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Variational theory of multilayer solid adsorption

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We present a simple variational theory describing the adsorption of successive solid layers on a homogeneous substrate. Infinitely far from the substrate the theory reduces to the self-consistent theory of Saito for the roughening transition. In agreement with recent Monte Carlo simulations a sequence of first-order transitions is found at low temperatures. However, at temperatures greater than the roughening temperature, all layers are adsorbed in a continuous manner.

Recently there have been several studies of the physical adsorption of atoms on a homogeneous periodic substrate.[1-5] While mean-field theory (MFT) applied to a lattice gas model has provided a useful guide to many features of the "wetting" transition,[4] it gives a qualitatively incorrect description of the effects of finite temperature fluctuations on the first-order "layering" transitions.[1-4] These transitions arise from the addition of successive layers of a solid adsorbate onto a strongly attractive substrate as the pressure is increased. This deficiency is closely related to the failure of MFT to predict a roughening transition[6] for the three-dimensional lattice gas interface, as was recognized by de Olivera and Griffiths.[1]

In this Communication we present a simple theory which treats in a qualitatively correct way the long-wavelength fluctuations affecting the layering and roughening transitions. The theory is in good agreement with available Monte Carlo (MC) simulations[2,3] and has already been used to help analyze the data in an experimental study of solid ^{4}He adsorbed on graphite.[5]

As in Ref. 1, an atom in the nth adsorbed layer is assumed to interact with the substrate by the attractive potential $u_n = -c/n^3$. (Atoms in the first layer may feel an additional attraction which we assume for simplicity is strong enough to give wetting at $T = 0$.) This attractive interaction can stabilize an adsorbed phase of finite thickness when the chemical potential (pressure) is less than the value which produces an adsorbed layer of infinite thickness.

The long-wavelength properties of the adsorbed solid-fluid interface are described by the following coarse-grained Hamiltonian, which is a simple generalization of that used to study the roughening transition[6]

$$H = \frac{J}{2} \sum_{j,\delta} (h_j - h_{j+\delta})^2 + \sum_j V(h_j) - \frac{J}{2} y_0 \sum_j \cos 2\pi h_j \ . \tag{1}$$

As discussed in detail by Weeks for the liquid-vapor interface,[7] the h_j indicate the distance from the substrate at coarse-grained substrate positions j, conveniently taken to form a square lattice, of the local Gibbs dividing surface separating solid and fluid regions when other degrees of freedom of the microscopic Hamiltonian are integrated out. The h_j can be visualized as the heights of interacting columns and give a description of the long-wavelength fluctuations of the interface.

The first sum in Eq. (1) over all columns j and nearest neighbors $j+\delta$ acts as a surface tension to favor flat surface configurations with all h_j equal. The second term, discussed below, gives the combined effects of the interaction with the substrate and the chemical potential deficit $\Delta\mu$ in terms of an effective column potential $V(h_j)$. Both these terms would appear in a treatment of the adsorption of a liquid layer. If the adsorbed phase is a solid, the third term which energetically favors integer (i.e., discrete) values of h_j is also needed. (Higher harmonics have a negligible effect on the theory described herein.) Although nonintegral h_j are possible in the coarse-grained picture, these must arise from averages over microscopic configurations having intracolumn steps and are of higher energy than the integer values. The dimensionless parameter y_0 determines the importance of this "discreteness" term at low temperatures and will be chosen to best fit experiment. At high temperatures, thermal fluctuations will greatly reduce the importance of this term and the adsorption isotherms are very similar for solid and for liquid adsorbates.

We assume, for the effective column potential,

$$V(h) = \Delta\mu h + \frac{c}{2}(h + \tfrac{1}{2})^{-2} + k_1 \ . \tag{2}$$

The chemical potential deficit $\Delta\mu$ acts as a uniform "magnetic field" on the column variables h, and the second term gives the effect of interactions with the substrate. We have approximated the coarse-grained average of the atomic interaction term u_n over configurations consistent with a given h by a trapezodial rule integration, treating n as a continuous variable. k_1 is an integration constant depending on c and any additional first layer interaction, whose precise value is unimportant in what follows. $V(h)$ has its minimum value at a height h_0 given by

$$h_0 = (\Delta\mu/c)^{-1/3} - \tfrac{1}{2} \ . \tag{3}$$

When the term involving y_0 in Eq. (1) is unimportant (e.g., a solid at high temperatures or a fluid), h_0 closely approximates the average position of the interface (average coverage) to be found for a given $\Delta\mu$.

We determine the behavior of the interface under more general conditions by use of the variational principle[8,9] for the free energy

$$\frac{A}{N} \leqslant \frac{A_0}{N} + \frac{1}{N}\langle H - H_0\rangle_0 \ , \tag{4}$$

where $\langle\ \rangle_0$ denotes a normalized ensemble average using an arbitrary reference Hamiltonian H_0. It is physically reasonable and mathematically very convenient to take H_0 as the simple quadratic form

$$H_0 = \frac{J}{2}\sum_{j,\delta}(h_j - h_{j+\delta})^2 + B\sum_j (h_j - \alpha)^2 \ . \tag{5}$$

The free parameters α (which gives the average position of the interface) and B (which controls the extent of the fluctuations about α) are chosen to minimize the free energy in Eq. (4). This method is a generalized and simplified version of the approach Saito[9] used to describe the roughening transition with $V(h) = 0$, where it gives remarkably accurate results for so simple a theory.

Since H_0 is quadratic, the Gaussian averages in Eq. (4) are easy to perform. Thus, defining $D_j = h_j - \alpha$, we have[9,7]

$$\langle \cos 2\pi h\rangle_0 = \cos 2\pi\alpha \exp[-\tfrac{1}{2}(2\pi)^2\langle D^2\rangle_0] \tag{6}$$

and

$$\langle V(h)\rangle_0 = V(\alpha) + \tfrac{1}{2}V^{(2)}(\alpha)\langle D^2\rangle_0 + \cdots \ , \tag{7}$$

on expanding $V(h)$ in a Taylor series about $h = \alpha$. Higher-order terms in this (strictly speaking, asymptotic) expansion of the potential are negligible except possibly very near the substrate. Finally, we note to a good approximation[7,9]

$$\langle D^2\rangle_0 \equiv \frac{1}{N}\left(\frac{\partial A_0}{\partial B}\right)_\alpha = -\frac{1}{2\pi^2}\left(\frac{T}{T_R}\right)\ln\beta \ , \tag{8}$$

where $\beta = b/(1+b)$ and $b = B/J\pi^2$. Here $T_R/J = 4/\pi$ is the bulk roughening temperature in the variational approximation.[9]

The minimum free energy in Eq. (4) comes from the b and α values which satisfy $\partial A/\partial b = 0$ and $\partial A/\partial\alpha = 0$. These conditions give our two basic equations

$$b = (\tfrac{1}{2})v^{(2)}(\alpha) + y_0\beta^{T/T_R}\cos 2\pi\alpha \ , \tag{9}$$

$$\frac{y_0}{\pi}\beta^{T/T_R}\sin 2\pi\alpha + v'(\alpha) + (\tfrac{1}{2})v^{(3)}(\alpha)\langle D^2\rangle_0 = 0 \ . \tag{10}$$

Here $v(\alpha) = V(\alpha)/J\pi^2$ with similar definitions for the derivatives of V. The variational equation[9] describing the bulk roughening transition is obtained by setting $v(\alpha) = 0$ and α integral.

The coupled Eqs. (9) and (10) have been solved numerically, and (as is often the case) when multiple solutions are found, the one giving the lowest free energy is chosen. These solutions are closely approximated by the solutions to a set of simpler equations derived below for which several analytic results can also be derived.

Let α_0 and b_0 denote the "continuum" solutions to Eqs. (9) and (10) which arise when $y_0 = 0$. [It is a fairly good approximation to set $\alpha_0 = h_0$ in Eq. (3) since the term involving $v^{(3)}(\alpha_0)$ in Eq. (10) makes only a small correction.] Expanding the averaged potential in Eq. (7) about α_0 and ignoring variations in the fluctuation term $\langle D^2\rangle_0$ we have, to second order in $\alpha - \alpha_0$,

$$\langle V(h)\rangle_0 = V(\alpha_0) + \tfrac{1}{2}V^{(2)}(\alpha_0)[(\alpha - \alpha_0)^2 + \langle D^2\rangle_0] \ . \tag{11}$$

Minimizing the resulting free energy and noting $b \ll 1$ for T near T_R, we find the simplified equations

$$b = (\tfrac{1}{2})v^{(2)}(\alpha_0) + y_0 b^{T/T_R}\cos 2\pi\alpha \ , \tag{12}$$

$$0 = (2\pi)^{-1}y_0 b^{T/T_R}\sin 2\pi\alpha + (\tfrac{1}{2})v^{(2)}(\alpha_0)(\alpha - \alpha_0) \ . \tag{13}$$

Again, the lowest free-energy solution is used in the case of multiple solutions. It is convenient to consider α as a function of the continuum position α_0 in the following qualitative discussion of the solutions to Eqs. (12) and (13).

When $\alpha_0 = n$ for n integral the results are particularly simple since Eq. (13) has the solution (always of lowest free energy) $\alpha = \alpha_0$. There is also a solution $\alpha = \alpha_0$ for $\alpha_0 = n + \frac{1}{2}$ but this solution has the lowest free energy only for $T > T_{c,n}$ with $T_{c,n} < T_R$. We find numerically that $T_{c,n}$ is a very weak and increasing function of n with $T_{c,n} \rightarrow T_R$ as $n \rightarrow \infty$. There are first-order transitions for $T < T_{c,n}$ where α jumps from near n to near $n+1$ as α_0 is increased. The slope $\alpha' \equiv d\alpha/d\alpha_0$ at the integer (and when stable) half-integer positions is given by $\alpha' = (\frac{1}{2})v^{(2)}(\alpha_0)/b$.

For $T = T_R$ we can solve Eq. (12) for b and substitute into Eq. (13) to get

$$\alpha=\alpha_0-\frac{y_0\sin 2\pi\alpha}{2\pi(1-y_0\cos 2\pi\alpha)} \quad . \tag{14}$$

It is easy to show that α is a continuous and invertible function of α_0 for $y_0 \leq \sqrt{3}/2=0.866$, which we assume in all that follows. Equation (14) thus gives continuous coverage for all layers at $T=T_R$ and predicts a universal profile $\alpha(\alpha_0)$ independent of layer number with slope $\alpha'=1\pm y_0$ for α integral (− sign) or half integral (+ sign). For $y_0=0.8$, which provides a good fit to the MC data,[10] the adsorption curve is thus quite flat at integral α_0 and rises much more steeply for α_0 half integral. Similarly, the fluctuations are smaller for integral α_0 and largest near half-integral coverage.

As T is increased, α rapidly approaches α_0. For example, on plotting α vs α_0, only very small ripples are seen at $T=1.3T_R$. For fixed $T>T_R$ there is also a weak layer dependence with the ripples decreasing and $\alpha\rightarrow\alpha_0$ as $n\rightarrow\infty$. Note from Eq. (12) that $b\rightarrow b_0=(\frac{1}{2})v^{(2)}(\alpha_0)$ at high temperatures and it is only at an infinite distance from the substrate that, strictly speaking, we have the vanishing of b and the diverging fluctuations which characterize the bulk roughening transition.[9,6]

One interesting but probably spurious prediction of Eqs. (12) and (13) is the existence of first-order transitions from near integral coverage to a region of stable fractional coverage centered about half layer positions. However, these modified first-order transitions occur only in the very narrow temperature range $T_{c,n}<T<T_R$ and the predicted fluctuations are large. Thus it may be very difficult to determine experimentally whether this detailed feature of the theory is correct.

In summary, the variational method has provided a very simple and qualitatively accurate description of many features of multilayer adsorption. In agreement with MC data[2,3] Eqs. (9) and (10), or the simplified versions (12) and (13), give an infinite number of first-order transitions at low temperatures with continuous coverage for all layers at temperatures above the bulk roughening temperature T_R. A detailed comparison of this theory with new MC results will be presented in another paper.[10]

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