LETTER TO THE EDITOR

Effects of quenched disorder on layering transitions

R Kariotis

School of Mathematical and Physical Sciences, University of Sussex, Brighton BN1 9QH, UK

Abstract. The influence of a static disordered substrate and a static disordered external field on thin-film layering transitions is investigated. We find that when the disorder is confined to the substrate alone, the influence appears only in the lowest transition line and acts to encourage film growth at finite temperatures. Random external fields influence thick, as well as thin, films and act to discourage the film development, resulting in a re-entrant-like effect.

Considerable progress has been made recently in understanding the statistical mechanics of thin films on substrates (for a thorough study up to 1982 see Pandit *et al* (1982); for a more recent review see Sullivan and Telo da Gama (1985)). At the same time, interest in the effects of static disorder in lattice models has received a great deal of interest (for a review of work in this area see Grinstein (1985)). A natural extension of these two fields, now receiving attention, is to investigate the influence of disorder on the properties of thin films (see, for example, Forgacs *et al* 1985). In this letter we investigate the effect of weak static disorder on the properties of thin films as a function of temperature and chemical potential. The model Hamiltonian used in the calculations is the classical three-dimensional lattice gas (Pandit *et al* 1982)

$$H_{LG} = \sum_{ij} J_{ij} n_i n_j + \sum_i [-\mu + V(i)] n_i \tag{1}$$

where J_{ij} is the nearest-neighbour coupling between sites i and j, μ is the chemical potential and n_i is defined to be either 0 or 1 if site i is empty or occupied respectively. V_i is the van der Waals attraction of the substrate on the individual adatom located at site $i = (i_x, i_y, i_z)$ and is assumed to be of the form $V_i = V(z) = u_0/z^3$ where z is the distance from the substrate. Disorder may appear either in the value of the nearest-neighbour coupling J (referred to as off-diagonal disorder), or in the form of an external (position-dependent) field added to μ (diagonal disorder). In what follows we will consider one special case of each of these two types of randomness.

The thermodynamic properties of the system are obtained from the free energy which is obtained from the average

$$F = -T\langle \ln(Z) \rangle \tag{2}$$

where Z is the partition function

$$Z = \mathrm{Tr}\, e^{-\beta H}. \tag{3}$$

The trace means sum over all possible configurations of occupied and unoccupied sites (the thermodynamic average), and the angle brackets indicate the sum over all

possible configurations of disordered bonds or external field values (the statistical average). The two averages are distinct and must (essentially) be performed in the order implied in the expression above (indicative of the two different timescales involved). It is possible to take advantage of the convenience of doing the statistical averaging first by using the replicated partition function (Emery 1975, Grinstein and Luther 1976, Edwards and Anderson 1975). This requires making the replacement

$$\ln(Z) = \lim_{n \to 0} (Z^n - 1)/n. \tag{4}$$

The effective Hamiltonian of the replicated system is similar in appearance to what it was previously:

$$H = \sum_{ij\alpha} J_{ij} n_i^\alpha n_j^\alpha + \sum_{i\alpha} [-\mu + V(i)] n_i^\alpha \tag{5}$$

where the summation over α is a summation over the n replicas and n_i^α is the replicated lattice gas variable at site i. Averaging can now be done over the partition function $Z(n)$ rather than $\ln(Z)$ so that the trace over the occupation numbers can be performed last.

We consider two types of disorder. First, suppose that the adsorption of the first layer, with bond strength J_z, is disordered. Typically, this may arise if the plane determined by the substrate has surface irregularities in it such as impurities or defects. Writing $J_z = J_0 + \delta J$, where $J_0 = \langle J \rangle$, the Hamiltonian can be split into two parts:

$$H = H_0 + \delta H \tag{6}$$

where δH contains the terms in H representing the binding of the adatoms in the first layer to the substrate. The average partition function can be written as the sum of the cumulants

$$\langle Z(n) \rangle = \text{Tr } e^{-\beta H_0} \exp\{-\beta\langle \delta H \rangle + \tfrac{1}{2}\beta^2[\langle \delta H^2 \rangle - \langle \delta H \rangle^2] + \cdots\}. \tag{7}$$

In everything that follows, we assume $\langle \delta H \rangle = 0$ and treat only even powers of δH. (Two additional possibilities arise in that the disorder may either be Gaussian or non-Gaussian; we will assume that the disorder is weak and Gaussian. Later we will comment on what physical effects may appear as the disorder becomes stronger and/or non-Gaussian.) The modification of the Hamiltonian now can be written

$$\langle \delta H^2 \rangle = \sum_{ik\alpha\beta} \langle \delta J \delta J \rangle n_i^\alpha n_k^\beta. \tag{8}$$

Assuming that the disorder at one site is uncorrelated with that at other sites (homogeneous disorder), the factor in brackets is zero except when $i = k$. Therefore the right-hand side of the equation simplifies to

$$\langle \delta H^2 \rangle = \gamma \sum_{i\alpha\beta} n_i^\alpha n_i^\beta \tag{9}$$

where $\langle \delta J \delta J \rangle = \gamma$, and the summation is now over all sites on the substrate. It is possible to convert the coupling *between* replicas into a modified coupling to the substrate *within* each replica by taking note of the following manipulations. The summation in equation (9) contains n terms like n^α and $n(n-1)$ terms like $n^\alpha n^\beta$ (α not equal to β). To begin perturbation theory using H_0 as the unperturbed Hamiltonian (recalling that H_0 is diagonal in replica space), we only keep terms of order n and γ, and rewrite the resulting trace as n^α times the average (on the ordered substrate) of the remaining

replica variable. This modification can then be added directly to the replicated H_0 giving an effective binding energy for the first layer of

$$J(\text{eff}) = J_0 - \tfrac{1}{2}\gamma\beta[1 - \langle n \rangle_0] \tag{10a}$$

where $\langle n \rangle_0$ is the average on the ordered substrate. Calculation of $\text{Tr}\, e^{-\beta H}$ can now be carried out by any of the methods used for the ordered substrate. Mean-field theory (de Oliveira and Griffiths 1978) is sufficient to show approximately how the μ against T phase plane is affected by the disorder and was used to obtain $\langle n \rangle_0$ giving

$$J(\text{eff}) = J_0 - \tfrac{1}{2}\gamma\beta P(\beta\varepsilon) \tag{10b}$$

where $P(x) = [1 + \exp(-x)]^{-1}$ and $\varepsilon = J_0(1 + Z) - \mu$. Z is the lattice coordination number. However, the re-entrant behaviour discussed in an earlier letter (Kariotis and Prentis 1986) can only be seen using the (cumulant form of the) real space renormalisation group which was described in that letter. Therefore, the results discussed below were obtained by evaluating the effective Hamiltonian, as we did previously. Before going into these results we will describe the example of diagonal disorder which can also be treated in a manner similar to that just given.

The second kind of disorder that we want to consider is that due to a random external field and involves adding to the Hamiltonian a term of the form

$$H_{\text{ex}} = \sum_{i\alpha} h_i n_i^\alpha \tag{11}$$

where h_i is a homogeneous random field and $\langle h_i h_j \rangle = \gamma \delta_{ij}$. This is essentially equivalent to the random field Ising model (RFIM) (see Grinstein (1985) for a review) except that in this case the presence of the substrate must be taken into account. This kind of disorder may be present when the substrate imperfections are longer-ranged than in the case treated above. For example, if the bulk substrate has a second species randomly distributed throughout, the effective van der Waals potential becomes a random variable. (In principle the disorder would then no longer be homogeneous; however, to lowest order in γ this contribution simply appears as a shift in the magnitude of J.) Calculation of an effective Hamiltonian proceeds as for the case of the disordered substrate, resulting in a modified chemical potential of the form

$$\mu(\text{eff}) = \mu + \tfrac{1}{2}\gamma\beta P(\varepsilon\beta). \tag{12}$$

Except for a change in sign, this result is similar in form to that for the case of the disordered substrate.

In figures 1 and 2 we have shown the results of these calculations and the main conclusion is that the disordered substrate acts to encourage, and the random field acts to inhibit, the growth of the film. Both effects are negligible at low temperatures and are strong only for thin films.

In figure 1, where the disorder is confined to the substrate alone, all influence appears entirely in the first layer transition. The second and subsequent layers are essentially unchanged. The fact that the disorder effectively increases the binding energy can be understood by the following argument. When a bond that is weaker than average is present, an adatom is less likely to be deposited at that site without necessarily discouraging adsorption on neighbouring sites. When a bond (stronger than average) is present, a single adatom is favoured, and once deposited acts to further encourage nearest-neighbour deposits even when the adjacent bonds are weak. Thus the fluctuation of bond strength above and below the average value does not have a
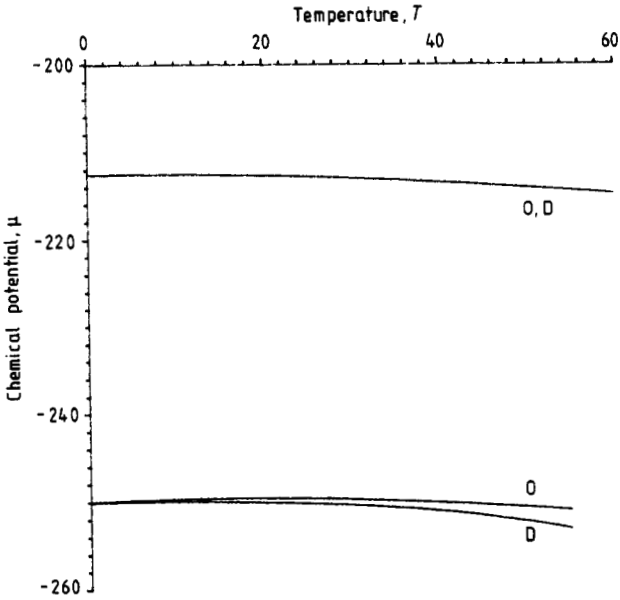
Figure 1. The μ against T plane for the lowest two first-order transition lines with (marked D) and without (marked O) a disordered substrate. The effect is essentially negligible along the line separating the first and second layer transitions.
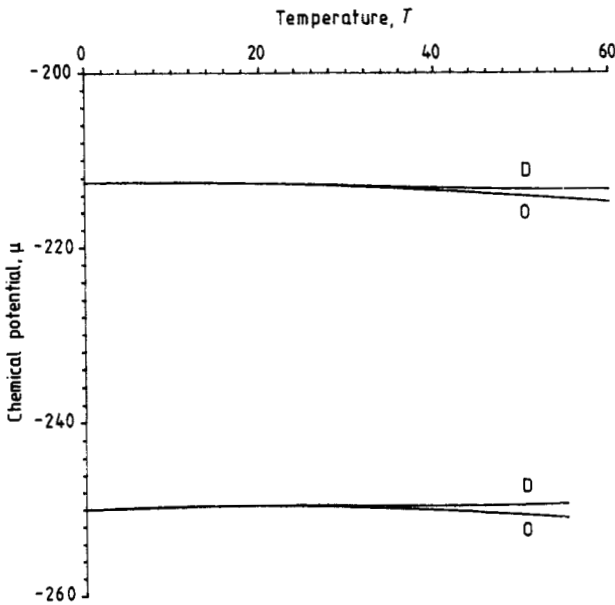

Figure 2. The μ against T plane for the lowest two first-order transition lines with (marked D) and without (marked O) a random external field. The calculation was performed assuming homogeneous local disorder.

symmetric effect on the favoured configurations at finite temperatures. At $T = 0$ this argument is not valid since it applies to an ensemble of configurations, hence at zero temperature the effect of fluctuations above and below the average coupling strength cancels out.

In figure 2, the slight re-entrant-like behaviour can be seen due to the disordered external field. Behaviour similar to this has recently been reported (Wagner and Binder 1986, Kariotis and Prentis 1986). The qualitative explanation of this effect, i.e. that this type of disorder inhibits rather than encourages film growth, follows along the same reasoning as in the disordered substrate but results in the opposite conclusion due to the fact that the chemical potential is a diagonal contribution to the Hamiltonian. Physically this means that if the chemical potential is locally weak, the probability of there being an adatom at that site is small even if the neighbouring sites are occupied.

In conclusion, we have shown that for weak disorder on the substrate, the development of the first layer at finite temperatures occurs at lower pressure. For disorder in the external field, film development at finite temperatures is inhibited most strongly in the first layer, and less so in subsequent layers. The case of strong and/or non-Gaussian disorder is much more complicated. Longer-range forces (for example, next-nearest-neighbour interactions) will be generated by the disorder, having either attractive or repulsive behaviour depending on the strength and the extent of the non-Gaussian properties. A study of the variety of effects that appear as these additional terms are included is presently being done.

References

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