Quasidendritic growth due to elastic fields

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Abstract

A model is proposed to explain the quasidendritic growth of Co islands deposited on a Pt(111) surface observed in the experiments made by Grütter and Dürrig in 1995. We simulate the growth of the Co islands using a Ginzburg–Landau approach. The elastic field is eliminated from the problem using the condition of mechanical equilibrium. The anisotropy of the lattice strain is shown to have a profound impact on the morphology of the domain growth. We first outline the method and the resulting equations. Preliminary numerical results showing a qualitative resemblance between their experimental results and our simulations are presented.

§1. Introduction

It is known that the domain morphology in phase-separating alloys can be strongly influenced by elastic fields (Khachaturyan 1983). These long-range fields originate from lattice misfit or the difference between the lattice constants of the two phases. Onuki (1989a, b), Nishimori and Onuki (1990) and Onuki and Nishimori (1991) introduced a Ginzburg–Landau approach to analyse the elastic effects in phase-separating alloys in a model B system (Hohenberg and Halperin 1977, Gunton et al. 1983). In their scheme, the elastic strain is a subsidiary tensor variable coupled to a conserved order parameter, the concentration c, in the free energy. They obtained a closed description of c by eliminating the elastic field from the condition of mechanical equilibrium. Sagui et al. (1994) applied this formalism to the study of the effect of an elastic field in an order–disorder phase transition described by dynamics corresponding to a model C system. The elastic field was coupled to both the concentration and the order parameter.

A recent experiment by Grütter and Dürrig (1995) illustrates the importance of the elastic field. They reported the observation of the dendritic growth of Co on Pt(111) surface. The dendrite arms are 3–5 nm wide, 0.20 nm high (a monolayer of Co) and can be up to 250 nm long. The lattice Co islands cause substantial surface strain which induces the reconstruction of the Pt(111) surface. These reconstructed areas act in turn as templates for the growth of the Co islands.

§2. Modelling of the quasidendritic growth

We simulate the growth of the Co islands on the Pt(111) using a similar Ginzburg–Landau approach. The field $\phi$ is unity when the atoms of Co are present and zero when the substrate is free of Co adatoms. An external driving force $h$
models the deposition of Co onto the Pt(111) surface. This driving force is assumed to be constant. The total free energy $\mathcal{F}$ is

$$\mathcal{F} = \int d\mathbf{r} \left( f(\phi, h, u_{ij}) + \frac{l_{\phi}^2}{2} |\nabla \phi|^2 \right),$$

where $l_{\phi}$ is a phenomenological constant. The bulk free-energy density $f(\phi, h, u_{ij})$ is given by

$$f(\phi, h, u_{ij}) = \frac{1}{4} \phi^4 + \frac{h - \frac{1}{3} \phi^3}{3} - \frac{h - \frac{1}{2} \phi^2}{2} + \frac{\epsilon_\phi^2}{2\alpha} \phi^2 + \epsilon_\phi \phi \nabla \cdot \mathbf{u} + f_{el},$$

where $\epsilon_\phi$ is the coupling constant between $\phi$ and $\nabla \cdot \mathbf{u}$ and $f_{el}$ is the elastic energy. The presence of the term $(\epsilon_\phi^2 / 2\alpha) \phi^2$ is clarified in the calculations below. $\alpha \equiv \kappa + \mu$ where $\kappa$ and $\mu$ are the bulk and shear moduli respectively. With this linear coupling, the Pt(111) surface is strained only when some Co atoms ($\phi = 1$) are present.

The dendritic pattern in the experiment of Grütter and Dürrig (1995) is due mainly to the anisotropy of the lattice strain. For simplicity, only a fourfold anisotropy is considered. The elastic energy for a two-dimensional crystal with the point-group symmetry of a square is given by (Landau and Lifshitz 1990)

$$f_{el} = \frac{1}{2} C_{11}(u_{xx}^2 + u_{yy}^2) + \frac{1}{2} C_{12}(u_{xx} u_{yy}) + C_{44} u_{ky}^2,$$

where $u_{ij} = \frac{1}{2}(\partial u_i / \partial x_j + \partial u_j / \partial x_i)$ is the elastic strain. This energy can be rewritten as (Sagui et al. 1994)

$$f_{el} = \frac{1}{2} \kappa (\nabla \cdot \mathbf{u})^2 + \mu \sum_{ij} \left( u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \mathbf{u} \right)^2 + \frac{1}{2} \beta \sum_i u_{ii}^2,$$

which is the isotropic elastic energy plus a part due to the square anisotropy. The elastic moduli are given by

$$\mu = C_{44}, \quad \kappa = C_{11} + C_{44}, \quad \beta = C_{11} - C_{12} - 2C_{44},$$

and the anisotropy is defined as $\xi \equiv \beta / C_{44}$. In this paper, we consider that the elastic moduli do not depend on the order parameter $\phi$.

The elastic field instantaneously relaxes to adjust to a given $\phi$. This is the condition of mechanical equilibrium,

$$\frac{\delta \mathcal{F}}{\delta u_i} = \sum_j \frac{\partial \sigma_{ij}}{\partial x_j} = 0.$$  \hspace{1cm} (6)

With the definition of the elastic stress tensor

$$\sigma_{ij} = \frac{\delta \mathcal{F}}{\delta u_{ij}} = (\epsilon_\phi \phi + \kappa \nabla \cdot \mathbf{u} + \beta u_{ii}) \delta_{ij} = 2\mu \left( u_{ij} - \frac{\delta_{ij}}{2} \nabla \cdot \mathbf{u} \right),$$

the condition of mechanical equilibrium in Fourier space is

$$i \mathbf{k} \cdot \hat{\mathbf{u}}(\mathbf{k}) = \frac{\epsilon_\phi \hat{\chi}(\mathbf{k}) \hat{\varphi}(\mathbf{k})}{1 + \kappa \hat{\chi}(\mathbf{k})},$$

\hspace{1cm} (8)
where we introduce
\[ \hat{\chi}(k) = \sum_{i} \frac{k_i^2}{\mu(1 + \zeta k_i^2)}. \]  
(9)

A linear approximation in the anisotropy \( \zeta \) gives
\[ i k \cdot \hat{u}(k) = \frac{\epsilon_\phi}{\alpha} \hat{\phi}(k) - \zeta \frac{\epsilon_\phi}{\alpha^2} \left( 1 - 2 \frac{k_x^2 k_y^2}{k^4} \right) \hat{\phi}(k) \]  
or in real space
\[ \nabla \cdot u = - \frac{\epsilon_\phi}{\alpha} \phi + \zeta \frac{\epsilon_\phi}{\alpha^2} \left( 1 - 2 \frac{\nabla_x^2 \nabla_y^2}{\nabla^4} \right) \phi. \]  
(10)

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Hence the anisotropy introduces a long-range interaction. In agreement with what Cahn (1961) has shown in the case of spinodal decomposition, if the system is isotropic and the elastic moduli are independent of \( \phi \), then the induced elastic field is simply proportional to \( \phi \) and thus there will be no long-range interaction present.

The part of the functional derivative of the free energy due to the elastic terms is
\[ \Delta_{\text{el}} = \epsilon_\phi \nabla \cdot u = - \frac{\epsilon_\phi^2}{\alpha} \phi + \beta \left( \frac{\epsilon_\phi}{\alpha} \right)^2 \left( 1 - 2 \frac{\nabla_x^2 \nabla_y^2}{\nabla^4} \right) \phi. \]  
(12)

Finally, the Langevin equation for the order parameter is
\[ \frac{\partial \phi}{\partial t} = - \Gamma_{\phi} \frac{\delta F}{\delta \phi} \]
\[ = - \Gamma_{\phi} \left[ \phi^3 + (h - \frac{3}{2}) \phi^2 - (h - \frac{1}{2}) \phi + \beta \epsilon_\phi^2 \left( 1 - 2 \frac{\nabla_x^2 \nabla_y^2}{\nabla^4} \right) - \frac{1}{\phi} \nabla^2 \phi \right], \]  
(13)

where \( \Gamma_{\phi} \) is the mobility and the coefficient \( \epsilon_\phi \) is redefined so that \( \epsilon_\phi \equiv \epsilon_\phi / \alpha \). The term \( (\epsilon_\phi^2 / 2 \alpha) \phi^2 \) in \( f_2(\phi, h, \phi) \) (equation (2)) cancels the isotropic part of the elastic contribution.

\section*{3. Numerical simulations}

Because of the term \( 1 / \nabla^4 \) in equation (13), it is necessary to go to Fourier space. The system size is \( 256 \times 256 \) and periodic boundary conditions are used throughout the simulations. The time integration is performed using the standard Euler method. We have neglected noise.

In the following simulations, \( \lambda = 0.33 \), \( \Gamma_{\phi} = 3 \) and \( \epsilon_\phi = 0.5 \). Also, \( \kappa = 0.9 \) and \( \mu = 0.3 \). The spatial mesh is taken to be \( \Delta x = \Delta y = 1.0 \) whereas \( \Delta t = 0.1 \). The time integration is performed using the standard Euler method. Finally, the external field is chosen to be \( h = 0.45 \).

The introduction of an anisotropy in the elastic moduli drastically changes the morphology of the \( \phi = 1 \) domains (hereafter called black domains) as well as the speed of growth. This is illustrated by the left-hand side of figure 1 where \( \beta = -0.1 \). After the black domain has reached a critical radius, we observe the growth of branches exhibiting a fourfold anisotropy. The growth of the black phase in front of the tip is greatly favoured. This can be visualized by the contour plot of \( \Delta_{\text{el}} \).
The contour plots are shown on the right-hand side of Figure 1. Lighter colours correspond to positive values of the functional derivatives. These positive regions repel the particles from the dark regions and the growth takes place preferentially in the darker regions of the contour plot. This quasidendritic growth is characterized by an absence of secondary branching.

The morphology of the growth is similar to that observed in the experiment of Grütter and Dürrig (1995), except that we used a square anisotropy to simplify the algebra.
§4. Conclusion

We have coupled the strain field to the order parameter in a model A system. By assuming that the elastic field relaxes very fast, we have expressed it in terms of the order parameter. We have shown how this relatively simple coupling drastically modifies the growth and the morphology when anisotropy of the elastic field was taken into account. This simple model allows us to recover some of the experimental results of Grütter and Dürig (1995), that is the quasidendritic growth of Co deposited on a Pt(111) surface. However, in order to facilitate our calculations, a fourfold anisotropy was used. Further work is in progress.

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References
