Simulating and Visualising Phase Transitions:
Models for Droplet Nucleation and Growth

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Abstract

Droplet nucleation occurs when a small fluctuation in a system forms and subsequently grows in magnitude. Raindrop formation is a familiar everyday example. Droplets can be modelled using a field equation such as the Cahn-Hilliard system [1, 2, 3]. Attempts to understand and describe growth processes in material physico-chemical systems are often made using nucleation theory, which works well in the dilute limit. The range of validity of nucleation theoretical models can be explored using microscopic simulation models in which nucleating clusters can be counted and measured exactly. The Becker-Doring nucleation theory is described and its range of validity is discussed for binary alloy simulations using the Kawasaki exchange model in various concentration regimes. Graph labeling and enumeration techniques are employed to study the range of sizes of clusters present in nucleating systems.

Droplet Formation

The Cahn-Hilliard model [1, 3] models the phase transition and domain separation of a binary alloy consisting of two types of atoms A and B, the ratio these atoms is known as the mass fraction. In a Cahn-Hilliard system with an extreme mass fraction, the dilute atom will form nuclei in the same way a real binary alloy nucleates. Figure: 1 shows a comparison between a Cahn-Hilliard system with an extreme mass fraction and an electron micro-graph of a real binary alloy.
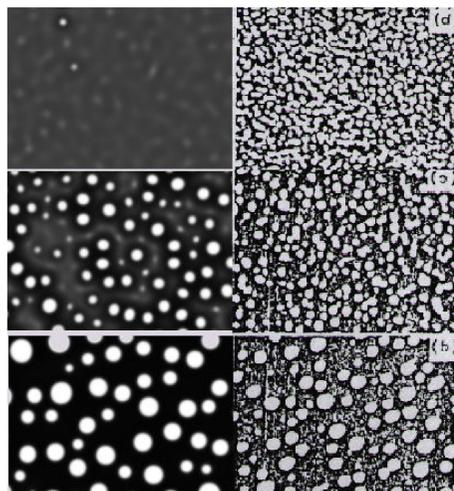

Figure 1: Cahn-Hilliard Simulation with a mass fraction of 25% on the left showing similar behaviour to the Electron Micro-graph on the right (J. Gunton).

Growth Laws

If l is the size of a cluster and the total system has cluster density of $n_l(t)$ per unit volume at time t, according to conservation of mass, the volume fraction V_f occupied by all the clusters is:

$$V_f(t) = \int n(t) d\mathbf{r} = V_{\text{total}} \sum_{l=0}^{\inf} n_l(t) \qquad (1)$$

To avoid infinities, this can be limited to $n_l\text{max}$ provided the maximum cluster size l^{max} is known. It is also useful to identify a special cluster size, denoted by l^* which will typically be the mean or median cluster size (or some other moment) in a distribution. Given that ϕ is the difference species or phases in a given system, we have $N(t) = \sum_{\phi=1}^{k} N_\phi(t)$ for k separate phases or species. Generally there will be one majority phase and the other phases form minorities against it as a background. This majority phase can be ignored or the vacancies on the background matrix or lattice can be treated as "particles" in their own right. Clusters can be compact or not but they always occupy some space and create an exclusion volume that cannot be occupied by other clusters. This constrains the density fractions of phases and not all arrangements and combinations are possible.

There are various processes we can consider for a system of clusters, it is convenient to consider nucleation theory based on growth and decay of clusters by monomer activation. This means the cluster size changes by ± 1 for growth and decay. In some systems this may be sufficient to explain all behaviours, but the probabilities of clusters breaking up or merging is non-zero even when size changes are considerably greater than unity.

The central assumption behind droplet and cluster theories of growth in binary solutions is that it is the heterophase or droplet fluctuations which lead to the decay of metastable states. These theories are generally formulated in the dilute limit, where a small volume fraction of solute material is uniformly distributed in the solvent as a single phase state. Following a quench, droplet fluctuations start the nucleation process, and these droplets then grow or shrink in size according to the condensation and evaporation mechanisms available.

A convenient starting point for this approach is that of [4], whereby a rate equation can be set up to describe changes in the cluster distribution function. Let the number of the minority-phase clusters with a mass of l A-atoms be denoted by $n_l(t)$ per unit volume at time t. The rate equation for condensation and evaporation processes can be written as:

$$\frac{dn_l(t)}{dt} = C_{l-1}^+ n_{l-1}(t) - C_l^+ n_l(t) +$$
$$C_{l+1}^- n_{l+1}(t) - C_l^- n_l(t), \quad l \geq 2$$
$$\frac{dn_l(t)}{dt} = C_1^+ n_1(t) + C_2^- n_2(t), \quad l = 1 \qquad (2)$$

The coefficients for condensation or growth of an l-cluster, C_l^+ and for evaporation or decay of an l-cluster, C_l^- are themselves functions of time. Their values must reflect the facts that we are only considering monomer activated processes, that is processes where a cluster increases or decreases its mass by a single atom, and that in a canonical simulation, the monomer population is finite. As clusters grow, the monomer population is depleted, and so C_l^+ will necessarily decease with time. Equation 2 can be rewritten using the detailed balance condition for growth and decay that states:

$$C_l^+ n_l^{eq} = C_{l+l}^- n_{l+l}^{eq} = W(l, l' = 1) \qquad (3)$$

Where $l' = 1$ denotes that we are only considering monomer activated processes, and W is the combined rate factor, and is strictly speaking time dependent itself, although it is treated here as constant in time. The rate equation is now parameterised by n_l^{eq}, the equilibrium or most probable cluster size distribution. The main task for a nucleation theory is to predict a form for this equilibrium cluster size distribution, by some approximation [5, 6]. It is sufficient here to suppose that the equilibrium cluster distribution can be written as:

$$n_l^{eq} = n_0 e^{-\triangle F_l k_b T} \qquad (4)$$

after Fisher, in which n_0 is a constant, and $\triangle F_l$ is the non-classical droplet free energy. This approach is essentially that of an ideal gas law for a non-interacting assembly of droplets, and is correct in the dilute limit[5]. Following [7], the rate equation can now be recast as:

$$\frac{dn_l(t)}{dt} = W(l-1,1)\left[\frac{n_{l-1}(t)}{n_{l-1}^{eq}} - \frac{n_l(t)}{n_l^{eq}}\right] + W(l+1,1)\left[\frac{n_{l+1}(t)}{n_{l+1}^{eq}} - \frac{n_l(t)}{n_l^{eq}}\right] \quad (5)$$

which is valid for $l \geq 2$, and expanding about l using:

$$\frac{n_{l\pm1}(t)}{n_{l\pm1}^{eq}} = \frac{n_l}{n_l^{eq}} \pm \frac{\partial}{\partial l}\frac{n_l}{n_l^{eq}} + \frac{1}{2}\frac{\partial^2}{\partial l^2}\frac{n_l}{n_l^{eq}} + \cdots$$
$$W(l-1,1) = W(l,1) - \frac{\partial}{\partial l}W(l,1) \qquad (6)$$

to yield:

$$\frac{\partial n_l(t)}{\partial t} = \frac{\partial}{\partial l}\left[W(l,1)\frac{\partial}{\partial l}\frac{n_l(t)}{n_l^{eq}}\right] = -\frac{\partial}{\partial l}J_l \qquad (7)$$

where J_l defines the *cluster current*. Since this is a continuity equation in cluster-size space $\{l\}$ it can be generalised by allowing the case $l' \geq 1$ where clusters grow or decay by more than one atom (see equation 8). By expanding the derivative in equation 8 and assuming Fisher's form n_l^{eq} in equation 4 we can derive equation 9 where R_l defines the cluster reaction rate for processes involving $l \rightleftharpoons l'$.

$$J_l = -\sum_{l'} l'^2 W(l, l') \frac{\partial}{\partial l}\frac{n_l(t)}{n_l^{eq}} \qquad (8)$$

$$J_l = -\left[R_l \frac{\partial}{\partial l} n_l(t) - \frac{\partial}{\partial l}\frac{\triangle F_l}{k_n T} R_l n_l(t)\right] \qquad (9)$$

$$R_l = \frac{1}{n_l^{eq}} \sum_{l'} l'^2 W(l, l') \qquad (10)$$

This illustrates that J_l contains two terms: a diffusive term: $-R_l\frac{\partial}{\partial l} n_l(t)$ and a drift term: $\frac{\partial}{\partial l}\frac{\triangle F_l}{k_n T}R_l n_l(t)$.

Only the drift term contains explicit dependence on the *form* of the equilibrium distribution. These two terms are of opposite sign, and it is supposed in cluster theories that there is a critical droplet size l^* at which the two terms are equal. For $l < l^*$ the drift term acts against the diffusion so that if a large droplet *does* form, it is likely to *decay* again. However, for the case when $l > l^*$ the drift term acts with the diffusion and hence super-critical droplets can grow steadily.

Following a quench to a metastable state, there is a transient time during which the cluster concentration $n_l(t)$ grows for clusters less than the critical cluster size $l \lesssim l^*$, until clusters saturate weakly at their equilibrium sizes. After this time lag, the nucleation current J_{l^*} around the maximum cluster size, has almost reached a steady state value known as *the* nucleation rate J.

So far the formulation of nucleation theory has only relied on the approximation of taking a specific form for the *unknown* droplet free energy function. Further progress can not be made without building in the restrictions mentioned earlier, of having a large *dilute* system, with a *fixed* monomer population density, and the additional constraint, that large droplets once formed, are removed from the system. This latter prevents all the solute material from precipitating out of solution and allows us to solve the steady state condition for the dilute system. Following Becker and Doring [7] and the requirement that the monomer population density is fixed, these constraints can be expressed by:

$$\lim_{l \to 0} \frac{n_l(t)}{n_l^{eq}} = 1 \qquad (11)$$

$$\lim_{l \to \infty} \frac{n_l(t)}{n_l^{eq}} = 0 \qquad (12)$$

for the removal of large droplets. The steady state cluster concentration n_l^{ss} can be obtained using:

$$\frac{\partial n_l^{ss}}{\partial t} = 0 \qquad (13)$$

requiring that $J_l \equiv J$ independent of l. Hence:

$$J = n_l^{eq} R_l \frac{d}{dl}\frac{n_l^{ss}}{n_l^{eq}} \qquad (14)$$

which gives:

$$\frac{n_l^{ss}}{n_l^{eq}} = J \int_l^\infty \frac{dl'}{R_{l'} n_{l'}^{eq}} \qquad (15)$$

with

$$J = \frac{1}{\int_0^\infty \frac{dl}{R_l n_l^{eq}}} \qquad (16)$$

using the boundary equations 11 and 12. If l^* is large, the free energy term in R_l can be expanded as a quadratic around l^* as:

$$\triangle F_l \approx R_{l^*} - \frac{1}{2} g k_b T (l - l^*)^2 \qquad (17)$$

where g is a constant. Equation 15 can be recast as:

$$\frac{n_l^{ss}}{n_l^{eq}} = \frac{1}{2}\{1 - \text{erf}\left(\frac{l - l^*}{\sqrt{\frac{g}{2}}}\right)\} \qquad (18)$$

The meaning of the parameter g is then to control the width of the region in which the ratio $\frac{n_l^{ss}}{n_l^{eq}}$ changes from unity to zero. This parameter is known as the Zeldovitch parameter [8].

The ratio in equation 18 varies with values of the Zeldovitch parameter g and implies that $\frac{n_l^{ss}}{n_l^{eq}}$ is close to unity around $l \lesssim l^*$ and goes to zero rapidly, for cluster sizes greater than l^*. This justifies the idea that the critical cluster size is a useful concept and can be employed as a cutoff on the full distribution.
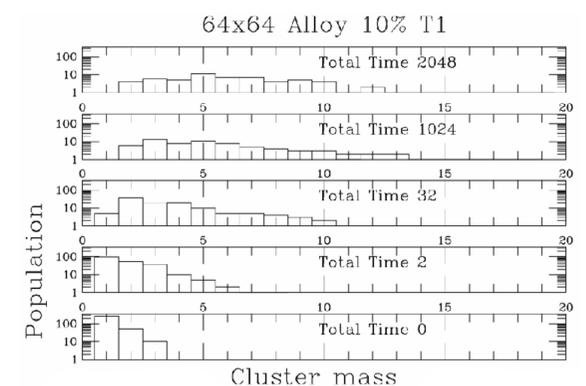

Figure 2: Cluster Distribution in 64x64 Alloy

Using the simulation configurations generated by the model it is possible to apply graph labeling and analysis methods [9] and to exactly enumerate clusters and histogram them by size. Figure X shows the cluster distributions as measured from a typical model system of a 64×64 binary alloy with minority phase concentration of 10% and at temperature $T = 2T_c$.

Discussion and Conclusions

Our simulations show that when the monomer population is depleted the distribution is no longer approximated by Fisher's exponential form. It is better described by a log-normal distribution or a Maxwellian distribution. This illustrates that although Fisher's exponential form for the free energy is useful at high temperatures, it breaks down for quenches to temperatures below the critical temperature. This is attributable to the depletion of the crucial monomers in the simulation, although this would in principle extend to other small mobile clusters, in a real alloy system. There are clearly other deficiencies with the Becker-Doring theory, as it fails to take proper account of the particle interactions.

Simulating and visualising[10] the phase transition in these model systems has made use of several computational resources. We are presently investigating the use of graphical processing units (GPUs) [11] to speed up the simulations and make it possible to simulate bigger and more realistic systems.

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