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Roughening transition temperature in the presence of an adsorbing fluid

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The effect on the roughening temperature T_R of an adsorbing fluid above the substrate is calculated. The partition function is evaluated for three models, the Ising model, the absolute solid-on-solid model, and the discrete Gaussian models, with the addition of a second species in vapor form above the surface. Then with the use of the duality transformation of José *et al.* and the renormalization-group method of Kosterlitz, a relationship between T_R and the chemical potential of the fluid is obtained. T_R is then expressed in terms of the ambient pressure by using approximate equations of state. It is found that a significant decrease in T_R may occur as the pressure is increased, and the conditions under which this effect might be observed are discussed.

I. INTRODUCTION

In a previous communication[1] it was noted that the equilibrium roughness of a solid surface will increase in the presence of an adsorbing gas if the preferred adsorption sites are the edges of the protrusions associated with the roughness. Therefore, one would also expect a lowering of the roughening transition temperature T_R. In this paper, we calculate T_R as a function of the chemical potential of the fluid above the surface, and of the adsorption energy. Three models are considered: First we discuss the simple Burton-Cabrera-Frank (BCF) picture,[2] which reduces to the two-dimensional Ising model; then we discuss the absolute solid-on-solid (ASOS) model and the discrete Gaussian model. The renormalization theories that have been established for the "pure" surface[3,4] are immediately applicable in the presence of the adsorbing fluid. The only change is that the energy J needed to create a step of unit height on the pure surface is replaced by a function J':

$$\frac{J'}{k_B T}=f(J/k_B T\ ,(\mu+|\epsilon|)/k_B T)\ ,$$

where μ is the chemical potential, $|\epsilon|$ is the adsorption energy, and k_B is Boltzmann's constant. The value of $K^*=(J'/k_B T)$ at T_R, the roughening temperature, is known from renormalization theory; therefore, T_R in the present case is the solution of the equation

$$K^*=f(J/k_B T_R\ ,(\mu+|\epsilon|)/k_B T_R)\ .$$

The relation between chemical potential, pressure, and temperature of the adsorbing fluid is then used to calculate the roughening temperature T_R as a function of pressure for the gaseous as well as liquid phases where applicable (i.e., where T_R is less than the gas-liquid critical temperature). As one might expect, substantial lowering of T_R occurs in the liquid range. Even if the free liquid is gaseous, the result for the liquid should still be the relevant one, once the adsorbate is several layers thick.

The physical system that we have in mind is that of a crystal surface (for example, silver) in contact with a gas of a different species (for example, carbon dioxide). Models of crystal growth must take into account the exchange of atoms between the substrate and the vapor (or solution) from which the deposit is being made. But it is also of practical interest to consider the effect of a second substance above the surface. In principle, competition between the two vapors is a complicated process; therefore, in this report we make the assumption that the second species has a significantly larger vapor pressure than the first. We also neglect interaction between the two gases and assume that a phenomenological treatment relating the chemical potential to the vapor pressure will be sufficient for our purposes. The second species can adhere to edges of protrusions so that there should be a decrease in T_R as the pressure is increased; the detailed behavior of the gas will not qualitatively influence this conclusion.

This paper is organized as follows. In Sec. II we discuss the calculations involved in obtaining T_R as a function of the chemical potential of the fluid for three distinct models: the Ising, the ASOS, and the discrete Gaussian models. The results are Eqs. (9) and (18). Since the second species is adsorbed at the edges of the substrate we expect the roughening effect to be enhanced as the pressure of the fluid is increased. Therefore, in Sec. III we apply approximate equations of state relating the chemical potential of the fluid to the pressure and temperature, enabling us to obtain T_R explicitly in terms of P. The results are plotted in Figs. 1—3.

II. INTERACTION BETWEEN THE FLUID AND THE SURFACE

A. BCF model

In 1951 Burton, Cabrera, and Frank proposed a two-level model of a crystal surface, in which the roughness energy between two neighbors is written as[2]

$$U(\sigma_i,\sigma_{i+\delta})=J\frac{1-\sigma_i\sigma_{i+\delta}}{2}\ . \tag{1}$$

In this expression, $J=\phi/2$ (ϕ is the binding energy of the crystal), and the variables $\sigma_i,\sigma_{i+\delta}$ take on the values ± 1. The summation index i runs over all sites of the lattice and $i+\delta$ runs over all nearest neighbors in the positive direction. Therefore, the roughness energy for the surface with a given distribution of $\{\sigma_i\}$ is

$$E=\sum_{i,\delta} U(\sigma_i,\sigma_{i+\delta}) \ . \tag{2}$$

Since the model is effectively the two-dimensional Ising model, the roughening transition temperature T_R is exactly known

$$\frac{kT_R}{J}=\frac{1}{\ln\cot(\pi/8)}\sim 1.135 \ . \tag{3}$$

In the presence of an adsorbate, we can write the energy for a given step distribution as

$$E=\frac{J}{2}\sum_{i,\delta}(1-\sigma_i\sigma_{i+\delta}) + \sum_{i,\delta} m_{i+\delta}\left[\frac{\epsilon_1}{2}(1+\sigma_i\sigma_{i+\delta})+\frac{\epsilon_0}{2}(1-\sigma_i\sigma_{i+\delta})\right] , \tag{4}$$

where $m_{i+\delta}=0,1$ is the number of adatoms, ϵ_1 is the adsorption energy at a smooth site, and ϵ_0 is the adsorption energy at a rough site. Including the possibility of adsorption at smooth sites evidently involves no extra work in this model. The grand partition function for the system is

$$Z=\sum_{\substack{\{\sigma_i\},\\ \{m_i\}}} \exp\left[-\frac{\beta J}{2}\sum_{i,\delta}(1-\sigma_i\sigma_{i+\delta}) +\beta\sum_{i,\delta} m_{i+\delta}\left[\frac{\epsilon_1'}{2}(1+\sigma_i\sigma_{i+\delta}) +\frac{\epsilon_0'}{2}(1-\sigma_i\sigma_{i+\delta})\right]\right] , \tag{5}$$

where $\epsilon_1'=\mu-\epsilon_1$, $\epsilon_0'=\mu-\epsilon_0$, and μ is the chemical potential of the adatom in equilibrium with its vapor.

For any well-behaved function $f(\sigma_i\sigma_{i+\delta})$, bearing in mind that $(\sigma_i\sigma_{i+\delta})^{2n}=1$, we have

$$f(\sigma_i\sigma_{i+\delta})=\tfrac{1}{2}[f(1)+f(-1)] + \tfrac{1}{2}\sigma_i\sigma_{i+\delta}[f(1)-f(-1)] \ .$$

We are now left with

$$Z=\sum_{\{\sigma_i\}} A\exp\left[\frac{\beta}{2}\sum_{i,\delta}\sigma_i\sigma_{i+\delta}\left[J+\frac{1}{\beta}\ln(1+e^{\beta\epsilon_1'}) -\frac{1}{\beta}\ln(1+e^{\beta\epsilon_0'})\right]\right] , \tag{6}$$

where

$$A=[e^{-\beta J}(1+e^{\beta\epsilon_1'})(1+e^{\beta\epsilon_0'})]^N$$

is independent of the configurations $\{\sigma_i\}$. It is clear from Eq. (6) that the roughness energy J in the BCF model is now replaced by J_{eff} through the following equation for all temperatures:

$$J_{\text{eff}}=J+\frac{1}{\beta}\ln(1+e^{\beta\epsilon_1'})-\frac{1}{\beta}\ln(1+e^{\beta\epsilon_0'}) \ . \tag{7}$$

Letting $\epsilon_1\to\infty$, i.e., $\epsilon_1'\to-\infty$ (which means that flat sites are not eligible for adsorption), this expression reduces to

$$J_{\text{eff}}=J-\frac{1}{\beta}\ln(1+e^{\beta\epsilon_0'}) \ . \tag{8}$$

Not surprisingly, this is also what we obtained for the ASOS model at low temperatures,[1] where step increments greater than 1 are unlikely.

The roughening transition temperature is now given by the solution of the following equation:

$$k_BT=1.135[J-k_BT\ln(1+e^{\beta|\epsilon_0|}e^{\beta\mu})] , \tag{9}$$

where $e^{\beta\mu}$ is a function of pressure P and temperature T. In the case of an ideal gas, for example, $e^{\beta\mu}=(P/T)\lambda^3$, λ is the de Broglie wavelength of a gas molecule at temperature T. Evidently, T_R is a function of (P,ϵ_0,J), and when $P=0$, $\mu=-\infty$, which means no adsorption is available, we recover the BCF value of T_R. In Fig. 1 we plot P vs T_R; the manner in which $e^{\beta\mu}$ is evaluated in terms of P and T will be discussed in Sec. III.

B. The ASOS and discrete Gaussian models

The partition function evaluated in Ref. 1 was

$$Z=\sum_{\{h_i\}}\exp[-\beta H+\beta\mu N(\Delta h_{i\delta})] , \tag{10}$$

where

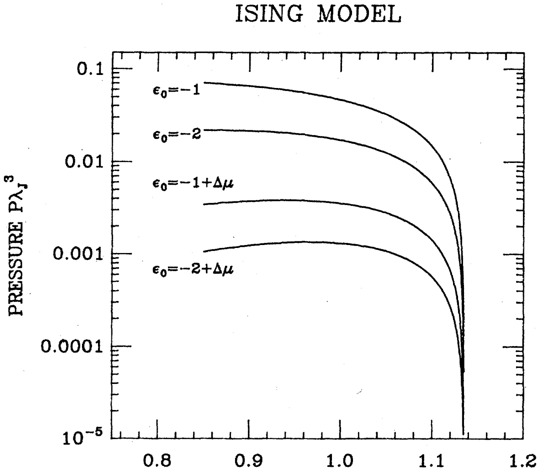

FIG. 1. The graph of P vs T_R in units of J for the Ising model. $\lambda_J=(2\pi\hbar^2/MJ)^{1/2}$. The adsorption energy ϵ is plotted once for $|\epsilon_0|=J$ and once for $|\epsilon_0|=2J$. Also shown are the same curves in the liquid region with a change in chemical potential $\Delta\mu=-2.57J$. The Lennard-Jones parameter u_0 was evaluated at $u_0=4.3J$.

$$H=J\sum_{i,\delta}|h_i-h_{i+\delta}|\ ,$$
$$N(\Delta h_{i\delta})=\sum_{i,\delta}m_{i\delta}\epsilon_0\ , \tag{11}$$
$$m_{i\delta}=\begin{cases}0,1 & \text{if } |h_i-h_{i+\delta}|\neq 0\\ 0 & \text{otherwise}\ .\end{cases}$$

δ is summed over all positive directions. With this particular Hamiltonian, called the ASOS model, these sums can be evaluated exactly, and the result is

$$Z=\prod_{i\delta}\int_0^{2\pi}\frac{d\phi_i}{2\pi}\mathfrak{z}_{i\delta}\ ,$$
$$\mathfrak{z}_{i\delta}=1+(1+e^{\beta\mu'})\frac{\cos(\phi_i-\phi_{i+\delta})-e^{-\beta J}}{\cosh(\beta J)-\cos(\phi_i-\phi_{i+\delta})}\ , \tag{12}$$
$$\mu'=\mu+|\epsilon_0|\ .$$

The indices run over all sites of the lattice, and there is one factor $\mathfrak{z}_{i\delta}$ for each bond between sites. In the limit of low temperatures, as has been pointed out by Weeks,[3(c)] the partition function takes a form similar to that of a classical planar Heisenberg ferromagnet. For our purposes, it is sufficient to expand $\mathfrak{z}$ in powers of the difference of the angles, giving

$$Z=\prod_i\int_0^{2\pi}\frac{d\phi_1}{2\pi}\exp\left[-\frac{K_{\text{eff}}}{2}\sum_{i,\delta}(\phi_i-\phi_{i+\delta})^2+O((\phi_i-\phi_{i+\delta})^4)\right]\ . \tag{13}$$

The effective coupling is

$$K_{\text{eff}}=\frac{1+e^{\beta\mu'}}{\cosh(\beta J)-1}\,\frac{\sinh(\beta J)}{\sinh(\beta J)+e^{\beta\mu'}(1-e^{-\beta J})}\ . \tag{14}$$

The index i refers to a lattice site, $i=(i_x,i_y)$, and δ is summed over all positive directions. In order to proceed with the analysis, we use the duality transformation of José *et al.*[4(a)] This has the effect of taking the original lattice with site variables ϕ_i defined on the interval $(0,2\pi)$ into an new lattice whose site variables φ_i run from $-\infty$ to $+\infty$

$$Z=\sum_{\{m\}}\left[\prod_i\int_{-\infty}^{\infty}d\varphi_i\right]\times\exp\left[-\frac{1}{2K_{\text{eff}}}\sum_{i,\delta}(\varphi_i-\varphi_{i+\delta})^2+2\pi i\sum_i m_i\varphi_i\right]\ . \tag{15}$$

In addition to the "spin-wave" variables φ, this transformation introduces a set of "vortex" variables m_i which range over all positive and negative integers. Introducing an extra term in the exponent, $\ln y_0 m_i^2$, the final form for the partition function is obtained by expanding in powers of y_0 [Refs. 3(c) and 4(a)]

$$Z=\left[\prod_i\int_{-\infty}^{\infty}d\varphi_i\right]\exp\left[-\frac{1}{2K_{\text{eff}}}\sum_{i,\delta}(\varphi_i-\varphi_{i+\delta})^2+y_0\cos(2\pi\varphi_i)\right]\ , \tag{16}$$

so that as in Ref. 3(c) we work with the spin-wave variables rather than the vortex variables. Defining the Green's function to be

$$\langle\varphi^2(q)\rangle^{-1}=G^{-1}(q)=\frac{q^2}{K_R}+m_R^2\ , \tag{17}$$

the renormalization-group method of Kosterlitz[4(b)] can be applied. The spin-wave correlation function $G(q)$ is not directly related to any quantity referring to the original lattice variables h_i; however, the recursion relations for the parameters K, y, and m are similar (though not identical) to those of Kosterlitz. We assume that the fixed point of the dual lattice corresponds to the critical point of the original lattice.

The equation for the fixed point value of K, denoted K^*, is

$$K=\frac{2}{\pi}+\pi K\exp\left[-\frac{\pi}{2}K\ln(8e^{2\gamma})\right]\ . \tag{18}$$

γ is Euler's constant. From this we find $K^*=0.7$ and can then obtain T_R, the roughening temperature, as a function of chemical potential, or less directly as a function of the pressure of the gas, by equating $K^*=K_{\text{eff}}$. (The results are plotted in Fig. 2.) Various values of the adsorption energy ϵ_0 are shown, each indicating a reduction of T_R as the pressure is increased.

For comparison, we have also treated the discrete Gaussian model

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

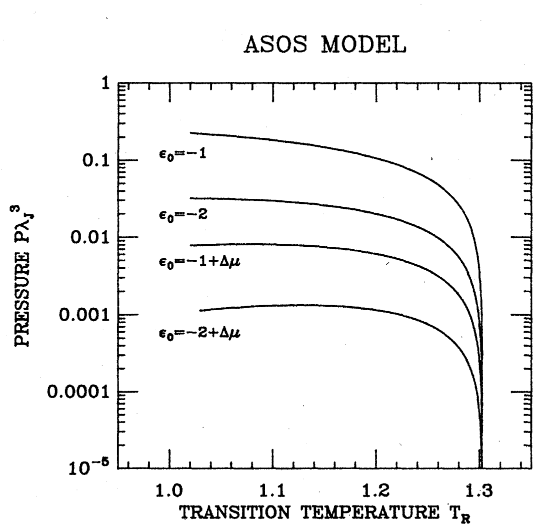

FIG. 2. The graph of P vs T_R for the ASOS model. The same as in Fig. 1 but with $\Delta\mu=-3.43$ and $u_0=5.1$.

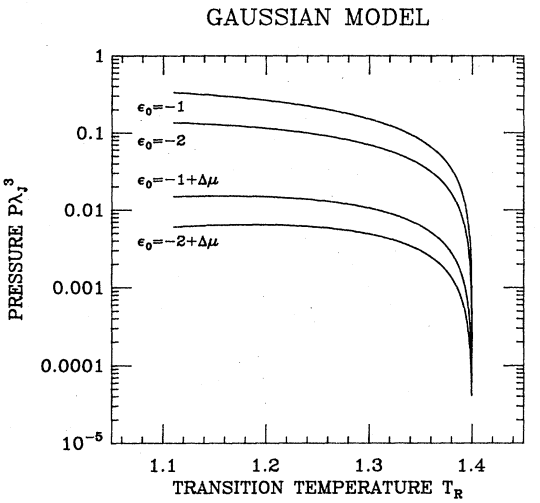

FIG. 3. The graph of P vs T_R for the discrete Gaussian model. The same as in Fig. 1 but with $\Delta\mu=-3.45$ and $u_0=5.4$.

where the variables h_i are restricted to integer values. This cannot be done analytically, but numerical values for K_{eff} are easily obtained. The plot of T_R vs P for this model appears in Fig. 3. For the Gaussian model the effective K is

$$K_{\text{eff}}=\frac{2\gamma B_2(\alpha)}{1+2\gamma B_0(\alpha)}\ ,\quad \alpha=2\ , \tag{19}$$

where

$$\gamma=1+e^{\beta\mu'}\ ,$$

and

$$B_k(\alpha)=\sum_{n=1}^{\infty}\exp\left[-\frac{J\beta}{2}n^{\alpha}\right]n^k\ .$$

In Fig. 4 we have plotted the potential energies used in the various models. The three are identical when $\Delta h=0,1$; thereafter the Ising model has the most potential energy, the ASOS the least. In Monte Carlo simulations,[5] the exact value of T_R depends on the details of the Hamiltonian. The particular form for the roughening energy as a function of temperature, $J(T)$, and the exponent that is used in the height difference $|h_i-h_j|^{\alpha}$ will determine where the transition occurs. Without reference to specific materials, we can only conclude that the above results ought to be applicable to a relatively wide range of physical systems.

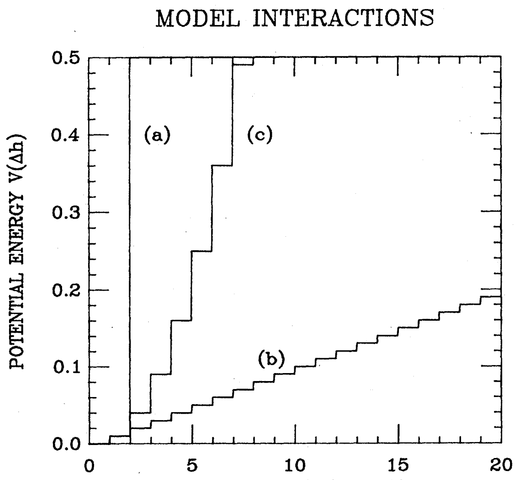

FIG. 4. The effective potential energy between neighboring sites in the (a) Ising model, (b) ASOS model, and (c) discrete Gaussian model.

III. CHEMICAL POTENTIAL OF THE GAS

At $P=0$, all three models are qualitatively similar. The primary difference is in the value of T_R, which is accounted for in the details of the Hamiltonian. Figures 1–3 show the dependence on pressure in the hypothetical case in which the gas is ideal and unable to liquify, and also the case of a van der Waals model in which liquification does occur; because the pressures involved are significant, it is necessary to take into account the liquification of the gas. This was done by starting with the chemical potential of the perfect gas at given pressure and temperature and adding to it the change $\Delta\mu(T,P)$ acquired along a trajectory in the P-T plane in passing from well within the gaseous to well within the liquid state (note that it is sufficient to calculate the change in going from well withing the gaseous phase *up to* —rather than beyond—the coexistence curve).

It is possible to determine the range of values of the van der Waals equation once we have an estimate of J for the substrate. If we use the virial coefficients a,b obtained from the Lennard-Jones potential,[6] the critical temperature for the van der Waals gas is given by

$$T_c=\left[\frac{2}{3}\right]^3\frac{a}{b}\simeq\left[\frac{2}{3}\right]^3u_0$$

(u_0 is the energy parameter in the 6-12 potential). Also we know that the triple point temperature is given by

$$T_t=\frac{1}{4}\frac{a}{b}\simeq\frac{u_0}{4}\ .$$

Therefore, we can fix limits on u_0 in order that the curve $P(T_R)$ crosses the critical curve $P(T)$ for the van der Waals equation. These values depend on T_R at $P=0$ (therefore, depend on the model used) and are given in Table I. In principle, these curves also depend on the par-

TABLE I. The relationship between maximum and minimum allowed values of Lennard-Jones energy u_0, given in units of J.

Model	T_R	$u_{\min}$	$u_{\max}$	$\Delta\mu_{\max}$
Ising	1.135	3.83	4.54	−3.29
ASOS	1.305	4.40	5.22	−3.78
Discrete Gaussian	1.400	4.73	5.60	−4.06

ticular value of ϵ_0, however, this dependence is very weak. A change of 1% was found in $u_{\max}$ when ϵ_0 had been increased by a factor of 50.

One important approximation has been made which requires a brief explanation. The gas-liquid phase transition was treated phenomenologically within the model of an unbounded van der Waals gas. The equation of state of a gas bounded by a smooth surface has been treated in the lattice-gas[7(a)–7(c)] and the Potts lattice-gas models.[7(d)] One simple improvement of our model would be to use the equation of state of Ref. 7(c) or 7(d). A truly complete treatment would simultaneously take into account roughening and the interactions considered in these references.

IV. CONCLUSION

In this paper, we have considered the effect of having a second fluid above a crystal surface near the roughening transition temperature. The adatoms generally can adhere to smooth sites or to the edges of protrusions on the surface, with characteristic energies. Only the latter process was investigated, and it was found that a decrease in roughening temperature T_R results. Phenomenological equations of state were employed to obtain T_R explicitly in terms of the vapor pressure of the fluid.

In conclusion, it can be seen from the graphs that once the gas is in liquid form, considerable decrease in the roughening temperature occurs for relatively little change in pressure. As a result, there is hope that this effect can be observed even if the transition temperature at low pressure is relatively high since the liquification causes a drastic increase in the effective adsorption energy. For a substrate with $J \sim 0.1$ eV, a proper choice of gas would require a material whose binding energy is about 0.5 eV, for which the van der Waals equation would predict a critical temperature of about 100 K.

ACKNOWLEDGMENT

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