Phase separation in elastically coupled binary alloys

Justin C. W. Song*
School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, 02138, USA

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I review some of the theory[1–4] behind microstructure formation in the phase separation of binary alloys, in particular how compositional changes in a material can be affected by elastic properties of the alloy. This is done by considering a Landau-Ginzburg theory of binary alloy with an elastic interaction and solving for the elastic interactions. I also describe how finite sized confined grains leads to supression of spinodal decompositon in an attempt to motivate how to think about polycrystallinity in binary alloys.

I. INTRODUCTION

When a metal mixture is cooled (slowly) below its alloying temperature there is a tendancy for it to phase separate into its constituent components. This phase separation is driven by the entropy of mixing in a solution and results in a whole vareity of alloy solid phases. There are two ways in which an alloy can phase separate. One is through spinodal decomposition, where small amplitude fluctuations throughout the alloy are amplified and take over the phase composition of the material. Another is nucleation and growth [8] where a critical nucleus size of a phase is needed (to overcome a nucleation barrier) for the phase separation to occur around this nucleus. In this article, we are interested in the former and will explore some aspects of spinodal decomposition in binary alloys.

Elastic interactions are important in the phase separation of binary alloys. Some dramatic demonstrations are the {111} or {100} planes chosen for spinodal decomposition [2] in cubic systems - which we shall review here - and percipitation of the harder phase in elastically inhomogeneous binary alloys [4, 5] . It is the long ranged elastic interaction, which is sensitive to composition distribution, shape and boundary conditions of the system, and its competition with short-range diffusion that is responsible for many of the microstructures observed in phase separated binary alloys.

Microstructure formation in alloys can have important technological implications for the strength of an alloy. For instance, the movement of dislocations can be impeded by grain boundaries as well as, to a lesser extent, boundaries between phases. Thus the microstructure in the alloy can change the plastic properties of the system much like how grain boundaries through the Hall-Pecth effect changes the yield strength of a material. This provides motivation to understand how the microstructure of an alloy might look like, which directions are dominant in the alloy and what the characteristic size of phase separation might be. In this article, we review a simple of theory of how elastic interactions selects a characteristic size for the phase separation as well as dominant direction of the phase separation.

II. LANDAU-GINZBURG MODEL

We consider the Landau Ginzburg model[2]

$$\beta H = \int_{\text{all space}} dr \Big[f(\phi) + \frac{\kappa}{2}(\nabla\phi)^2 + f_{el} \Big], \tag{1}$$

where $f(\phi) = T/2\phi^2 + u\phi^4$ is the usual Landau-Ginzburg free energy density, $\phi \in [-1, 1]$ is the composition of the alloy and $\mathbf{u}$ is the displacement field. We consider the elastic free energy for cubic crystals, f_{el}, which is given by

$$\begin{aligned} f_{el} = \frac{C_{11}}{2}\Big((\epsilon_{xx} - \alpha\phi)^2 + (\epsilon_{yy} - \alpha\phi)^2 \Big) \\ + C_{12}(\epsilon_{xx} - \alpha\phi)(\epsilon_{yy} - \alpha\phi) + 2C_{44}\epsilon_{xy}^2. \end{aligned} \tag{2}$$

where $\epsilon_{ij} = \frac{1}{2}\Big(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\Big)$. The composition of the alloy is coupled to the strain field in a bi-linear term $\propto \alpha\phi(\nabla u)$[3]. Here we represent it as a modification of the diaganol strains. The physical origin of the coupling between the fields is the lattice mismatch between the 2 constiuents of the binary alloy. Note that there is no coupling when the composition $\phi = 0$ because the average lattice mismatch in that situation is zero and the diagonal term of the elastic energy reduces to just its usual form[6].

Evidently, what we have here is two fields coupled to each other. In general, to solve for the configurations of $(\phi, \mathbf{u})$ - in the saddle point approximation - one would have to find the configuration of $(\phi, \mathbf{u})$ that minimize the free energy. However, this is a hard problem. Fortunately, elastic relaxations tend to be far faster than the compositional changes in the alloy. Imagine slowly cooling an alloy from a liquid melt to below the critical temperature - here given by $t = 0$ - the phase separation of alloy into its constituent components would be governed by diffusive transport and hence the timescale of this change is far longer than the time it takes for the elastic strains to reach mechanical equilibrium. Hence, we can safely assume (and thus impose) that on time

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*Electronic address: `jcwsong@fas.harvard.edu`

scales of compositional changes of the alloy, mechanical equilibrium is always satisfied. This means that[6]

$$\frac{\delta F}{\delta u_i} = 0. \tag{3}$$

This gives us equations for mechanical equilibrium:

$$-(C_{11}+C_{12})\alpha\frac{\partial\phi}{\partial x} + C_{11}\frac{\partial\epsilon_{xx}}{\partial x} + C_{12}\frac{\partial\epsilon_{yy}}{\partial x} + 4C_{44}\frac{\partial\epsilon_{xy}}{\partial y} = 0 \tag{4}$$

$$-(C_{11}+C_{12})\alpha\frac{\partial\phi}{\partial y} + C_{11}\frac{\partial\epsilon_{yy}}{\partial y} + C_{12}\frac{\partial\epsilon_{xx}}{\partial y} + 4C_{44}\frac{\partial\epsilon_{xy}}{\partial x} = 0 \tag{5}$$

We can use a potential to solve for this by writing $\epsilon_{ij} = \frac{\partial^2 W}{\partial x_i \partial x_j}$[4]. This gives us the solution

$$\nabla^2 W = \frac{2\alpha}{B}\tilde{\phi} \tag{6}$$

where $B = (C_{11}+C_{12})/(C_{11}+C_{12}+4C_{44})$ and $\tilde{\phi}$ is used to denote fluctuations away from the saddle point homogenous solution - the spatial derivative of ϕ is only sensitive to the fluctuations about a homogeneous composition. Eqn. 6 is the cause of the long-range interaction that considering elasticity in the system gives. The solution to this in two-dimensions is a logarithmic decay and in 3-dimensions it is a $1/r$ decay. Now, substituting this solution into Eqn. 1, we first note that to first order, this modifies the quadratic term in the composition ϕ (with a positive number), and hence depresses the critical temperature such that the critical temperature (which used to be at $t = 0$) is now

$$t_c = -(C_{11}+C_{12})\alpha^2 \tag{7}$$

where we have used the saddle point approximation. It is nice note that it is the compressibility modulus $(C_{11}+C_{12})$ that feeds into this suppression. We note that in making this saddle approximation we note that since Eqn. 6 would have a right hand side equal to zero, there is no contribution from the elastic terms (no "charge" in the system). Cahn [2] first noted a depression in the critical temprature when he treated the case for isotropic elasticity.

Second, we can look for the maximally unstable modes of the system by first making a fluctuation in the composition ϕ. This is given by the usual $\phi = \phi_0 + \tilde{\phi}$ where ϕ_0 is the saddle point solution at a given temperature. Next, we expand out only keeping terms up to quadratic order. Re-writing the composition fluctuation in terms of their fourier modes, $\tilde{\phi}(q)$, we are in a position to rewrite the elastic contribution. We note that Eqn. 6 gives a relationship between the fourier modes of $W(q)$ and the fourier modes of the composition fluctuations $\tilde{\phi}(q)$ such that

$$-q^2 W(q) = B\tilde{\phi}(q) \tag{8}$$

Specifying 2-dimensions as we did for the elasticity, Eqn. 1 becomes Eqn. 9 below

$$\beta H = \int \frac{d^2q}{(2\pi)^2}\frac{1}{q^4}\Big\{\big[(\frac{\kappa}{2\xi^2}+\alpha B)q^4 + (-C_{11}+C_{12}+2C_{44})q_x^2 q_y^2 + \frac{\kappa}{2}q^6\big]|\tilde{\phi}(q)|^2 + \alpha\phi_{hom}B\tilde{\phi}(q)\Big\} \tag{9}$$

where $\kappa/2\xi^2 = (T + 2t_c + 12\phi_0^2 u)$ and ϕ_{hom} is the composition in the homogeneous phase (which is $t > t_c$). One thing we note immediately is that $\tilde{\phi}(q)$ appears in both the first and second powers. This is explained by thinking about the significance of ϕ_{hom}. We first note that for the alloy, the order parameter is a conserved order parameter. That is the total integral of order parameter over all space should give the same number above and below the transition temperature. This is simply because of the conservation of the number and type of metal constituents in the alloy. So if we are in a situation where the homogeneous phase ($t > t_c$) is a 50-50 composition of the two metals, this means that ϕ_{hom} is zero. We consider this case. The variance is given by

$$\langle|\tilde{\phi}(q)\tilde{\phi}(q')|^2\rangle = \frac{2\pi^2\delta_{q,q'}}{(\frac{\kappa}{2\xi^2}+\alpha B) + \gamma q_x^2 q_y^2/q^4 + \frac{\kappa}{2}q^2} \tag{10}$$

where we have rewritten $\gamma = -C_{11}+C_{12}+2C_{44}$. There is already different from the gaussian model that we're used to. In particular it is anisotropic, and the anisotropy depends on γ. We shall elaborate on this later. However, like the gaussian model, the maxima is still at $q = 0$. This, however, is at the infinite time limit where the system has sampled all possible configurations. What is commonly the case, however, is for spinodal decompostion in the alloy to be dominated by the kinetics. To study this, we use the Cahn-Hilliard equation [7, 8]

$$\frac{\partial\phi}{\partial t} = \mu\nabla^2\frac{\delta F}{\delta\phi} \tag{11}$$

where the dynamics of the compositional evolution is governed by a diffusive process. μ is the diffusive mobility. Writing this in k-space for our system we find that this

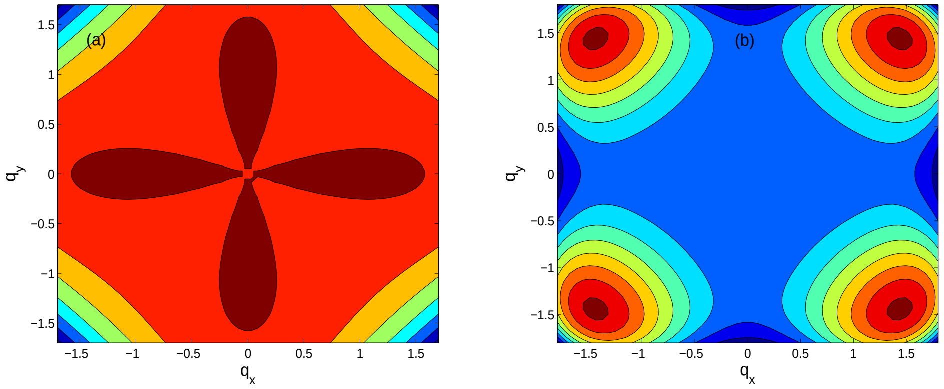

FIG. 1: Plot of the maximas of the $\omega(q)$. (a) shows $\gamma > 0$ where the maximal lobes are located in the q_x and q_y directions. (b) shows $\gamma < 0$ where the maximal nodes are located in the 45 degree direction. Dark red indicates maximum value in the colour plot and blue indicates the minimum value in the colour plot. Obviously, the value continues to decrease as we go to higher values of $|q|$, however, the colour bar only indicates values inside the image.

becomes

$$\frac{\partial\tilde{\phi}(q)}{\partial t} = \mu\omega(q)\tilde{\phi}(q) \tag{12}$$

where we have done the linearized - this is the same as keeping the energy to quadratic order that we did earlier. The solution to this equation becomes

$$\phi(q,t) = \phi(q,t=0)\exp(\mu\omega(q)t) \tag{13}$$

where the dispersion $\omega(q)$ is given by

$$\omega(q) = \Big[-(-\frac{\kappa}{2\xi^2} + \alpha B)q^2 - \gamma q^2 \sin^2(2\theta) - \frac{\kappa}{2}q^4\Big] \tag{14}$$

where the negative sign was added because of the ∇^2 of the Cahn-Hilliard equation. Note that the coefficient of the first term (together with the negative sign) is positive. When $\gamma > 0$ fluctuation amplitude maxima is along the q_x and q_y directions (4 lobes). When $\gamma < 0$, the maxima is along the 45 degree direction. This is shown in Fig. 1 where we plot the dispersion $\omega(q)$. Because the early stages of spinodal decompostion are dominated by the kinetics, the points of maximum dispersion amplitude are amplified more than the other fluctuations. We find that the modes q with maximum amplitude are *exponentially* ampified because. Hence, the typical microstructure in such alloys is either in the q_x, q_y directions or in the 45 degree rotated orientation. As can be seen in Fig. 1, this is controlled by the sign of γ. Using other arguments invovling the directions with the least elastic energy, Cahn[2] shows this same relation. We can also write down where the maximum q mode occurs and this is

$$|q_{\max}| = \begin{cases} \frac{1}{\sqrt{2}}(\frac{\kappa}{2\xi^2} - \alpha B)^{\frac{1}{2}} & \gamma > 0 \\ \frac{1}{\sqrt{2}}(\frac{\kappa}{2\xi^2} - \alpha B - \gamma)^{\frac{1}{2}} & \gamma < 0 \end{cases} \tag{15}$$

It is interesting to note that the maxima q mode don't occur at the same magnitude. This is due to the different amount of elastic energy needed to contort the system in the shear $\{xy\}$ directions as opposed to the longitudinal $\{xx\}, \{yy\}$ directions. What is clear from this analysis, is that a characteristic size is adopted from a kinetic effect and was not there at equilibrium. We expect that as $t \to \infty$ the alloy can move towards a solution where we have the zero mode as the largest mode. However, in many cases the system trapped in a *metastable* state and doesn't leave it. It is also clear that even without elastic interactions one would also have a maximally unstable mode. However, this would be at very small wavelengths (large q). What the elasticity did was to make these wavelengths larger and the cubic part addded anisotropy to the decomposition directions.

A. Finite sizes

One consequence of having phase decomposition that is dominated at early time by the kinetics is that finite sized effects can affect whether or not one gets phase separation. Consider the dispersion relation in Eqn. 14. At small $|q|$ $\omega(q)$ is positive. Next note that at large $|q|$, we have that $\omega(q)$ is negative. So for a finite range between zero and some q_c^e - where e denotes elastic - we have that $\omega(q)$ is positive and hence in kinetics will be amplified. However, for $q > q_c$, these will have exponentially smaller amplitudes and as mentioned earlier will be exponentially diminished. If we consider a system with a finite size a, this will impose a $q_a \sim 1/a$ such that $q < q_a$ cannot be supported by the system. So if $q_a > q_c^e$, then none of the wavelengths will be amplified, and phase separation via spinodal decomposition cannot happen. In such a case, only nucleation and growth can allow for phase separation of the alloy system. q_c^e for our system can be obtained as

$$|q_c^e| = \begin{cases} (\frac{\kappa}{2\xi^2} - \alpha B)^{\frac{1}{2}} & \gamma > 0 \\ (\frac{\kappa}{2\xi^2} - \alpha B - \gamma)^{\frac{1}{2}} & \gamma < 0 \end{cases} \qquad (16)$$

Again the critical size is different for the two different directions that preferred by the crystal when γ changes sign. We note that such critical q_c also exists in the original landau ginzburg theory without elastic interactions - this is a consequence of incipient surface tension[1]. However, at a given temperature (such that phase separation should occur in both cases with and without elastic interactions), the critical $q_c^s = (\kappa/2\xi^2)^{1/2}$ arising from surface tension effects is larger than the q_c^e arising from elastic effects (because αB is positive) if we consdier $\gamma > 0$. Hence, we expect to see such a critical size from the elastic effects at larger grain sizes than ones which are due purely to incipient surface tension. However, if $\gamma < 0$, this may not be the case, as seen from eqn. 16.

III. REMARKS ON POLYCRYSTALLINE ALLOYS

We can use this intuition on finite size effects in binary alloys to motivate how to think about polycrystalline alloys. One notes, that if a grain is oriented very differently from its surrounding grains it is effectively clamped by the surrounding grains. What this means is that the fluctuation modes $\tilde{\phi}(q)$ that are needed for it to phase separate via spinodal decomposition cannot extend out to beyond its grain boundaries because if the orientations of the surrounding grains are sufficiently mismatched, then the maxmimally unstable lobe (here we concern ourselves with the direction) of the grain we're concerned with is not the maximally unstable lobe of the surrounding grains. To illustrate this a little more we consider just a bi-crystalline case where one grain is embedded inside a larger crystal with their orientations mismatched. If we decrease the size of the grain embedded inside, such that $1/a_{\mathrm{grain}} < q_c^e$, then there will no longer be anymore unstable (that is positive $\omega(q)$) modes left to decompose to. This grain will no longer decompose via spinodal decomposition. It can, however, decompose via other mechanisms such as nucleation and growth. One thing that might happen is that since the crystal emedding the grain is large, it will phase separate via spinodal decomposition. However, at the grain boundaries betweenn the grains (between large cyrstal and embedded small grain), we find that there is a cost to maintaining phase boundary between the phase decomposed region (outside, in the large crystal) and phase non-decomposed region (inside, embedded grain). This may give rise to phase separation which grows from the boundaries. Clearly more can be done on this, in particular to show how the change in size of the grain affects the stability of the modes inside the embedded grain if we fix a particular orientational mismatch.

IV. SUMMARY

I summarize what I have done. I've reviewed how to couple an elastic field to composition field in a landau-ginzburg model. Here we saw that this produced a suppression of the critical temperature. In addition, via kinetics, this produced a characterisitic size for the phase separation that was specific to the elastic interaction, and dominant directions in the spinodal decomposition. We used to idea of unstable modes to motivate finite size effects where sizes below a critical size $\sim 1/q_c^e$ do not spinodally decompose. Using this intuition we concluded that for grains embedded deep inside a crystal with an orientational mismatch, spinodal decompostion is suppressed, and other mechanisms become more important.

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