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LETTER TO THE EDITOR

Re-entrant phenomena in thin film layering transitions

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Abstract. The μ against T plane is studied for the lattice gas and ASOS models of a two-dimensional interface using both the cumulant expansion version of the real space renormalisation group and low temperature perturbation theory. Contrary to results obtained using the Migdal-Kadanoff approximation re-entrant behaviour (at fixed μ) is seen. The same models in one dimension have also been solved (numerically) and similar effects are seen, supporting the two-dimensional results.

In recent years considerable progress has been made in the understanding of thick and thin film growth (for reviews see Pandit *et al* (1982) and Sullivan and Telo da Gama (1985)). Phenomena such as layering (de Oliveira and Griffiths 1978), wetting (de Gennes 1985) and roughening (Weeks 1980) have all been investigated using a variety of theoretical tools such as thermodynamics (Sullivan 1979, Cahn 1977), mean-field theory (Hauge and Schick 1983), Monte Carlo simulation (Ebner 1980, 1981) and renormalisation group (Saam 1983, Nightingale *et al* 1984, Kroll and Lipowsky 1982, Fisher and Huse 1985).

Most theoretical calculations use models which, for convenience, ignore certain excited modes of the interface. Huse *et al* (1985) have pointed out that overhangs and bubbles, while unimportant on length scales larger than the bulk correlation length, nevertheless influence the critical properties of the interface. Kariotis and Suhl (1985) considered the influence of surface irregularities on the roughening transition. In particular, the work of Nightingale *et al* uses an effective column potential of

$$\begin{aligned} V(h) &= -B - A/h^2 \qquad h > 0 \\ &= 0 \qquad\qquad\quad h = 0 \end{aligned} \tag{1}$$

where h, a positive integer, is the column height and A and B are parameters that represent the adatom-substrate and the adatom-adatom interaction. The form of this potential excludes the possibility of fluctuations in the surface of the deposited adatoms. In this letter we consider the effects that these surface excitations have on the phase diagram in the μ against T plane.

The Hamiltonian for the ASOS (absolute solid-on-solid) model is given by (Nightingale *et al* 1984, Weeks 1980)

$$H = J \sum_{ij} |h_i - h_j| + \sum_i [-\mu h_i + V(h_i)] \tag{2}$$

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where h_i is a non-negative integer and represents the column height above the substrate at site i. μ is the chemical potential of the adatoms and $V(h)$ is the (single-column) potential energy for a column of height h. $V(h)$ contains effects due both to the adatom–substrate and adatom–adatom interactions. A discussion of the form in equation (1) (which we will use below) is given by Nightingale *et al.* The approximation that this represents is that surface fluctuations not included in $V(h)$ can be accounted for in the nearest-neighbour term in H. The result leads to a tractable form for the partition function which can be evaluated using real space renormalisation group (RSRG) techniques in the Migdal–Kadanoff (MK) approximation. The phase diagram in the μ against T plane that is found within the MK approximation shows boundaries that separate regions of integral film thickness, and whose behaviour is monotonically decreasing with increasing temperature. No re-entrant behaviour appears; that is, there are no regions in which $\mu(T)$ along the phase boundaries increases as T increases.

We have calculated the phase diagram using the cumulant expansion form of the RSRG and found that, contrary to the statement made by Nightingale *et al*, the slope of the phase boundaries is not monotonic, suggesting the existence of re-entrant behaviour. This effect was then compared with calculations done on one-dimensional models, and also with those performed using low temperature perturbation theory. In both cases the re-entrant behaviour was found. The manner in which these results were obtained is as follows.

In order to perform an RG calculation we use an $N \times N$ matrix which represents the interaction between two neighbouring sites that are in states n_1 and n_2 respectively (n_1, n_2 are one of N possible states at each site). The ASOS nearest-neighbour interaction is

$$H_{ij}(n_1, n_2) = J|n_1 - n_2| + V(n_1) + V(n_2) - \mu(n_1 + n_2). \tag{3}$$

This determines the initial interaction. The first renormalised and subsequent interactions are obtained using the single diagram of the cumulant expansion (see Niemeyer and van Leeuwen 1974) shown in figure 1. The projection operator which was used

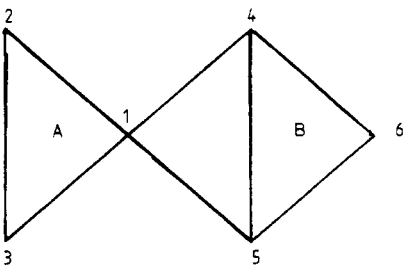

Figure 1. The first diagram in the cumulant expansion of the real space renormalisation group. The three sites which make up cell A have heights n_1, n_2 and n_3. Those of cell B have heights n_4, n_5 and n_6.

takes the 'height' of the cell to be the average of the three height variables of the individual sites that make up the cell:

$$P(h_A, \{h_i\}) = \delta[h_A - \tfrac{1}{3}(h_1 + h_2 + h_3)]. \tag{4}$$

The renormalised interaction is given by

$$H'(k, l) = 2\langle H(n_1, n_4)\rangle - T \ln[Z_0(k) Z_0(l)] \tag{5a}$$

where

$$Z_0(l) = \mathrm{Tr}\, e^{-\beta H_A} P(l, \{h_i\}). \tag{5b}$$

$\beta = 1/T$ and H_A is the 3-site Hamiltonian for cell A (see figure 1):

$$H_A = H_{12}(n_1 n_2) + H_{23}(n_2 n_3) + H_{31}(n_3 n_1). \tag{6}$$

H is an $N \times N$ matrix, where N is the maximum height allowed for the height variables h_i (taken to be 20). Transitions between states in which $\langle h \rangle = l$ and $\langle h \rangle = l + m$ are determined by the initial values of T and μ where the behaviour $H(l, l) \to -\infty$ makes a transition to $H(l+m, l+m) \to -\infty$, all other diagonal elements being less negative.

The results of the cumulant version of the RSRG applied to the ASOS Hamiltonian are shown in figures 2(a) and (b). Figure 2(a) is equivalent to figure 1 of Nightingale *et al* but in this case, the coexistence lines separating regions of different film thickness can be seen to bulge upward very slightly for thin films. If one were to express the pressure in terms of μ as

$$\mu = T \ln(P/P_0) - T \ln(T/T_0)^{5/2} \tag{7}$$

this would literally require that in some regions of the phase plane (for fixed μ) a decrease in film thickness would result with increasing T, and hence P. This effect is even more pronounced in figure 2(b) where the scale of the energy has been decreased by a factor of 10, resulting in the appearance of a low temperature triple point. The bulging seems to become smaller as the film thickness increases.

In addition to the ASOS model we have also investigated a similar calculation carried out on the lattice gas model (de Oliveira and Griffiths 1978) in order to determine if the re-entrant effect is particular to the ASOS model. In this theory the Hamiltonian is

$$H = \sum_{ij} V_0 n_i n_j + \sum_i [-\mu + V(i)] n_i \tag{8}$$

where the indices i, j refer to the three-dimensional coordinate of each site (which may be either occupied ($n = 1$) or not ($n = 0$)). $V(i)$ is the van der Waals potential, $V(i) = u_0/i^3$. The RSRG works the same here as in the ASOS model except that the 'state' of each column is assigned an integer that unambiguously determines which sites within the column are occupied or not. For the ASOS, a height h fixes exactly the state of the column; for the lattice gas, a 'binary' number is given by

$$L_A = \sum_{i=1}^{N} n_i^A 2^{i-1} \tag{9}$$

where each n_i^A is a site variable in column A at the ith layer above the substrate. Thus $L_A = 0$ corresponds to zero layers on the substrate, $L_A = 1$ corresponds to one layer, $L_A = 3$ corresponds to two, $L_A = 7$ to three, etc. Once the set of states are given their respective L_A values, an interaction matrix $H(L_A, L_B)$ between column A in state L_A and column B in state L_B can be constructed using the Hamiltonian (8). When H is thus obtained, the RSRG is applied as before, and the results are shown in figure 3.

For temperatures below the critical temperature, the layering transitions occur in a well ordered sequence. The critical temperatures $T_c(n)$ are of course functions of the van der Waals parameter u_0 and the height above the substrate, and the behaviour in this region is considerably complex, but the transition from layered to striped behaviour is distinct. This effect was first discussed in the context of interface behaviour by Huse *et al* (1985) and a more detailed study of this model will be given elsewhere

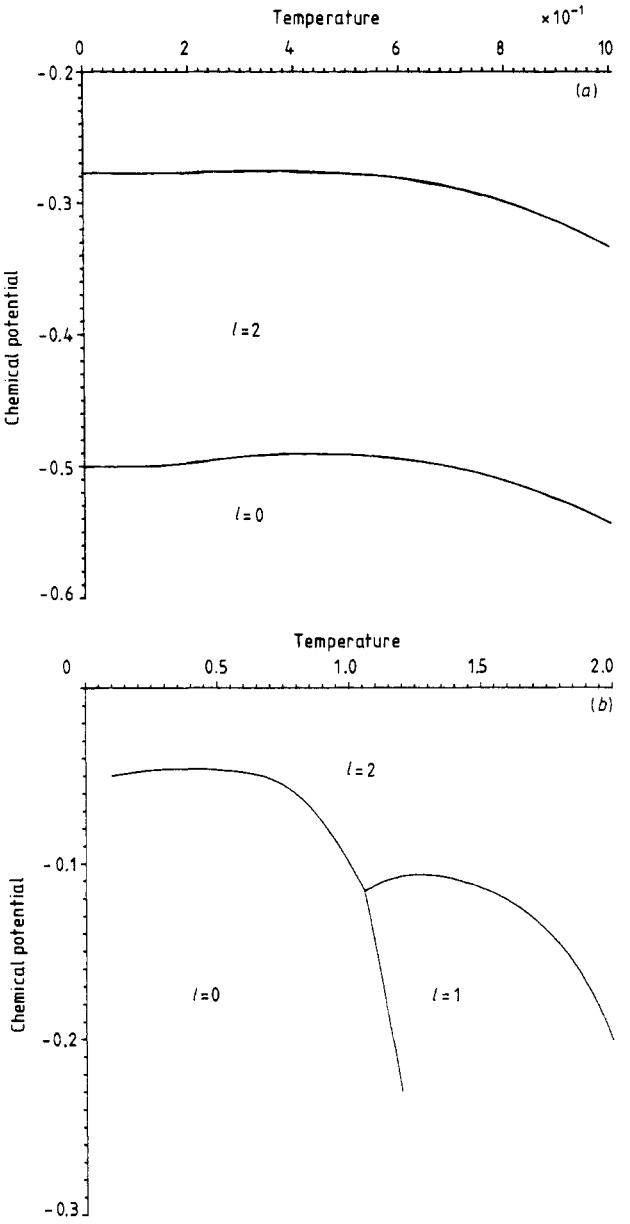

Figure 2. (*a*) The μ against T phase plane showing the phase boundaries separating states of different film thickness. For comparison, we chose $A=-2.0$ and $B=1.5$ as in figure 1 of Nightingale *et al* (1984). (*b*) The same as in (*a*) with $A=-0.2$ and $B=0.15$.

(Kariotis and Prentis 1986). For the purpose of the present study, it is sufficient to observe that the re-entrant effect is clearly present along the phase boundary separating zero and two layers, and zero and one stripe.

We turn now to the case of calculations on one-dimensional models. It is conceivable that the re-entrant behaviour which results from the above transformation is not a real physical effect but rather arises from the nature of the approximation itself.

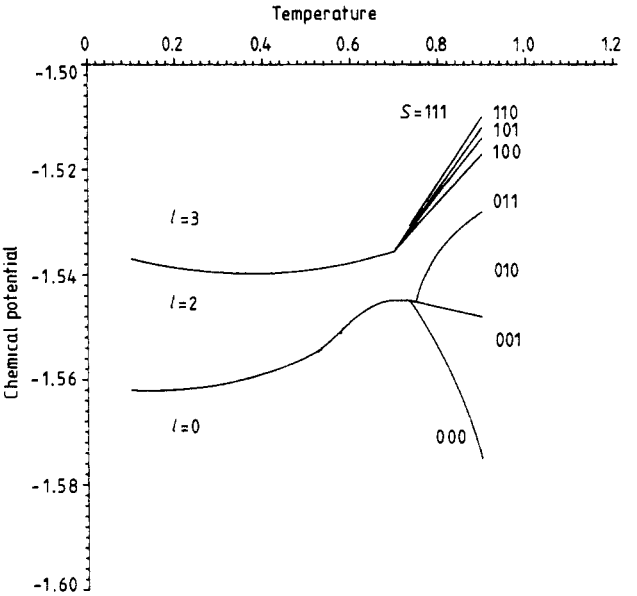

Figure 3. The μ against T phase plane for the lattice gas model. To the left of the critical temperatures, the phase boundaries separate states with distinct film thickness of $l=0$, $l=2$, $l=3$. To the right of the critical temperatures striped phases occur, denoted $S=000$, $S=001$, etc.

Kaufman and Griffiths (1983) have shown that for second-order phase transitions the usual form of the cumulant expansion violates thermodynamic convexity in the low temperature region. Although our method (which is used here only for first-order transitions) does not generate a free energy as the iteration proceeds, it is necessary to be sure that the re-entrant effect is not in some sense a result of the properties of the transformation. In order to check this, we have also investigated the one-dimensional ASOS Hamiltonian which can be solved exactly (albeit numerically). The partition function in this case is written as a product of 'transfer' matrices, which means that beginning with the definition

$$Z = \mathrm{Tr}\, \mathrm{e}^{-\beta H} \tag{10}$$

where

$$H = \sum_i H_{ii+1}$$

the trace can be re-expressed in the form

$$Z = \sum_{\{n_i\}} \prod_{i=-\infty}^{\infty} \mathrm{e}^{-\beta H_{ii+1}}. \tag{11}$$

Each site variable is a non-negative integer $n = 0, 1, 2, \ldots$. The matrix $\exp[-\beta H_{ii+1}(n_1, n_2)]$ can be diagonalised (numerically) in the same manner used for the Ising model (see Pathria 1972 p 419). If we write the largest eigenvalue as $\lambda_1 = \exp(E_1)$, then the coverage (or film thickness) is given by

$$l = \langle h \rangle = T\, \partial E_1 / \partial \mu. \tag{12}$$

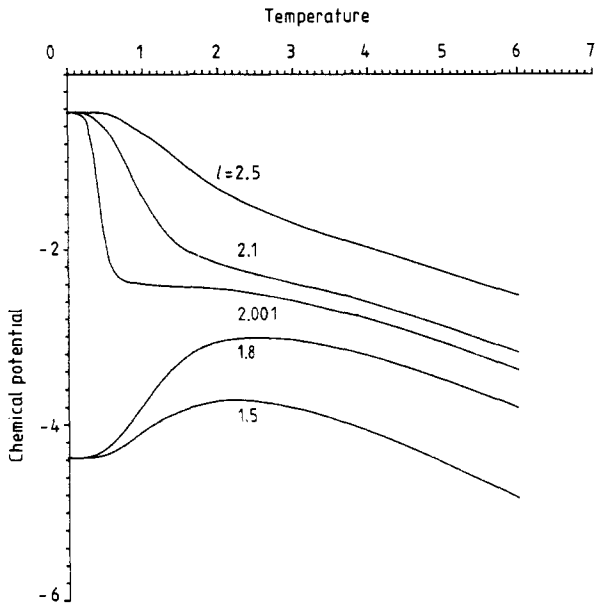

Figure 4. The μ against T phase plane for the one-dimensional ASOS Hamiltonian. The values used were $A=-5$, $B=10$ and V was taken to be linear in h^{-3} rather than h^{-2} because of the change in dimension of the substrate.

This is plotted in figure 4 for the ASOS model where contours of fixed coverage clearly exhibit the re-entrant effect. Qualitatively similar results were found with the lattice gas.

Finally, we consider a low temperature perturbation theory calculation which was performed on the ASOS Hamiltonian in three (bulk) dimensions. The free energy, F, of the system for small T can be calculated for a film of thickness l and $l+1$ each, and then at coexistence $F(l)=F(l+1)$. From this an expression for $\mu(T)$ on the phase boundary can be obtained. To lowest order in the expansion parameter $\exp(-\beta 4J)$, we found that the re-entrant effect will not appear at all for thick films but that it does appear for the phase boundaries separating layers of thickness $l=0$ and $l=1$, and $l=1$ and $l=2$ respectively if $-A>\frac{1}{2}B$. This is in accord with the results shown in figure 2(a) which indicate that the effect becomes increasingly smaller as the film becomes thicker.

Hauge and Schick (1983) have shown that there exists a Clausius-Clapeyron equation for the phase boundaries in the μ against T plane separating layers of thickness l_1 and l_2

$$\frac{\mathrm{d}\mu}{\mathrm{d}T}=-\frac{\Delta S}{\Delta l} \tag{13}$$

where ΔS is the change in entropy between layer l_2 and l_1 and Δl is the change in thickness. If we consider a boundary separating two regions that differ in thickness by 1 then

$$\mathrm{d}\mu/\mathrm{d}T=-(S_2-S_1). \tag{14}$$

S_2 and S_1 are the entropy of the thicker and thinner layers respectively. If the thicker film has greater entropy than the thinner one, then the phase boundaries must have

negative slope. The re-entrant effect which we have described above suggests that there is, at sufficiently low temperatures, a region where $S_2 < S_1$. The physical explanation behind this is as follows. The entropy density of an ideal gas is

$$s = (\tfrac{5}{2} - \mu/T)n \tag{15}$$

where n is the number density. For small T and large (negative) μ, which necessarily means thin film, the entropy of the gas plus film is dominated by the gas. As T increases at fixed μ the entropy density of the gas may increase slightly but the total entropy of the gas plus film can become still larger if more volume is made available to the gas, i.e. if the film becomes thinner. As T increases further, the entropy of the gas begins to make a smaller contribution to the total entropy of the combined system and it is the film that determines the overall value. At that point, the slope of the phase boundaries will be negative.

In summary, we have shown, using renormalisation group and perturbation theory calculations on two two-dimensional models and exact numerical calculations on these models in one dimension, that re-entrant behaviour in the μ against T phase plane appears for thin films. The explanation of the effect is that at low pressure and temperature, the entropy density of the gas is sufficient to favour a thin film over a thicker one.

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