle \Pi, \delta[h_i - h(t, \{\xi_i(t)\})] \pi \rangle\), where \(h(t, \{\xi_i(t)\})\) is the solution to the Langevin equation for a particular realization of the noise.

Any noise average can be expressed as an ensemble average over the \(P\) distribution, according to:

\[
\langle F[\{h_i(t, \{\xi_i(t)\})\}] \rangle = \int \mathcal{D}h \Pi \delta[h_i - h(t, \{\xi_i(t)\})] F[\{h_i\}] = \int \mathcal{D}h \Pi \delta[h_i - h(t, \{\xi_i(t)\})] F[\{h_i\}] = \langle F[\{h_i\}] \rangle_P. \quad (5.6)
\]

It is shown in detail in Appendix B that, upon assuming a Gaussian for \(P\), the average surface height \(\bar{h}(t)\) and the pair correlation in momentum space \(g(p,t)\) are found to obey the equations

\[
\frac{d\bar{h}(t)}{dt} = \frac{\beta}{\tau} \left[ \Delta \mu - 2 \pi y_2 \sin(2 \pi \bar{h}(t)) \exp \left(-\frac{\pi^2}{N} \sum_p g(p,t)^{-1}\right) - 4 \pi y_4 \sin(4 \pi \bar{h}(t)) \exp \left(-\frac{\pi^2}{N} \sum_p g(p,t)^{-1}\right) \right], \quad (5.7)
\]

\[
\frac{dg(p,t)^{-1}}{dt} = -\frac{4}{\tau} g(p,t)^{-1} \left[ \lambda(p) - g(p,t) + 2 \pi^2 \beta y_2 \cos(2 \pi \bar{h}(t)) \exp \left(-\frac{\pi^2}{N} \sum_p g(p,t)^{-1}\right) \right. \\
+ \left. 8 \pi^2 \beta y_4 \cos(4 \pi \bar{h}(t)) \exp \left(-\frac{\pi^2}{N} \sum_p g(p,t)^{-1}\right) \right]. \quad (5.8)
\]

Equations (5.7) and (5.8) form a set of coupled equations which appears hard to solve. As in Ref. 12, we decouple these two equations by neglecting the effect of a time-dependent \(h\) on the evolution of \(g(p,t)\), which is then identified with the equilibrium \(g(p)\) (quasistationary approximation). In this way, we wind up with:

\[
\frac{d\bar{h}(t)}{dt} = \frac{\beta}{\tau} \left[ \Delta \mu - \text{sgn}(y_2) \Delta \mu_c \sin(2 \pi \bar{h}(t)) \right. \\
\left. - \Delta \mu_c' \sin(4 \pi \bar{h}(t)) \right], \quad (5.9)
\]

where

\[
\Delta \mu_c = 2 \pi |y_2| \left[ 1 + (\pi \xi)^2 \right]^{-\pi |y_2|}, \quad (5.10)
\]

\[
\Delta \mu_c' = 4 \pi y_4 \left[ 1 + (\pi \xi)^2 \right]^{-\pi |y_2|}. \quad (5.10)
\]

The form of the solution critically depends upon \(\Delta \mu_c\) and \(\Delta \mu_c'\). A special case is when \(\xi\) is infinite (PR, when critical, and the rough phase). In this case, \(\Delta \mu_c = \Delta \mu_c' = 0\) and Eq. (5.9) is easily solved as \(\bar{h}(t) = (\beta \Delta \mu / \tau^2) t\), which describes continuous growth. This is well known,\(^{17,18}\) and also found in Monte Carlo simulations of restricted SOS models.\(^{4,23}\)

The behavior of \(\Delta \mu_c\) and \(\Delta \mu_c'\), for \(T \leq T_{PR}\) and \(C < C^*\), is easily found to be:

\[
\Delta \mu_c = 2 \pi |y_2| (\pi \xi)^{-2T/T_{PR}}, \quad \Delta \mu_c' = O(\Delta \mu_c^2). \quad (5.11)
\]
$\Delta \mu_c$ is called the depinning field since the crystal does not grow for $\Delta \mu < \Delta \mu_c$ (see below). At first sight, it is puzzling that, according to Eq. (5.11), $\Delta \mu_c$ close to $T_R$ appears to be set by the energy scale $y_2$ (the bare surface pinning potential) rather than $J$ (the renormalized pinning potential), as it should be on physical grounds. For example, Nozieres and Gallet\textsuperscript{18} showed that the depinning field

$$\Delta \mu_c \sim \frac{\gamma a^2}{\xi^2}, \tag{5.12}$$

where $\gamma$ is the renormalized surface stiffness at $T_R$, and $a$ (here = 1) is the step height. Since $\gamma a^2 = \frac{2}{5}k_BT_R$,\textsuperscript{18} which in turn equals $2J$, one has $\Delta \mu_c \sim 2J/\xi^2$. However, a simple algebraic manipulation [see Eq. (3.13)],

$$J \pi(t - T_R^\pm) \approx J \frac{\pi}{2y_2} (\pi \xi)^{-2}, \tag{5.13}$$

shows that

$$\Delta \mu_c = \frac{J}{\pi \xi^2}, \tag{5.14}$$

that is, our result for $\Delta \mu_c$ below roughening is in fact in full agreement with Eq. (5.12), and is correctly controlled by $J$ and not by $y_2$.

Next, let us consider what happens to the depinning field just below and just above $T_{PR}$. There are no previous results about this. For $T_{PR} > 4/T_R$, PR is critical and we find from Eqs. (5.10) and (3.16):

$$\Delta \mu_c \sim |T - T_{PR}|^{\omega}, \quad \Delta \mu'_c \sim |T - T_{PR}|^{4T_{PR}/(T_R - T_{PR})}, \tag{5.15}$$

where $\omega = T_R/(T_R - T_{PR})$ is the same exponent as for the free energy [cf. Eq. (3.30)], and is typically much larger than 1. It follows that pinning of the flat surface to integer height values and that of the DOF surface to half-integer height values close to PR is much stronger in comparison with that found below roughening. A glance at Fig. 1, for example, shows that $\xi^2$ will grow large only very close to $T_{PR}$, which implies, via Eq. (5.14), that only there does $\Delta \mu_c$ truly become small.

Finally, we find that the role of $\Delta \mu'_c$ is irrelevant: since $4T_{PR}/(T_R - T_{PR}) > \omega$ [cf. Eq. (3.31)], there exists a neighborhood of $T_{PR}$ where $\Delta \mu'_c \ll \Delta \mu_c$, meaning that $\Delta \mu'_c$ can be neglected at least sufficiently near criticality.

We now wish to compute $\tilde{h}(t)$. Equation (5.9) is exactly solvable when $y_2 = 0$.$\textsuperscript{12}$ We set $\tilde{h}(0) = 0$ and distinguish between $\Delta \mu > \Delta \mu_c$ and $\Delta \mu < \Delta \mu_c$. In case (a), we find

$$\tilde{h}(t) = \frac{1}{\pi} \arctan \left[ \frac{\text{sgn}(y_2) \Delta \mu_c + D \tan \left( \frac{\pi \beta D}{\tau} - \frac{\text{sgn}(y_2) \arctan \Delta \mu_c}{D} \right) \right] + n, \tag{5.16}$$

for $(n-1)(\pi/\beta D) + t_0 < t < n(\pi/\beta D) + t_0$, $n$ integer, with $D = \sqrt{\Delta \mu_c^2 - \Delta \mu_c^2}$ and $t_0 = (\pi/\beta D) \left[ \frac{1}{2} + (1/\pi) \text{sgn}(y_2) \arctan(\Delta \mu_c/D) \right]$. $\tilde{h}(t)$ is a stepwise increasing function of time with step period $\pi/\beta D$. The increase becomes linear as $\Delta \mu$ grows to infinity, $\tilde{h}$ is never stationary; however, its rate of increase is minimum at $\tilde{h} = \frac{1}{2} + k$, $k$ integer, when $y_2 > 0$ (smooth phase); or at $\tilde{h} = \frac{1}{2} + k$, $k$ integer, when $y_2 < 0$ (DOF phase). This feature is different from results of restricted SOD simulations, where the staircase plateaus occur rather accurately at integer or half-integer numbers (when $T < T_{PR}$ or $T > T_{PR}$, respectively).\textsuperscript{1,23}

Below the critical depinning field (case b), $\Delta \mu < \Delta \mu_c$, one finds

$$\tilde{h}(t) = \frac{1}{\pi} \arctan \left[ \frac{\text{sgn}(y_2) \Delta \mu_c - D}{\Delta \mu} \frac{e^{2\pi \beta D/\tau} - 1}{e^{2\pi \beta D/\tau} - \text{sgn}(y_2) \Delta \mu_c - D} \right], \tag{5.17}$$

with $D = \sqrt{\Delta \mu_c^2 - \Delta \mu_c^2}$. When $y_2 > 0$ (flat surface), the denominator is always positive and $\tilde{h}$ increases monotonically up to $1/\pi \arctan(\Delta \mu_c - D)/\Delta \mu$. When $y_2 < 0$ (DOF surface), the solution to Eq. (5.9) is again similar to that for $y_2 > 0$. However, as $\tilde{h}$ crosses $\frac{1}{2}$ at $(\pi/2\beta D) \ln[(\Delta \mu_c + D)/(\Delta \mu_c - D)]$, the right-hand side of Eq. (5.17) adds another 1, eventually leveling off at a value $< 1$. Hence, in this regime there are no oscillations and the crystal does not grow (in reality, the growth mechanism would be nucleation, which is, however, beyond the scope of our theory). Hence $\Delta \mu_c$ really represents the threshold which the driving force must ultimately overcome in order to cause continuous crystal growth. Similar is the outcome of a renormalization-group treatment of the growth mode near roughening;\textsuperscript{18} a sufficiently large $\Delta \mu$ is needed in order to observe continuous (i.e., substantial) growth for $T < T_R$, whereas an infinitesimal $\Delta \mu$ suffices for $T > T_R$.

The last point to discuss is what happens when including $\Delta \mu'_c$. It turns out that this factor has little influence on the evolution of $\tilde{h}$ as compared to $\Delta \mu_c$ (some numerical results can be found in Fig. 3). As before, we ask what are the values of $\tilde{h}$ when its slope is minimum. Alternatively, we
VI. ADSORPTION ONTO AN ATTRACTIVE SUBSTRATE

The theory above is for a free surface. However, the main experimental claims of surface preroughening have been made for thin multilayer films of rare-gas solids adsorbed on attractive substrates. These data show that the film thickness, i.e., the average quantity of adsorbed matter, is, below the roughening temperature, a staircaselike function of chemical potential. More specifically, it is a function of the difference \( \Delta \mu \) between the chemical potential of the bulk interface and that of the film (not to be confused with the quantity \( \Delta \mu \) of Sec. V, which is just the opposite). Roughly, these layering jumps occur between integer layer numbers at low temperatures, and disappear due to roughening at high temperatures. In detail, however, a reentrant behavior was observed in Ar, for example: the jumps first disappear at about 82% of the melting temperature; then they reappear above this temperature, but this time between roughly half-integer layer numbers; finally they disappear for good at about 94% of the melting temperature, where roughening is known to take place. Other subtler features in the layering phase diagram of Ar have also been reported, in the form of zigzagging heat-capacity peaks joining low- and high-temperature layering transition lines. A very similar reentrant layering behavior has also been found recently in a grand-canonical Monte Carlo simulation for Lennard-Jones particles.

Den Nijs first suggested that the reentrant first-order layering transitions should be indicative of PR of the bulk interface. More recently, Weichman and Prasad provided a renormalization-group theory of adsorption which compares well with the experiments. Here we show that our variational theory is capable of accounting in detail for this rich adsorption phase diagram. To this end, we follow earlier work by Weeks, who studied the standard case, without PR. We use the extended sine-Gordon Hamiltonian augmented by a term \( \Sigma V(h) \) describing the influence of the substrate. The substrate potential mainly serves to define a mean film thickness, \( h_0 \), diverging as \( \Delta \mu \) goes to zero. This can be accounted for by using the Weeks prescription for the potential,

\[
V(h) = \Delta \mu h + \frac{c}{2h^2},
\]

with \( c > 0 \), and where the heights are zero at the substrate. The first term in Eq. (6.1) favors the gas phase with respect to the solid, and thus works against adsorption, whereas the second term describes van der Waals attraction by the substrate. Near its point of minimum, \( h_0 = (\Delta \mu/c)^{1/3} \), \( V(h) \) is approximated by

\[
V(h_0) + \frac{1}{2} V''(h_0)(h-h_0)^2.
\]

with \( V''(h_0) \sim (\Delta \mu/c)^{6/3} \). For simplicity, we assume form (6.2) to be valid in general (the error made is small in the thick-film limit).

In the same spirit of Sec. III, we estimate the free energy of our model [Hamiltonian \( H + V(h) \)] using the Bogoliubov inequality, Eq. (3.4). We obtain...
\[
\frac{1}{N} \left( \sum_i V(h_i) \right)_0 = V(h_0) + \frac{1}{2} V''(h_0) \left( \frac{1}{N} \sum_i (h_i - h_0)^2 \right)_0 = V(h_0) + \frac{1}{2} V''(h_0)(\bar{h} - h_0)^2 + \frac{V''(h_0)}{16\pi\beta J} \ln[1 + (\pi\xi)^2],
\]

(6.3)

and then, using earlier results [see Eq. (3.7)], we arrive at the free-energy functional

\[
\beta \Delta f^* = \beta V(h_0) + \frac{\beta}{2} V''(h_0)(\bar{h} - h_0)^2 + \frac{V''(h_0)}{16\pi J} \ln[1 + (\pi\xi)^2] + \frac{\pi}{8} \ln[1 + (\pi\xi)^{-2}]
\]

\[- \beta y_2 \cos(2\pi\bar{h})[1 + (\pi\xi)^2]^{-(\pi/4\beta J)} - \beta y_4 \cos(4\pi\bar{h})[1 + (\pi\xi)^2]^{-(3\pi/4\beta J)},
\]

(6.4)

with \(\xi\) and \(\bar{h}\) being selected so as to minimize \(\Delta f^*\). Necessary conditions for this are

\[
V''(h_0)(\bar{h} - h_0) + 2\pi \sin(2\pi\bar{h})[1 + (\pi\xi)^2]^{-(\pi/4\beta J)}\{y_2 + 4y_4 \cos(2\pi\bar{h})[1 + (\pi\xi)^2]^{-(3\pi/4\beta J)}\} = 0
\]

(6.5)

and

\[
J \xi^{-2} = \frac{V''(h_0)}{2} + 2\pi^2 y_2 \cos(2\pi\bar{h})[1 + (\pi\xi)^2]^{-(\pi/4\beta J)} + 8\pi^2 y_4 \cos(4\pi\bar{h})[1 + (\pi\xi)^2]^{-(\pi/4\beta J)}.
\]

(6.6)

These equations must be solved numerically. When more than one solution is found, the such is chosen that provides the minimum \(\Delta f_{\text{bond}}(T, \Delta \mu)\) of \(\Delta f^*\).

In Sec. VII we solve Eqs. (6.4)–(6.6) numerically in a number of selected cases. However, one can even go beyond the quadratic approximation (6.2). For example, if we keep up to fourth-order terms in the expansion of \(V(h)\) around \(h_0\), then Eq. (6.4) must be modified as follows:

\[
\beta \Delta f^* = \beta V(h_0) + \frac{\beta}{2} V''(h_0)(\bar{h} - h_0)^2 + \frac{\beta}{6} V'''(h_0)(\bar{h} - h_0)^3 + \frac{\beta}{24} V''''(h_0)(\bar{h} - h_0)^4
\]

\[
+ \frac{V''(h_0) + V'''(h_0)(\bar{h} - h_0) + \frac{1}{2} V''''(h_0) (\bar{h} - h_0)^2}{16\pi J} \ln[1 + (\pi\xi)^2] + \frac{V''(h_0)}{512\pi^3 \beta J^2} \ln^2[1 + (\pi\xi)^2]
\]

\[- \beta y_2 \cos(2\pi\bar{h})[1 + (\pi\xi)^2]^{-(\pi/4\beta J)} - \beta y_4 \cos(4\pi\bar{h})[1 + (\pi\xi)^2]^{-(3\pi/4\beta J)}.
\]

(6.7)

Equations (6.5) and (6.6) are then replaced by

\[
V''(h_0)(\bar{h} - h_0) + \frac{V''(h_0)}{2}(\bar{h} - h_0)^2 + \frac{V''(h_0)}{6}(\bar{h} - h_0)^3 + \frac{V''(h_0) + V'''(h_0)(\bar{h} - h_0)}{16\pi \beta J} \ln(1 + (\pi\xi)^2) + 2\pi \sin(2\pi\bar{h})
\]

\[
\times [1 + (\pi\xi)^2]^{-(\pi/4\beta J)}\{y_2 + 4y_4 \cos(2\pi\bar{h})[1 + (\pi\xi)^2]^{-(3\pi/4\beta J)}\} = 0
\]

(6.8)

and

\[
J \xi^{-2} = \frac{1}{2} \left[ \frac{V''(h_0) + V'''(h_0)(\bar{h} - h_0) + \frac{1}{2} V''''(h_0) (\bar{h} - h_0)^2}{32\pi \beta J} \ln[1 + (\pi\xi)^2]
\]

\[
+ 2\pi^2 y_2 \cos(2\pi\bar{h})[1 + (\pi\xi)^2]^{-(\pi/4\beta J)} + 8\pi^2 y_4 \cos(4\pi\bar{h})[1 + (\pi\xi)^2]^{-(\pi/4\beta J)}.
\]

(6.9)

respectively. We postpone a discussion of third- and fourth-order corrections to results obtained within the quadratic approximation until the end of Sec. VII.

VII. NUMERICAL RESULTS: ADSORBED FILM ON A SUBSTRATE

First we consider the case \(T_{PB} > T_{pb}/4\). To be specific, we take \(T_{PB} = 0.5\), \(C = 0.5J\), and \(y_4 = 0.1J\) (see Fig. 1 for the bulk-interface behavior). We set \(c = J\) in what follows. A typical low-temperature adsorption isotherm is plotted in Fig. 4 \((T = 0.4)\). Here we show both \(\xi\) and \(\bar{h}\) as a function of \(h_0\). Besides a less interesting behavior at large \(\Delta \mu\), we see sharp jumps of the film height \(\bar{h}\) between nearly integer values every time \(h_0\) equals an integer-plus-one-half, and without any loss of continuity for \(\Delta f_{\text{bond}}\). This is the film coun-
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The cusp is found for $h_0 = (\Delta \mu/c)^{-1/2}$ (also drawn as a continuous line through the $\bar{h}$ data), along the adsorption isotherm $T = 0.4$, for $T_{PR} = 0.5$. Sharp jumps of $\bar{h}$ between integer values signal the crossing of first-order layering transition lines.

FIG. 4. Variational correlation length $\xi (\times)$ and height $\bar{h}$ (□), during growth, as a function of $h_0 = (\Delta \mu/c)^{-1/2}$ (also drawn as a continuous line through the $\bar{h}$ data), along the adsorption isotherm $T = 0.4$, for $T_{PR} = 0.5$. Sharp jumps of $\bar{h}$ between integer values signal the crossing of first-order layering transition lines.

The counterpart of the bulk-interface smooth phase, whose degeneracy is removed by a nonzero $\Delta \mu$ which selects among pure states the one with the nearest height to $h_0$. At every $\bar{h}$ jump, a cusp is found for $\xi$, which becomes less and less sharp as $h_0$ grows, until $\xi$ attains the bulk-interface value (1.2394 for $T = 0.4$). Moreover, from Fig. 5 we see that jumps are also found in the numerical $\Delta \mu$ derivative of $\Delta f_{\text{best}}$: this is not surprising, given that $(\partial \Delta f_{\text{best}}/\partial \Delta \mu)_\beta$ is the variational estimate of the average film width (to be compared with $\bar{h}$ in Fig. 4) when the original $V(h)$ is used [Eq. (6.1)]. Starting from $h_0 = 1.5$, half-integer values of $h_0$ define first-order transition lines ending in noncritical points whose temperatures $T^{(1.5)}, T^{(2.5)}, T^{(3.5)} \ldots$ eventually converge to $T_{PR}$ as a power law, $T_{PR} = T^{(\pi/2)} \sim T^{(\pi/2)}$, with $p_1(T_{PR}) = 2.510$.

FIG. 5. Variational estimate of $\bar{h}$ through the $\Delta \mu$ derivative of $\Delta f_{\text{best}}$, for $T = 0.4$ and $T_{PR} = 0.5$. The small discrepancies from Fig. 4 are due to the quadratic approximation of the substrate potential [cf. Eq. (6.2)].

In Fig. 6, the behavior at $T = 0.6$ (the DOF phase in the bulk interface) is reported. It is similar to Fig. 4, but now $\bar{h}$ and $(\partial \Delta f_{\text{best}}/\partial \Delta \mu)_\beta$ jump between half-integer values every time $h_0$ is an integer. This is the adsorbed film remnant of the DOF phase. As before, $\xi$ shows a cusp whenever $\bar{h}$ jumps, and increases eventually until the bulk value 2.7797. Starting from $h_0 = 2$, integer values of $h_0$ define first-order transition lines starting at temperatures $T^{(2)}, T^{(3)}, T^{(4)}, \ldots$, which converge to $T_{PR}$ as a power law, $T^{(n)} - T_{PR} \sim n^{-p_2(T_{PR})}$, with $p_2(T_{PR}) = 2.502$. Weichman and Prasad gave a renormalization-group estimate of the same exponent, $p_1(T_{PR}) = p_2(T_{PR}) = 4 - [\pi/K_5(T_{PR})] = 2.429$, which is encouragingly similar to ours. Finally, the transition lines terminate in noncritical end points at temperatures $T^{(2)}, T^{(3)}, T^{(4)}, \ldots$, which converge to $T_R$ as $T_R = T^{(n)} \sim (\ln n)^{-r}$, with $r = 1.406$ (for comparison, the renormalization-group estimate is $r = 2$).

Lastly, we study the behavior at $T_{PR}$ (see Fig. 7). Here both $\xi$ and $\bar{h}$ grow monotonically with $h_0$, and there is no first-order line ever crossed. To sum up, coming from low temperature, first-order layering transitions disappear just below $T_{PR}$, only to reappear soon after. At higher temperature, they disappear again, and for good, when roughening is reached. The ensuing phase diagram is shown in Fig. 8.

Next we study the growth of the adsorbed film under conditions where the bulk PR is first order ($T_{PR} < T_R/4$). We use $T_{PR} = 0.25, C = 0.5J$, and $y_4 = 0.1J$ [see Fig. 2 for the behavior at the bulk interface]. A typical low-temperature adsorption isotherm is plotted in Fig. 9 (T = 0.2). The main difference with respect to Fig. 4 is in the supplementary step around $h_0 = 1.5$, which is found in the $\bar{h}$ staircase [and in $(\partial \Delta f_{\text{best}}/\partial \Delta \mu)_\beta$ as well], signalling a more complex behavior than before. A more accurate analysis shows that the two additional first-order points actually belong to new transition lines, one of which (and precisely that at lower $h_0$, line A) bifurcates at $T \approx 0.238$ into two first-order lines (one ending at $T = 0.269$ with vanishing $\bar{h}$ jump, and the other at
\[ T = 0.273 \] enclosing a region where \( h_{\bar{\theta}} = 1.25 \). The other transition line \((B)\) joins the first reentrant line on the DOF side of the phase diagram \( \approx \) see below in this section \( \approx \) at \( T \approx 0.2919 \). Other details are similar to the \( T_{PR} = 0.5 \) case: \( \xi \) has a cusp at every \( h_{\bar{\theta}} \) jump, growing eventually until the bulk value \( 0.4978 \); the first-order lines at \( h_0 = 1.5, 2.5, 3.5, \ldots \) terminate in noncritical end points, whose temperatures \( T_{(1.5)}, T_{(2.5)}, T_{(3.5)}, \ldots \) converge to \( T_{PR} \) as a power law, \( T_{PR} \approx T_{\xi}^{(1/2)} \approx 0 \), with \( q_1 \approx 4.405 \).

The phase with coverage \( h_{\bar{\theta}} = 1.25 \) is an unexpected realization of Den Nijs's \( \theta \)-DOF phase,\(^{26,19}\) in the presence of a strong substrate. We now wish to understand how it comes about. It is shown in Appendix A that \( \theta \)-DOF phase solutions characterized by some fractional coverage \( h_{\bar{\theta}} \) generally do exist as local free-energy minima [cf. Eq. (A31)]. Without a substrate, however, they can be global minima only if \( y_4 < 0 \). This is a rather common circumstance, although models which realize it have only recently been discussed.\(^{19}\)

What we find here is that a strong attractive substrate and a large correlation length \( \xi \) can stabilize a phase \( h_{\bar{\theta}} = 1.25 \) near \( PR \), even when \( y_4 > 0 \). The key factor is that \( \xi \) tends to develop maxima at coverage \( h_{\bar{\theta}} = (2n + 1)/4 \). This can be seen directly in Figs. 10 and 11, and understood in Eq. (6.6), for \( y_2 = 0, y_4 > 0 \). Since \( \cos(4\pi h_{\bar{\theta}}) = -1 \) at this \( h_{\bar{\theta}} \), the last term cancels part of \( V'' \), hence \( \xi \) becomes large. Given a large \( \xi \) and a strong substrate \( V'' \), consider, for example, the total free energy (6.4) for \( y_2 = 0, y_4 > 0, \) at \( h_0 = 1.25 \). We see that \( h_{\bar{\theta}} = \frac{1}{4} \) can prevail because the main destabilizing \( y_4 \) term is reduced by a large \( \xi \), so that the main stabilizing \( V'' \) term (which vanishes only at \( h_{\bar{\theta}} = \frac{1}{2} \) but is otherwise positive) can
VARIATIONAL THEORY OF PREROUGHENING

In this paper, we have introduced a mean-field variational theory of preroughening (PR) of crystal surfaces, which generalizes previous approaches devoted to roughening. We find that many features of both preroughening and roughening are well described in this simple theory. In particular, PR of a rigid lattice model is correctly predicted to be a nonuniversal second-order transition, at least when $T_{PR} > T_R/4$. In this case, the theory connects the critical exponents and the roughness parameter at PR to the ratio of the two temperatures. For $T_{PR}$ below this threshold value, PR is predicted to become first order, in agreement with Ref. 3.

Surface dynamics is also described by the theory. Growth take over. A more physical way to rationalize a quarter-coverage $\theta$-DOF phase is to note that close to $(2n + 1)/4$ the substrate acts to renormalize the value of $\gamma_4$, which may become effectively negative.

In Fig. 10 the $T=0.3$ isotherm is shown. A very similar behavior to that of Fig. 6 is found: $\tilde{h}$ jumps (and the $\Delta \mu$ derivative of $\Delta f_{best}$ behaves the same) between half-integer values every time $h_0$ takes an integer value; correspondingly, $\xi$ has a cusp, while increasing with $h_0$ up to the bulk value 0.8376. Starting from $h_0 = 2$, integer values of $h_0$ define first-order transition lines originating at $T'(1), T'(3), T'(4), \ldots$, which converge to $T_{PR}$ as $T'(0) - T_{PR} \sim n^{-q_2}$, with $q_2 = 3.802$. Weichman and Prasad gave an estimate of 4 for $q_1 = q_2$, which is close to ours. The transition lines survive only below the roughening temperature; they end in noncritical points at $T'(1), T'(3), T'(4), \ldots$, showing a nonmonotonic trend to $T_{PR}^g(0.25)$.

The $T=0.25$ isotherm (Fig. 11) gives a conclusive indication of the overall structure of the film phase diagram when $T_{PR} < T_R/4$. At $T_{PR}$, there is a radically different behavior than that represented in Fig. 7. Besides the pair of jumps which occur when the fork stemming from line A is crossed, further jumps of $\tilde{h}$ are found at $h_0 = 1.75 + (n/2)$ ($n = 0, 1, 2, \ldots$), the former at the crossing of line B, and the others along the “zipper” that joins the $T<T_{PR}$ first-order lines to the $T>T_{PR}$ first-order lines. In the end, the phase diagram of the film looks like Fig. 12.

The “zippering” behavior found for $T_{PR} < T_R/4$ is quite similar to the experimental results, as well as to the outcome of renormalization-group theory. In fact, the zipper which is present in the phase diagram of argon films strongly suggests first-order PR of Ar(111). We note that for the Ar(111) surface $T_{PR} = 69$ K, $T_R = 80$ K, so the condition $T_{PR} < T_R/4$ is far from being verified. We conclude that there must be other physics, not contained in our modeling, and probably not contained in any rigid lattice model, which is at work in making quantitatively the PR of Ar(111) first order.

Finally, we add some remarks on the changes introduced in the foregoing results when including third- and fourth-order terms in the substrate potential. We considered, in particular, the isotherms plotted in Figs. 4 and 11. Actually, only minor changes have to be noted (i.e., no further transition line is found). In both cases, the main quantitative corrections come about, as expected, for low $h_0$. First of all, $\tilde{h}$ jumps will occur at slightly lower $h_0$ values than before, with appreciable differences only for large $\Delta \mu$. This suggests a small bending downwards of all the transition lines in Figs. 8 and 12. More important, each time a transition line is crossed, the correlation length also makes a jump (while a cusp was seen before). Moreover, the first (and most important) $\xi$ maximum is slightly depleted. Finally, the numerical agreement between $\tilde{h}$ and $(\partial f_{best}/\partial \Delta \mu)$ considerably improves, and this provides a successful check of internal consistency of our numerical procedure.

VIII. CONCLUSIONS

When $T_{PR} < T_R/4$, the theory predicts a new phase diagram for $T_{PR} < T_R/4$, which is similar to the experimental results, as well as to the outcome of renormalization-group theory. In fact, the zipper which is present in the phase diagram of argon films strongly suggests first-order PR of Ar(111). We note that for the Ar(111) surface $T_{PR} = 69$ K, $T_R = 80$ K, so the condition $T_{PR} < T_R/4$ is far from being verified. We conclude that there must be other physics, not contained in our modeling, and probably not contained in any rigid lattice model, which is at work in making quantitatively the PR of Ar(111) first order.

Finally, we add some remarks on the changes introduced in the foregoing results when including third- and fourth-order terms in the substrate potential. We considered, in particular, the isotherms plotted in Figs. 4 and 11. Actually, only minor changes have to be noted (i.e., no further transition line is found). In both cases, the main quantitative corrections come about, as expected, for low $h_0$. First of all, $\tilde{h}$ jumps will occur at slightly lower $h_0$ values than before, with appreciable differences only for large $\Delta \mu$. This suggests a small bending downwards of all the transition lines in Figs. 8 and 12. More important, each time a transition line is crossed, the correlation length also makes a jump (while a cusp was seen before). Moreover, the first (and most important) $\xi$ maximum is slightly depleted. Finally, the numerical agreement between $\tilde{h}$ and $(\partial f_{best}/\partial \Delta \mu)$ considerably improves, and this provides a successful check of internal consistency of our numerical procedure.

VIII. CONCLUSIONS

In this paper, we have introduced a mean-field variational theory of preroughening (PR) of crystal surfaces, which generalizes previous approaches devoted to roughening. We find that many features of both preroughening and roughening are well described in this simple theory. In particular, PR of a rigid lattice model is correctly predicted to be a nonuniversal second-order transition, at least when $T_{PR} > T_R/4$. In this case, the theory connects the critical exponents and the roughness parameter at PR to the ratio of the two temperatures. For $T_{PR}$ below this threshold value, PR is predicted to become first order, in agreement with Ref. 3.

Surface dynamics is also described by the theory. Growth
is continuous at both PR and roughening (when not first order), as well as—or course—in the whole rough phase; in all other cases, the growth mode is layer by layer. In this regime, there is a threshold which the driving force must overcome in order for the crystal to become depinned and start growing, both below and above $T_{PR}$. This is the direct extension to preroughening of the known result, obtained by Nozières and Gallet in the simple sine-Gordon model, and by Kotrla and Levi in a kinetic solid-on-solid model, that the interface mobility for a finite driving force is enhanced just below the roughening temperature. The behavior of the depinning field close to $T_{PR}$ is critical, with the same exponent of the free energy.

Finally, we find that the variational approach can reproduce many of the subtle features of the layering phase diagram of noble gases adsorbed on an attractive substrate. In particular, if parameters are chosen such that bulk PR is first order, clear evidence is found for the zippering behavior observed in the experiments and also predicted by renormalization-group arguments. A substrate-induced $\theta$-DOF phase is also predicted, leading to a quarter-coverage region in the phase diagram.

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APPENDIX A: VARIATIONAL FREE ENERGY

In this appendix, we compute some surface quantities which are averages over the ensemble specified by the quadratic Hamiltonian $H_0$ in Eq. (3.3), with continuous heights. We first simplify the notation by defining a matrix $V$, such that

$$
\frac{\beta J}{2} \sum_{i,\delta} (h_i - h_{i+\delta})^2 = \sum_{x,y} h_x V_{x,y} h_y = hVh.
$$

(A1)

We use $x, y, \ldots$, as well as $i, j, \ldots$, throughout this section to indicate the sites of a square lattice. Equation (A1) yields

$$
V_{x,y} = \beta J (4 \delta_{x,y} - \delta_{|x-y|,1}) = V_{y,x}.
$$

(A2)

Translational invariance of $V$ imposes the existence of plane-wave eigenvectors

$$
\sum_y V_{x,y} e^{ip\cdot y} = \lambda(p) e^{ip\cdot x},
$$

(A3)

with eigenvalues

$$
\lambda(p) = 2 \beta J (2 - \cos p_x - \cos p_y).
$$

(A4)

(we choose a unitary horizontal lattice spacing). We use periodic boundary conditions to fix the $p$ values. For a rectangular $L_x \times L_y$ box, we have $p = (n_x/L_x) b_x + (n_y/L_y) b_y$, with $n_x = 0, 1, \ldots, L_x - 1$, $n_y = 0, 1, \ldots, L_y - 1$, $b_x = 2 \pi e_x$, and $b_y = 2 \pi e_y$.

Using orthogonality of plane waves, Eq. (A3) can be easily solved in $V_{x,y}$, as

$$
V_{x,y} = \frac{1}{N} \sum_p \lambda(p) e^{ip\cdot (x-y)}.
$$

(A5)

A similar formula gives the inverse-matrix elements

$$
V^{-1}_{x,y} = \frac{1}{N} \sum_p \frac{e^{ip\cdot (x-y)}}{\lambda(p)}.
$$

(A6)

The infrared divergence in Eq. (A6) can be healed up by introducing a small mass term which must eventually be set to zero when evaluating measurable quantities like, for instance, the pair correlations [see Eq. (A11) below].

In order to calculate thermodynamic averages over quadratic Hamiltonians, the Gaussian integral

$$
\int D\Phi e^{-\frac{1}{2} \phi V \phi + \frac{1}{2} \phi J \phi} = \pi^{N/2} (\det V)^{1/2} e^{-\frac{1}{2} \phi J \phi}.
$$

(A7)

is useful, where $V$ is any positive-definite matrix, $h = \{ \ldots, h_i, \ldots \}$, and $b$ is any complex $N$-component vector. We used the notation $D\Phi = \prod_p (\pi \lambda(p))^{1/2}$. Observe that det $V$ is simply the product of the $V$ eigenvalues (all positive). In particular

$$
\int D\Phi e^{-\frac{1}{2} \phi V \phi} = \pi^{N/2} \prod_p (\pi \lambda(p))^{1/2}
$$

(A8)

is the partition function $Z_{CG}$ of the continuous Gaussian (CG) model, which is rough at any temperature. This can be seen from the expression for the average square height difference:

$$
\langle (h_x - h_y)^2 \rangle = \frac{1}{Z_{CG}} \sum_p \frac{1 - e^{ip\cdot (x-y)}}{\lambda(p)} \sim \frac{1}{\beta J} |x-y|.
$$

(A9)

Using the result

$$
\int D\Phi \phi V \phi = \frac{1}{N} \sum_p \frac{1 - e^{ip\cdot (x-y)}}{\lambda(p)} \sim \frac{1}{\beta J} |x-y|,
$$

(A10)

one finally obtains

$$
\langle (h_x - h_y)^2 \rangle = \frac{1}{N} \sum_p \frac{1 - e^{ip\cdot (x-y)}}{\lambda(p)} \sim \frac{1}{\beta J} |x-y|.
$$

(A11)

which diverges at large distance, although as slow as a logarithm.

Another matrix we introduce is $W$, defined through

$$
\frac{\beta J}{2} \sum_{i,\delta} (h_i - h_{i+\delta})^2 + \beta J \xi^{-2} \sum_i h_i^2 = hWh.
$$

(A12)

It is fairly simple to show that

$$
W_{x,y} = \beta J (4 + \xi^{-2}) \delta_{xy} - \delta_{|x-y|,1}
$$

(A13)

and

$$
\sum_y W_{x,y} e^{ip\cdot y} = g(p) e^{ip\cdot x},
$$

(A14)
with
\[
g(p) = 2\beta J \left( 2 - \cos p_x \cos p_y + \frac{\xi^2}{2} \right). \quad (A15)
\]
At variance with $\lambda(p)^{-1}, g(p)^{-1}$ acquires a mass term $\xi^2$ in the large-$N$ long-wavelength limit
\[
\beta J g(p)^{-1} \approx \frac{1}{p^2 + \xi^2}. \quad (A16)
\]
The outcome of this is that a term like $J \xi^2 \sum h_i^2$ in the Hamiltonian makes the surface flat, since it gains a finite correlation length $\xi$. This follows from the estimate of the average square height difference at large distance, $|x-y| \gg \xi$. \[
\langle (h_x-h_y)^2 \rangle = \frac{1}{N} \sum_p \frac{1}{g(p)} \ln \frac{\pi \xi}{2|x-y|} \left[ e^{-\langle|x-y|/\xi\rangle} \right]. \quad (A17)
\]
Given all of the above, we calculate the right-hand side of Eq. (3.4). The first ingredient we need is
\[
\beta F_0 = -\frac{1}{2} \int \ln \left[ \pi g(p)^{-1} \right]. \quad (A18)
\]
Then, using $h' = h_i - \bar{h}$, we have
\[
\beta (\mathcal{H} - \mathcal{H}_0) = hVh - h'Wh' + \beta y_2 \sum [1 - \cos(2\pi h_i)] + \beta y_4 \sum [1 - \cos(4\pi h_i)]. \quad (A19)
\]
The average of the first part of Eq. (A19), given the formula $\Sigma_y V_{x,y} = 0$ and using Eq. (A10), comes out as
\[
\langle hVh - h'Wh' \rangle = \langle h'(V - W)h' \rangle = \sum (V_{x,y} - W_{x,y}) \times \langle h_x h_y \rangle = \frac{1}{2} \sum (V_{x,y} - W_{x,y}) W_{x,y}^{-1}
\]
\[
= \frac{1}{2} \sum g(p)^{-1} \lambda(p) - 1. \quad (A20)
\]
Then it follows from Eq. (A7) that
\[
\langle e^{ibh} \rangle = e^{i\bar{h}b} e^{-|1/b|h^{-1}b}, \quad (A21)
\]
with $b\bar{h} = \bar{h} \Sigma_i b_i$. In particular:
\[
\langle e^{\pm 2\pi i/\hbar} \rangle = e^{\pm 2\pi i\bar{h}} e^{-|\pi/\hbar|^2 N^2 \Sigma g(p)^{-1}}. \quad (A22)
\]
Collecting together all the foregoing results, we finally obtain
\[
\beta F^* = \beta F_0 + \beta (\mathcal{H} - \mathcal{H}_0) = \sum \ln \left[ \pi g(p)^{-1} \right] + \frac{1}{2} \sum g(p)^{-1} \lambda(p) - 1 + N \beta y_2 \left[ 1 - \cos(2\pi h_i) \right] \left[ 1 - \cos(4\pi h_i) \right] \left[ \frac{4\pi^2}{N} \sum g(p)^{-1} \right]. \quad (A23)
\]
Choosing $g(p)$ and $\bar{h} = \langle h_i \rangle_0$ as free parameters, we select them by requiring that $\beta F^*$ be minimum. A necessary condition for that is to have $\delta F^* = 0$, from which
\[
g(p) = \lambda(p) + 2\pi^2 \beta y_2 \cos(2\pi \bar{h}) \exp \left[ -\frac{\pi^2}{N} \sum g(p)^{-1} \right] + 8\pi^2 \beta y_4 \cos(4\pi \bar{h}) \exp \left[ -\frac{4\pi^2}{N} \sum g(p)^{-1} \right]. \quad (A24)
\]
and
\[
\sin(2\pi \bar{h}) \left[ y_2 + 4y_4 \cos(2\pi \bar{h}) \exp \left[ -\frac{3\pi^2}{N} \sum g(p)^{-1} \right] \right] = 0. \quad (A25)
\]
Among the solutions to the two joint equations (A24) and (A25), we must ultimately choose the one providing the absolute minimum of $\beta F^*$. In turn, this gives those $\bar{h}(T)$ and $\xi(T)$ that qualify the thermodynamic phases of the surface as described by the Hamiltonian (3.1).

We can further simplify Eqs. (A24) and (A25) by making explicit the $\xi$ dependence. In the thermodynamic limit, a sum $\Sigma_p F(p)$ is evaluated as $N \int \frac{d\mathbf{p}}{(2\pi)^3} F(p)$.
\[
= \frac{N}{2\pi} \int f_{\beta A} d\mathbf{p} \left( 2\pi^2 \right)^3 F(p). \quad \text{We thus find}
\]
\[
-\frac{1}{2} \sum \ln \left[ \pi g(p)^{-1} \right] = -\frac{N}{\beta} \ln \frac{\pi}{\beta} + \frac{N}{\beta} (\pi^2 + \xi^{-2}) \times \ln(\pi^2 + \xi^{-2}) + \frac{N}{\pi} \xi^{-2} \ln \xi - \frac{N}{8} \pi. \quad (A26)
\]
From Eq. (A25), we obtain three possible choices for $\tilde{h}$:

1. $\tilde{h} = \ldots, -2, -1, 0, 1, 2, \ldots,$

2. $\tilde{h} = \ldots, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \ldots$.

3. $\cos(2\pi\tilde{h}) = -\frac{y_2}{4y_4}[1 + (\pi\xi)^{2}]^{3\pi/4\beta J}$.

Solutions of type (1) correspond to the ordered flat surface, and those of type (2) to the disordered flat (DOF) surface.

Type (3), finally, corresponds to the so-called $\theta$-DOF surface.\textsuperscript{26,3,19} In particular, a necessary condition for solutions (3) to be valid is $\xi = 1/\pi[4(4y_4)/(y_2)]^{1/4\beta J}(\pi/2 - 1)/2$.

Plugging Eq. (A31) into Eq. (A30), we obtain three possible expressions for the free energy:

\[
\beta \Delta f^*_1 = \frac{\pi}{8} \ln[1 + (\pi\xi)^{2}] - \beta y_2[1 + (\pi\xi)^{2}]^{-(\pi/4\beta J)} - \beta y_4[1 + (\pi\xi)^{2}]^{-(\pi/\beta J)},
\]

\[
\beta \Delta f^*_2 = \frac{\pi}{8} \ln[1 + (\pi\xi)^{2}] + \beta y_2[1 + (\pi\xi)^{2}]^{-(\pi/4\beta J)} - \beta y_4[1 + (\pi\xi)^{2}]^{-(\pi/\beta J)},
\]

\[
\beta \Delta f^*_3 = \frac{\pi}{8} \ln[1 + (\pi\xi)^{2}] + \frac{\beta y_2^2}{8y_4}[1 + (\pi\xi)^{2}]^{\pi/2\beta J} + \beta y_4[1 + (\pi\xi)^{2}]^{-(\pi/\beta J)}.
\]

We immediately see that free energy of type (3) may become relevant in presence of a strong substrate (see Sec. VII). For a free surface, and with $y_4 > 0$, we can ignore this, and the $\xi$ functional to minimize becomes

\[
\beta \Delta f^* = \frac{\pi}{8} \ln[1 + (\pi\xi)^{2}] - \beta y_2[1 + (\pi\xi)^{2}]^{-(\pi/4\beta J)} - \beta y_4[1 + (\pi\xi)^{2}]^{-(\pi/\beta J)},
\]

with $\tilde{h}$ being an integer for $T < T_{PR}$ and a half-integer for $T > T_{PR}$. Similarly, Eq. (A24) can be rewritten as

\[
J \xi^{2} = 2\pi[1 + (\pi\xi)^{2}]^{-(\pi/4\beta J)} + 8\pi^2 y_4[1 + (\pi\xi)^{2}]^{-(\pi/\beta J)}.
\]

Minimization of the variational free energy (A33) is discussed in Sec. III, together with the analysis of the solutions to Eq. (A34).

Our final comment is about the lattice geometry. One may ask whether the above conclusions retain their validity if a different host lattice is used. In particular, here we consider the case of a triangular lattice. We expect that only nonuniversal quantities like the transition temperatures depend upon the lattice geometry. In order to prove this, we start from Eqs. (A2) and (A4). In the hypothesis of a triangular host lattice, they are to be modified as follows:

\[
V_{xy} = \beta J(6\delta_{xy} - \delta_{|x-y|,1})
\]

and

\[
\lambda(p) = 2\beta J\left[3 - \cos p_x\cos \left(p_x^2 + \frac{3}{2}\right) - \cos \left(p_x\frac{3}{2}\right)\right] = \frac{3}{2} \beta J p^2.
\]

respectively. Similarly, Eq. (A16) becomes

\[
\beta J g(p)^{-1} = \frac{1}{\frac{1}{2}p^2 + \xi^{-2}},
\]

with different wave vectors than before. They now read $p = (n_x/L_x)\mathbf{b}_x + (n_y/L_y)\mathbf{b}_y$, with $\mathbf{b}_x = 2\pi[\mathbf{e}_x - (1/\sqrt{3})\mathbf{e}_y]$ and $\mathbf{b}_y = (4\pi/\sqrt{3})\mathbf{e}_y$. In particular, the area of the first Brillouin zone is now $(2\pi\sqrt{2/3})^2$, and the rule for summing up over all wave vectors becomes:

\[
\frac{1}{N} \sum_p F(p) = \frac{\sqrt{3}}{2} \int_{BZ} \frac{dp}{(2\pi)^2} F(p) = \frac{\sqrt{3}}{4\pi} \int_0^{2\pi/3} p F(p) dp = \frac{1}{2\pi} \int_0^{2\pi/3} p' F\left(\sqrt{2/3} p'\right) dp'.
\]

Given Eq. (A38), and defining $J' = \sqrt{3} J$, $\xi' = \xi^{-2}/\sqrt{3}$, we see that any expression involving only sums of $g(p)$ functionals, like the free energy (A23), becomes equivalent to its square-lattice form if we just replace $J$ with $J'$ and $\xi$ with $\xi'$. In this way, the theory exposed above is still valid [with the only exception of Eq. (A17), to which Eq. (A38) is not directly applicable], but with a new temperature scale $(J'/k_B$ instead of $J/k_B$) and also a rescaled correlation length. In
particular, surface roughening on the triangular lattice would occur at $4\sqrt{3}/\pi$ (in units of $J/k_B$).

**APPENDIX B: FOKKER-PLANCK EQUATION**

This appendix is meant to help the reader follow our derivation, which is formally somewhat different from that of Saito,$^{12}$ even if close in its essence. We derive differential equations for the average height and the pair-correlation function in nonequilibrium conditions when a Gaussian ansatz is made on the height distribution function $P(h_j,t)$, abbreviated as $P(h,t)$. The latter obeys the Fokker-Planck equation (5.5), which we here reproduce for the reader’s convenience:

$$\frac{\partial P(h,t)}{\partial t} = \frac{\beta}{\tau} \sum_i \delta \left( P \frac{\delta \mathcal{H}}{\delta h_i} + \frac{1}{\beta} \frac{\delta P}{\delta h_i} \right). \tag{B1}$$

Here $\mathcal{H}$ contains a term $-\Delta \mu \Sigma h_i$ which makes the crystal grow at the expense of the vacuum. Note that the stationary solution to Eq. (B1) for $\Delta \mu=0$ is $P_{eq}(h) \propto \exp(-\beta \mathcal{H})$, which ensures Boltzmann fluctuations at equilibrium.

We denote as $\langle \cdots \rangle_p$ the average $\int \mathcal{D}h \ P(h,t) (\cdots)$ over the height distribution. First we calculate the evolution of the height at a given site of the lattice:

$$\frac{d}{dt} \langle h_j \rangle_p = \int \mathcal{D}h \left[ \frac{\delta \mathcal{H}}{\delta h_j} + \frac{1}{\beta} \frac{\delta P}{\delta h_j} \right] = -\frac{\beta}{\tau} \left[ \frac{\delta \mathcal{H}}{\delta h_j} \right]_p,$$  

where we used the fact that $P$ goes to zero at infinity. Then, we consider the second cumulant $\langle (h_i - \langle h_i \rangle_p)(h_j - \langle h_j \rangle_p) \rangle_p$, whose first-order time derivative reads

$$\int \mathcal{D}h \left[ \frac{\delta \mathcal{H}}{\delta h_i} \right]_p = -\frac{\beta}{\tau} \left[ \frac{\delta \mathcal{H}}{\delta h_i} (h_i - \langle h_i \rangle_p) \right]_p + \frac{1}{\beta} \left\{ \frac{\delta \mathcal{H}}{\delta h_i} (h_i - \langle h_i \rangle_p) - \frac{1}{\beta} \delta j \right\}. \tag{B3}$$

Equations (B2) and (B3) are to be made explicit by specifying the form of $P$. We make two assumptions.$^{12}$ (1) Homogeneity, $\langle h_i \rangle_p = \overline{h}(t)$; and (2) Gaussian distribution for the heights, i.e., $P(h,t) \propto \exp(-\Sigma_i [h_i - \overline{h}(t)]W_{ij}[h_j - \overline{h}(t)])$, with $W_{ij} = W_{ji} = W_{i+k,j+k}$. This last assumption is not bad, provided the system is not much far from equilibrium. Using

$$\frac{\delta \mathcal{H}}{\delta h_i} = 2J \sum_p (h_i - h_{i+\delta}) + 2\pi y_2 \sin(2\pi h_i) + 4\pi y_4 \sin(4\pi h_i) - \Delta \mu,$$  

we readily obtain

$$\frac{d\overline{h}(t)}{dt} = \frac{\beta}{\tau} \left[ \Delta \mu - 2\pi y_2 \sin(2\pi \overline{h}(t)) \exp \left\{ -\frac{\pi^2}{N} \sum_p g(p,t)^{-1} \right\} - 4 \pi y_4 \sin(4\pi \overline{h}(t)) \exp \left\{ -(4\pi^2/N) \sum_p g(p,t)^{-1} \right\} \right], \tag{B5}$$

where the following resolution was used:

$$W_{xy}^{-1}(t) = \frac{1}{N} \sum_p e^{ip \cdot (x-y)} g(p,t). \tag{B6}$$

Note that in the absence of any driving force the system gradually approaches equilibrium, and Eq. (B5) gives back Eq. (A25).

Then we need the evolution equation of $g(p,t)$. To this end, we use Eq. (B3) which we now make less cumbersome. First, we have [cf. Eq. (A10)]

$$\langle [h_i - \overline{h}(t) ][h_j - \overline{h}(t)] \rangle_p = \frac{1}{2} W_{ij}^{-1}(t). \tag{B7}$$

Upon inserting Eq. (B4) into Eq. (B3), we are led to evaluate $\langle [h_i - \overline{h}(t) ] \sin(2\pi h_j) \rangle_p$. Using the same trick as in Eq. (A10), we obtain

Likewise, we have

$$\langle [h_i - \overline{h}(t) ] \cos(2\pi h_j) \rangle_p = \frac{1}{2} W_{ij}^{-1}(t) \times \exp \left\{ -\frac{\pi^2}{N} \sum_p g(p,t)^{-1} \right\} \tag{B9}$$
\[ \langle [h_i - \bar{h}(t)] \sin(4 \pi h_i) \rangle_p = 2 \pi W_{ij}^{-1} \cos[4 \pi \bar{h}(t)] \times \exp \left( - \frac{4 \pi^2}{N} \sum_p g(p,t)^{-1} \right). \]

Finally, using Eqs. (B7) and (A4), we obtain
\[ \left\{ \sum_\delta (h_i - \bar{h}_i + \delta)[h_j - \bar{h}(t)] \right\}_p = \frac{1}{2} \sum_\delta (W_{ij}^{-1} - W_{i+\delta,j}^{-1}) = \frac{1}{2} \beta J \lambda(p) W_{ij}^{-1}. \]

Collecting together all partial results, and using \( \delta_{xy} = (1/N) \sum_p e^{ip(x-y)} \), we find, in the end
\[ \frac{d}{dt} g(p,t)^{-1} = - \frac{4}{\pi} g(p,t)^{-1} \times \left[ \lambda(p) - g(p,t) + 2 \pi^2 \beta y_2 \cos[2 \pi \bar{h}(t)] \right] \times \exp \left( - \frac{\pi^2}{N} \sum_p g(p,t)^{-1} \right). \]

Again, in stationary conditions, Eq. (B12) gives back the equilibrium result (A24).

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13 See, for example, J. D. Weeks, in Ordering in Strongly Fluctuating Condensed Matter Systems, edited by T. Riste (Plenum, New York, 1980).
22 See, for example, N. Goldenfeld, Lectures on Phase Transitions and the Renormalization Group (Addison-Wesley, Reading, MA, 1992), Chap. 8.