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Energetics of surface roughness and adsorption

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Usually, rough surface sites are preferred in adsorption processes. The gain in adsorption energy to some extent compensates for the roughening energy, favoring an increase in roughness.

The equilibrium between a gas over the surface of a solid and the atoms adsorbed on it, in the range of monatomic coverage, is given by the so-called Langmuir isotherm,[1] most easily derived from detailed balance considerations. In this, as well as in more elaborate derivations, the surface sites available for adsorption are considered fixed and not subject to thermodynamic "recoil" due to the adsorbate. In fact, in the most common treatment, all atomic cells on the surface are taken to be identical and equally capable of adsorption.

However, it is quite usual for adsorption to occur preferentially at irregularities in the surface structure[2] (e.g., at ledges), presumably because of greater bonding opportunities there. Thus, the energy cost of supporting an irregular feature in the surface can to some extent be met by the bonding of an adatom. This means that for sufficiently large adsorption energies, one should expect an increase in surface roughness over the roughness appropriate to equilibrium without adsorbate. In this paper we present a simple assessment of this effect for low temperatures. Extension to higher temperatures and a discussion of the effect on the roughening transition is left for a later publication.

As an extreme example, let us assume that adsorption is allowed only at a site that differs in height from at least one neighboring site. Referring to Fig. 1, the roughness energy in a state with a given distribution of heights h_{ij} of the various sites is

$$E_R = J \sum_{ij} (|h_{ij} - h_{ij-1}| + |h_{ij} - h_{i-1j}|) \ , \tag{1}$$

where the sites are considered ordered (with increasing i for fixed j and vice versa).

The adatom occupation numbers of the sites are taken to be

$$m_{ij} = \begin{cases} 0 & \text{if } h_{ij} - h_{ij-1} = 0 \\ 0, \text{ or } 1 & \text{if } h_{ij} - h_{ij-1} \neq 0 \ , \end{cases} \tag{2}$$

$$n_{ij} = \begin{cases} 0 & \text{if } h_{ij} - h_{i-1j} = 0 \\ 0, \text{ or } 1 & \text{if } h_{ij} - h_{i-1j} \neq 0 \ . \end{cases}$$

It is convenient to introduce the notation (see, e.g., Weeks[3]):

$$p_{ij} = h_{ij} - h_{ij-1} \ ,$$
$$q_{ij} = h_{ij} - h_{i-1j} \ . \tag{3}$$

These p's and q's obey[4]

$$p_{ij} + q_{ij-1} - p_{i-1j} - q_{ij} = 0 \ . \tag{4}$$

In writing the partition function Z (the grand partition function with respect to the adatoms), we allow for the constraint (4) by means of the representation

$$\delta_{k0} = \frac{1}{2\pi} \int_0^{2\pi} d\phi e^{ik\phi} \tag{5}$$

of the Kronecker δ. We have

$$Z = (2\pi)^{-N} \int_0^{2\pi} \sum_{ij} d\phi \prod_{ij} \sum_{\text{all configurations}} \exp\left(-\sum_{ij} [\beta J(|p_{ij}| + |q_{ij}|) + i\phi_{ij}(p_{ij} - p_{i-1j} + q_{ij-1} - q_{ij})] + \beta\mu' \sum_{ij} (m_{ij} + n_{ij}) \right) \ . \tag{6}$$

Here, $\beta = (k_\beta T)^{-1}$ and $\mu' = \mu + |\epsilon|$, where μ is the chemical potential of the adatom in equilibrium with its vapor, and $\epsilon = -|\epsilon|$ is the adsorption energy. Also, $N = L \times M$, L and M being the side lengths of the lattice. Carrying out the sums over the P's and q's gives

$$Z = (2\pi)^{-N} \int_0^{2\pi} \prod_{ij} d\phi_{ij} Z_{ij} \ , \tag{6a}$$

where

$$Z_{ij} = \left(1 + (1 + e^{\beta\mu'}) \frac{\cos(\phi_{ij} - \phi_{i+1j}) - e^{-\beta J}}{\cosh\beta J - \cos(\phi_{ij} - \phi_{i+1j})} \right)$$
$$\times \left(1 + (1 + e^{\beta\mu'}) \frac{\cos(\phi_{ij} - \phi_{ij+1}) - e^{-\beta J}}{\cosh\beta J - \cos(\phi_{ij} - \phi_{ij+1})} \right) \ . \tag{6b}$$

At low temperatures, retaining only the first order in $e^{-\beta J}$

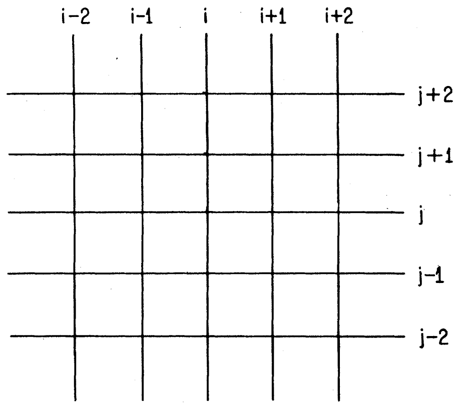

FIG. 1. Labeling of lattice sites.

gives

$$Z_{ij}=(1+A\cos\phi_{ij}\cos\phi_{i+1j}+A\sin\phi_{ij}\sin\phi_{i+1j})\times(1+A\cos\phi_{ij}\cos\phi_{ij+1}+A\sin\phi_{ij}\sin\phi_{ij+1})\ , \tag{6c}$$

where $A=2(1+e^{\beta\mu'})e^{-\beta J}$. Associating a "$C$" with a nearest-neighbor link $(ij;ij+1)$ or $(ij;i+1j)$, etc., carrying a cosine product, and an "S" with a link $(ij;ij+1)$ or $(ij;i+1j)$, etc., carrying a sine product, we see that only closed graphs with either nothing but "C"-type bars or nothing but "S"-type bars survive integration over the ϕ's.

Counting all possible such graphs is difficult. A crude approximation is obtained by counting the smallest squares only. For these

$$Z=\sum_{l=0}^{N}\sum_{n=0}^{l}\frac{N!}{(N-l)!l!}\frac{l!}{(l-n)!n!}Z^l\ , \tag{7a}$$

where $Z=(1+e^{\beta\mu'})^4e^{-4\beta J}$, is the contribution of a single admissible square, of which there are l, n of these l being "C"-type squares. This formula overcounts by admitting neighboring squares that share one or more sides. The effect of this overcounting is to some extent mitigated by the fact that larger closed graphs have been omitted. In this approximation, we find

$$Z=[1+2(1+e^{\beta\mu'})^4e^{-4\beta J}]^N \tag{7b}$$

and then the mean number of kink sites is

$$\langle N_{\text{kink}}\rangle=-\frac{\partial}{\partial\beta J}\ln Z=\frac{8N(1+e^{\beta\mu'})^4}{e^{4\beta J}+2(1+e^{\beta\mu'})^4}\ , \tag{8}$$

while the number of adatoms is

$$\langle N_{\text{ad}}\rangle=\frac{\partial}{\partial\beta\mu'}\ln Z=\frac{8N(1+e^{\beta\mu'})^3e^{\beta\mu'}}{e^{4\beta J}+2(1+e^{\beta\mu'})^4}\ . \tag{9}$$

Note that, not surprisingly

$$\langle N_{\text{ad}}\rangle/\langle N_{\text{kink}}\rangle=e^{\beta\mu'}/(1+e^{\beta\mu'})\ ,$$

which, bearing in mind the relation between gas pressure and chemical potential, is the same formula as the Langmuir coverage.

The apparent coverage, however, is

$$\frac{\langle N_{\text{ad}}\rangle}{N}=\frac{8e^{\beta\mu'}(1+e^{\beta\mu'})^3}{e^{4\beta J}+2(1+e^{\beta\mu'})^4}=\frac{8e^{-\beta\epsilon}fP(1+e^{-\beta\epsilon}fP)^3}{e^{4\beta J}+2(1+e^{-\beta\epsilon}fP)^4}, \tag{10}$$

where $e^{\beta\mu}=fP$ is the Tetrode-Sackur formula, with

$$f=\left(\frac{2\pi\hbar^2}{m}\right)^{3/2}(k_BT)^{-5/2}$$

and P the gas pressure above the surface. Also the concentration of rough sites is

$$\frac{\langle N_{\text{kink}}\rangle}{N}=\frac{8(1+e^{\beta|\epsilon|}fP)^4}{e^{4\beta J}+2(1+e^{\beta|\epsilon|}fP)^4}\ . \tag{11}$$

For very large P or $|\epsilon|$, (11) gives the unphysical result $\langle N_{\text{kink}}\rangle/N=4$. Undoubtedly this is due to the overcounting becoming severe in that limit. It is clear, however, that for J and $|\epsilon|$ comparable, the increase in roughening due to adsorbate can be considerable.

We note one result that is exact in the low-temperature limit ($k_BT<<J$). Formula (6c) then shows that the presence of adsorption can be characterized by an effective roughening energy

$$J_{\text{eff}}=J-k_BT\ln(1+e^{\beta\mu'})\ . \tag{12}$$

Finally, the results for θ and $\langle N_{\text{kink}}\rangle/N$ in the case when "smooth" sites are also eligible for adsorption (but with less binding energy) are found to be

$$\theta=\frac{\langle N_{\text{ad}}\rangle}{N}=\frac{(1+e^{\beta\mu''})^3e^{\beta\mu''}-\dfrac{6e^{\beta\mu''}e^{-4\beta J}(1+e^{\beta\mu'})^4}{1+e^{\beta\mu''}}+8e^{\beta\mu'}e^{-4\beta J}(1+e^{\beta\mu'})^3}{(1+e^{\beta\mu''})^4+2(1+e^{\beta\mu'})^4e^{-4\beta J}}\ , \tag{13}$$

$$\frac{\langle N_{\text{kink}}\rangle}{N}=\frac{8(1+e^{\beta\mu'})^4}{(1+e^{\beta\mu''})^4e^{4\beta J}+2(1+e^{\beta\mu'})^4}\ , \tag{14}$$

where $\mu'=\mu-\epsilon'$, $\mu''=\mu-\epsilon''$, ϵ' and ϵ'' being the adsorption energies at rough and smooth sites, respectively.

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[1] See, e.g., J. M. Blakely *et al.*, in *Surface Physics of Materials, Vol. 1*, edited by J. M. Blakely (Academic, New York, 1975).

[2] B. Lang, R. W. Joyner, and G. A. Somorjai, Surf. Sci. **30**, 454 (1972); Netzer and Wille, *ibid.* **74**, 547 (1978).

[3] John Weeks, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum, New York, 1980).

[4] In one-dimensional case, there is no similar constraint for the height difference. Hence, the calculation of Z can be carried out rigorously and trivially. The result is $Z=[1+2(e^{\beta\mu'}+1)/(e^{\beta J}-1)]^N$.