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In this paper we discuss mathematical, numerical and atomistic models of growth at surfaces through a number of examples. It is shown how such models have often been successful in predicting the structures that are observed experimentally. Different kinds of models are often complementary to each other. Mathematical models can give guidance on the long-time behaviour of the system but often need help from more detailed simulation to decide what to assume about the underlying microscopic processes. Despite their success, such models still have a long way to go. In particular, they need to address the question of how to predict the effective properties of coatings. Here experimental data are not always available, and guidance from theory is greatly needed.

1. Introduction

Interfaces are not thermodynamically stable objects. Surfaces are inevitable, but most real surfaces are not the minimum energy surfaces one could predict from a Wulff plot. Grain boundaries, voids, texture are not inevitable and a microstructure containing such features is what it is only because of the history of its making. Since the mechanisms of growth of such features depend on what is already there, this suggests that such mechanisms also depend on the detailed history of the problem. This is correct, and much effort has gone into trying to build models to explain growth at surfaces and other interfaces. Such models encounter two fundamental difficulties.

First, growth takes place on a variety of timescales. The detail of why an atom goes in one place rather than another is the proper subject of a microscopic simulation; molecular dynamics or Monte Carlo. However, the long-time behaviour may have features of its own that do not apparently depend on such details. Here a continuum approach is the more obvious starting point. Many problems are not so easily categorised; they are too slow to be tackled readily by running a detailed simulation for a long period yet the details of the process are too important to be dealt with by the crude averaging that a continuum model almost always uses. Here a wide variety of models have been used. These usually attempt to isolate some important features of the problem and incorporate them in a computer model. These are the main subject of this paper and a number of examples will be given later.

Second, the growth at a particular point on the surface may be affected by what happens far away from the growth point. A particular example of this is shadowing. If we consider a rough surface grown from a flux of particles projected onto it at an angle, parts of the 'valleys' will be shielded from the incoming particles by the

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'mountains'. Such an effect is not difficult to treat by a computer model, but presents great difficulties for mathematical modelling because the effect is non-local. The part of the surface doing the blocking could be at a considerable distance from that being blocked.

Many of the models in the literature attempt to reproduce the observed features of the microstructure. It is clearly necessary to do this, although the fact that a model produces something that looks like experiment is not a guarantee that the model is correct. However, what is often wanted, particularly in coatings, is not the prediction of the appearance of the coating, but its properties, particularly its properties as a function of the process parameters. The properties most often wanted are the Young's modulus, Poisson ratio, thermal expansion and thermal conductivity. This requires a step beyond that taken by most modelling.

2. Solid–liquid interfaces

The growth of solids in liquids was first considered by Stefan and a vast literature has grown from it. The original Stefan problem was the advance of an ice sheet across an undercooled pond. Consider the interface between a solid and its own liquid. The properties of both phases are usually considered to be the same. The melt is undercooled and so solid forms. Heat is generated at the interface by the release of latent heat. We therefore write the equations

$$\partial T/\partial t = \varLambda \nabla^2 T \tag{2.1}$$

and, at the liquid–solid interface, we have

$$[-C_{\mathrm{p}} \varLambda \hat{n} \nabla T] = v_{\hat{n}} L, \tag{2.2}$$

where $\varLambda$ is the thermal diffusion coefficient, C_{p} the specific heat, L the latent heat of fusion and $v_{\hat{n}}$ the velocity of advance of the interface where $\hat{n}$ is the normal to the interface pointing into the liquid. In general the interface will be curved. To discuss this, we must add an assumption about the microscopic processes at the interface. The normal assumption is that they are so fast that the system can be assumed to be in local thermodynamic equilibrium. This gives a relation between the temperature at a curved interface, T_{c}, and the temperature at the planar interface, T_{p}:

$$T_{\mathrm{c}} = T_{\mathrm{p}}(1-\gamma\kappa/L), \tag{2.3}$$

where γ is the surface tension and κ is the inverse curvature. What then is the rate of advance of the interface? The solutions to this problem are discussed by Kessler *et al.* (1988) and Brener & Mel'nikov (1991). We do not consider here the detailed mathematical treatments of the problem (for which see the references above) but make a few qualitative comments on the results.

The planar case is completely unstable. This is because, if bumps spontaneously form, they will lose heat more effectively than the surroundings and therefore grow. Ivantsov presented an approximate solution; that of a growing parabolic tip. Dendrites do have approximately this shape, but this solution is still unstable. Further progress has only been possible by simplifying the problem using a local approximation (discussed by Kessler *et al.*). This shows the fundamental importance of surface tension which, in effect, selects only the fastest growing of the solutions and can explain why dendritic structures occur. The Ivantsov problem is of such interest because it shows the wide range of behaviour that can result from so simple a system. The concentration of mathematical effort has led to an understanding of the structure of the growths, provided simplifying assumptions are made.

We have considered the Ivantsov equations as a continuum model. They are also the basis of a numerical model; diffusion-limited aggregation (see Meakin (1987) for an introduction and original references; most work is based on Witten & Sander (1981)). This model considers a cluster in a medium of particles executing random walks. If they hit the cluster they stick to it. The diffusion equation for the probability of an incoming particle is therefore

$$\partial u/\partial t = D\nabla^2 u, \tag{2.4}$$

where D is the diffusion coefficient. The boundary conditions are $u(r,t) = 0$ at the cluster surface and $u(r_\infty, t) = u_\infty$ far away from the cluster. If the cluster is a solid of density ρ, the average velocity of advance normal to the surface, v_n is given by $\rho v_n = D\,\partial u/\partial n$. These are the Ivantsov equations without surface tension. The instabilities noted there are suppressed by two cut-offs. The finite size of the lattice on which the simulation is performed gives a lower cut-off; the diffusion length gives an upper one. Noise is introduced into the system by the fact that individual particles are deposited. This is amplified into the characteristic 'fingers' seen in such growths by the instabilities. Indeed, Honjo *et al.* (1986) have produced a system that passes from the dendritic form to the 'fingers' of the diffusion-limited aggregation model. Matsushita *et al.* (1984, 1985) have shown that the patterns produced in the electro-deposition of zinc strongly resemble the simulations made using this model. Unfortunately, the only point of comparison given is the fractal dimension.

3. Solid–gas interfaces

These interfaces have frequently been studied by atomistic simulation. Direct simulation of growth processes has also been attempted; molecular dynamics simulations of molecular beam epitaxy have been reviewed by Das Sharma (1988). We shall not consider these in detail, but continue to discuss the approach used in §2. There are, however, two important differences from those cases. The first is that the initial surface is given; it is the substrate on which the coating is made. The second is that coatings are made by a far wider variety of methods than those seen in liquid/surface interfaces. As one might expect, the microstructure of the result depends on the method used to form it. Even using one method, the microstructure can vary greatly depending on the precise conditions used. We shall consider two examples, sputtering and molecular beam epitaxy.

Thornton (1977) divides the microstructure of coatings produced by sputtering into four regions characterized by the ratio of the temperature of the substrate to the bulk melting temperature of the coating; T/T_{M}. For $T/T_{\mathrm{M}} < 0.3$, the microstructure is columnar with fine grains but also many voids. At higher temperatures, $0.3 < T/T_{\mathrm{M}} < 0.5$, surface diffusion becomes important and the coating has larger grains and fewer gross defects. Beyond this region, bulk diffusion and recrystallization occur producing a structure resembling that of material grown from the melt. A transition zone is often observed in the region of $T/T_{\mathrm{M}} = 0.3$.

The most obvious feature of the microstructure of these coatings is the columns. These often obey the *tangent rule*. If α is the angle of incoming particles to the normal to the interface and β the angle of the columns in the coating, $2\tan\beta = \tan\alpha$. Columns are only observed for sizeable values of α. For near-normal incidence a 'cauliflower' structure is obtained (Messier & Yehoda 1985). For very high values of the angle of incidence, the tangent rule fails (Bensiman *et al.* 1984); a better approximation is $\beta = \alpha - 17$ (degrees).

Sputtered coatings are made by projecting particles at the surface. It is not difficult to model this. The ballistic model throws particles at a surface; when they hit the surface they stick to the place they strike. Henderson *et al.* (1974) showed that this model produces a set of columns and voids that resemble sputtered coatings. It even predicts the tangent rule (Leamy & Dirks 1978). Unfortunately, as Kim *et al.* (1978) pointed out, the scale of the predicted microstructure is wrong by several orders of magnitude. It is a good illustration of a general point made by Meakin (1987). It is necessary to produce a microstructure that looks right; it certainly is not sufficient. In this case, the problem arises because the model assumes that when an incoming particle hits the growing coating, it sticks where it hits. In fact, measurements of the sticking coefficient (S. J. Bull, personal communication) give values of about 0.1 under the conditions where coatings are formed. Simulations have been performed with low values of the sticking coefficient (Kim *et al.*). These do give more reasonable values for the density; however, as the sticking coefficient is lowered, the columns become less visible although a more detailed analysis of the results shows that they are still there. The fractal dimension of the coating is unaltered (Meakin 1983).

These results show that the behaviour of the impinging particles is not the only factor in the growth of coatings. Completely different behaviour has been observed when surface diffusion is dominant. Van der Drift (1967) has argued that this, together with the assumption that only the growth rate of crystallites normal to the interface is important, can explain the morphology of a wide range of coatings. Crystallites with the fastest growing orientation perpendicular to the interface then dominate the structure (platelets 'stand on end' for example). The fastest growing orientation is not the same as the fastest growing surface; it is well known that such surfaces 'grow out'.

This suggests that a growth model must contain both the manner in which particles arrive at the surface and a surface diffusion term (or at least some term that anneals out the instabilities produced by the simple growth model). This, however, says nothing specific about the geometry of the surface. If we are building a numerical model, this will be dealt with automatically. However, if we are using a mathematical model, something specific must be done. In the case of sputtered films, the most obvious geometrical effect is shadowing. The vapour atoms come in from all directions, and the local growth rate is roughly proportional to the solid angle of exposure of the site. The general shadowing effect is very difficult to include in a mathematical model, but more local effects of surface shape can be introduced. An example of this is the explanation of the tangent rule by Leamy & Dirks (1978).

The Eden model (see Bruinsma *et al.* (1990) for references) assumes that the local surface grows in the direction normal to itself at a given rate. If we assume that the coating is grown on a flat substrate, this implies that growth perpendicular to the substrate is faster at slopes in the surface than at hills or valleys. This is the basis of the KPZ equation (Karder, Parisi & Zhang 1986). This is a growth law for the height of the coating, h,

$$\partial h/\partial t = \sigma\nabla^2 h + J + \lambda(\nabla h)^2 + \eta(r,t), \tag{3.1}$$

where σ is the surface energy, λ a coefficient, J the rate of arrival of material and $\eta(r, t)$ represents the noise caused by the arrival of particles (as in the diffusion-limited aggregation model). The first term has an annealing effect; this could be mediated either by evaporation/condensation or reconstruction (Edwards & Wilkinson 1982). The third term is the lowest order contribution of the Eden model. The equation also incorporates the solid-on-solid approximation which states that the system contains no overhangs (see Conrad (1992) for an extended discussion of the approximation and its use in simulations).

This model, and developments of it, has been studied in great detail. Since it does not contain any effects of shadowing, it is not suitable for sputtering and cannot predict columnar growth. Although the model would seem closer to molecular beam epitaxy, Das Sharma & Tamborenea (1991) have shown that this is only superficially so. The crucial difference is that any relaxation effects in such models are instantaneous, whereas models of molecular beam epitaxy have a further timescale imposed on them by the effects of surface diffusion. In a later paper, Lai & Das Sharma (1991) suggest that a possible model equation for molecular beam epitaxy is

$$\partial h/\partial t = -\lambda_1 \nabla^4 h + \lambda_2 \nabla^2 (\nabla h)^2 + \eta(r, t). \tag{3.2}$$

Both the first two terms can be interpreted as modelling competition between surface diffusion and bonding effects. An equation like this shows both the strength and the weakness of the mathematical approach. It is possible to analyse an equation like this to obtain general features of the growth; in this case the scaling relations among the growth exponents. However, there is no unique connection between the form of the terms in the equation and any physical process and no way of predicting the relative importance of various terms.

As an example of how one can produce similar equations by quite different mechanisms, let us turn back to the question of shadowing in sputtered films. Karunasiri *et al.* (1989) have considered the following model equation

$$\partial h/\partial t = -D\, \partial^4 h/\partial r^4 + J\theta(r, h) + \eta(r, t). \tag{3.3}$$

The first term represents the surface diffusion; D is the surface diffusion coefficient. The second term is the incoming particle flux where $\theta(r, h)$ is the angle of exposure of a site at r, h and $\eta(r, t)$ is the noise term. The solid-on-solid approximation is used here as above. If the shadowing term dominates, the system evolves into an approximately self-similar 'mountain' landscape. Whether this happens depends on the ratio D/J. For large enough values, it should be possible to grow flat coatings. As the authors note, the restriction to one dimension may exaggerate the shadow effect, but the idea of a transition to a rough surface is not implausible. Mazor *et al.* (1988) came to similar conclusions by their Monte Carlo model. They also investigated the coarsening of the microstructure of the film using Monte Carlo methods to be discussed in the next section. The results illustrate the argument of Van der Drift that the surfaces growing fastest in the vertical direction dominate the problem.

4. Solid–solid interfaces

Growth is not just something that occurs at surfaces. In this section we consider the simulation of grain boundary growth. Here, as before, we are not attempting to calculate the properties of ions at individual grain boundaries, but rather are using models to gain understanding of the behaviour of the system as a whole. The experimental position has been reviewed by Atkinson (1988). The basic result is that for isothermal annealing, the mean grain size $\bar{R}$ grows as

$$\bar{R} = kt^n \tag{4.1}$$

at long times. The constant k has an Arrhenius dependence on temperature, but the activation energy is not identifiable with any simple atomic process. n is the grain boundary exponent. It is the purpose of most theories to calculate this.

The grain boundary network coarsens because it is always energetically favourable to eliminate grain boundaries. The problem is, however, complicated by the topology of the network; the way a given boundary moves is affected by the behaviour of other boundaries connected to it. Theories to explain the behaviour are of two kinds; the mean field theories, such as those of Hillert (1964) and Louat (1974) and the Monte Carlo simulations developed by Anderson *et al.* (1984). We will approach the problem by way of the simulations.

In this method the microstructure is modelled on a mesh. Each mesh point is assigned a spin; these spins will label the different possible orientations of a grain in a growing lattice. There must be a large enough number of possible spin orientations so that grains of like orientation do not meet each other. In practice 30–40 orientations is enough. The grain boundary energy is modelled using the many-spin Potts hamiltonian

$$H = -J \sum_{NN} (\delta_{S_i S_j} - 1) \tag{4.2}$$

where J is a parameter (in principle temperature dependent) and the sum is over all nearest neighbours. The system is then allowed to evolve by flipping the spins using standard Monte Carlo techniques. It is important to ensure that the system has reached the true long-time behaviour. Early work did not do this and obtained growth exponents of about 0.4, in disagreement with models like those of Hillert (1964) which assumed that the driving force for coarsening was the reduction of grain boundary energy. Later simulations (Anderson *et al.* 1989) obtained exponents of 0.5 in agreement with Hillert.

Hillert's theory solves the continuity equation for the probability distribution in a network, given the equation of motion of the radii of the grains. This he took to be

$$v(r,t) = \partial r/\partial t = c(u)/\bar{r} - 1/r \tag{4.3}$$

where $u = r/\bar{r}$. The first term represents grain growth due to the influx of material from neighbouring grains; the second term represents grain shrinkage by surface tension. Hillert took $c(u) = 1$, a mean field theory for all grains. However, the simulations of Frost *et al.* have shown deviations from mean field behaviour; large grains cluster near small grains and vice versa. Mulheran (1992*a*) has analysed the results from simulations to suggest that a reasonable approximation to $c(u)$ is simply $0.6u$. This gives much better agreement with the frequency distribution functions obtained from simulations.

Mulheran (1992*b*) has argued that a different mechanism drives grain growth at short time scales and has investigated the random walk theory of Louat (1974). This suggested that the evolution of the network was by the random motion of the grain boundaries. Mulheran showed that Louat's conclusion that the growth exponent was 0.5 is true only in the one-dimensional case; in two dimensions the exponent is $\frac{1}{3}$ and in three dimensions $\frac{1}{4}$. Since simulations obtain low growth exponents for short runs, this suggests that both mechanisms might operate in this region. By using the grain migration model of Feltham (1957) Mulheran has shown that this is a reasonable conclusion.

Simulations of this kind have been used to probe a wide variety of microstructural behaviour in solids. Their main use to date has been to test the assumptions behind the mean field theories often used, and suggest improvements. The most obvious difficulty is that, since there is no reliable method of fixing the value of J, their predictive power is limited.

5. Obtaining effective properties from simulations

It is known that the microstructure affects the properties of materials, and there are many comments to this effect (see, for example, Dirks & Leamy 1977). However, detailed studies of the variation of properties with microstructural features are rare. Examples are given by Hoffman *et al.* (1991) and Håkansson *et al.* (1991). In this section we consider briefly how knowledge of the microstructure can be used to obtain material properties. The theories that have been evolved face an awkward choice; either one performs a very crude average (in which case the effect of the microstructure is washed out) or one attempts to perform a complete analysis (which requires so much data about the details of the microstructure that it is almost impossible to obtain it). The cases of thermal conductivity and elastic properties illustrate the dilemma.

Maxwell (1873) showed that for a dilute two-phase system containing spherical inclusions, the effective thermal conductivity, K, is given by

$$K/K_0 = (1-p)/(1+0.25p), \tag{5.1}$$

where K_0 is the thermal conductivity of the pure material and p is the volume fraction of the inclusions. This result ignores both the shapes of the inclusions and their possible interaction. More recent work has attempted to consider inclusions of arbitrary shape. Here most of the interest has been in the effect of porosity. A collection of the most commonly used results is given by Schulz (1981). As she notes, for highly porous materials, it is not enough to know gross features such as the pore fraction; the detailed structure of the material becomes important. Such effects also appear in empirical attempts to correlate porosity and thermal conductivity (Ebel & Vollath 1988). A similar point is made by Lu & Kim (1990) in their analysis of the effective thermal conductivity of composites where the inclusions have very high conductivity. To obtain their results to order p^2, they require the pair distribution function for the inclusions. This is only obtainable analytically for simple model systems. It is not easy to obtain from experiment and has rarely, if ever, been attempted.

A similar line of argument obtains for elastic properties and stresses. A review of the effect of microstructure on stresses on thin films is given by Doerner & Nix (1988). The first level of approximation is again to consider only the volume fractions of the constituents. A review of the various results obtainable is given by Hale (1975). Beyond that, information about the inclusion distribution functions is required. If this is available, a method of obtaining effective elastic properties is discussed by Ferrari & Johnson (1989). However, now the full distribution function of the inclusions is needed. This method has been used, together with a numerical model, to obtain effective elastic properties and stresses for a plasma-sprayed zirconia coating (Ferrari *et al*. 1991). This suggests that the use of a model can overcome the major difficulty with using sophisticated effective medium approaches; it can provide the data about the microstructure that such theories require.

6. Conclusions

Many different approaches have been used in the attempt to simulate the growth at surfaces. The various methods used are often complementary. Mathematical models are often used to check the long-time behaviour of simulations. The simulations can give guidance on what mathematical models should assume about the underlying behaviour. In some cases the numerical models can pose the kinds of questions that can be tackled by atomistic simulation; the question of sticking coefficients or the mechanism of grain boundary motion for example.

Most models attempt to predict the structure of interfaces or coatings. However, as we have tried to suggest, the prediction of patterns and structure, though useful, is not sufficient. If these models are really to be useful to those attempting to produce coatings, they need to predict properties. There are a number of cases where this is now being done. More are needed, both to test the models against hard data and to help experimentalists to produce better coatings.

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