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Abstract. Aspects of the size dependence of phase separation in small bimetallic solid clusters are investigated using Monte Carlo simulations. The interatomic interactions are described approximately using the effective-medium theory. For the Ag–Cu system, which in the bulk shows phase separation for a broad range of mixing ratios up to the melting temperature, we find a strong size dependence of the maximum temperature where phase separation is possible. We also find that for clusters smaller than a critical cluster size N_0 of about 270 atoms there is no phase separation at all. The results are discussed in terms of a simple continuum model, which is found to be adequate for describing the main characteristics of the problem. Using the simple model we propose a description of N_0 as a function of the interface and mixing energies of an alloy, which can be used to estimate N_0 for other bimetallic alloys.

1. Introduction

Many intermetallic alloys show phase separation. In a range of temperatures and mixing ratios the two components segregate out to form two separate phases consisting predominantly of one of the components. In the bulk these effects are very well established and understood to a certain extent [1]. The question that we are addressing in the present paper is that of what happens in small metal particles. Consider a cluster of an alloy with some linear dimension r at a temperature and chemical composition making phase separation energetically favourable for a bulk system. On phase separation, the free energy decreases by an amount scaling approximately as r^3. At the same time the system has to 'pay' an amount of interface free energy scaling approximately as r^2. The scaling of these competing free energies is expected to induce a size dependence of the transition temperature and, especially, to give rise to a limiting cluster size r_0, beneath which phase separation does not occur.

Apart from providing new challenges to our understanding of alloys, small metal particles are increasingly used in the form of powders in metallurgical processes. Many metal catalysts are also intermetallic alloys, and to control the composition at the surface of such a catalyst particle, it is of paramount importance to have an understanding of the distribution of the two (or more) components in the cluster.

It is only within the last few years that simulations of metal clusters using reasonably accurate models for the interatomic interactions have become possible. The structure and melting of metal clusters has been studied for a number of systems [2, 3, 4]. Cluster alloys and in particular surface segregation has been studied by Yang and DePristo [4].

In the present paper we focus primarily on the effect of cluster size on phase separation in the interior of a bimetallic alloy cluster. Using the effective-medium theory to calculate the interatomic interactions we have made a series of Monte Carlo simulations of the phase separations as a function of the particle size and temperature. We will show that there is indeed a strong size dependence of the phase separation, and we will explicitly calculate the critical size below which there is no phase separation. We have chosen the Ag–Cu system to illustrate the effects that we will be discussing. This model system has a prominent miscibility gap in its bulk phase diagram and has the additional feature of displaying interesting size effects in the size range where computer simulations are feasible. We expect that the conclusions from the study of this system will prove to be more general, though.

In the following, we first introduce a simple phenomenological model of phase separation in bulk alloys and clusters. The model is useful in displaying the important questions to be studied in the simulations and will be used in a discussion of the simulation results. We then go on to discuss the simulation method and results of the simulation for the Cu-Ag system. Finally, in section 4 we conclude and use the simple model to make qualitative predictions for the size dependence of phase separation for other bimetallic alloys.

2. A simple cluster model

To establish a more firm intuition about the influence of the competition between interfacial and bulk energies on the equilibrium properties of an alloy cluster and quantify the discussion, we present a very simple thermodynamic model. A similar model has been reviewed earlier by Ollis [5] in connection with the surface structure of bimetallic catalysts. The model provides analytical and numerical results, which we relate to the qualitative and quantitative results of our Monte Carlo studies.

The simplest description of the energetics in solid alloys is provided by regular solution theory. This picture arises when approximating the cohesive energy by a sum of constant pairwise bond energies in combination with a mean-field approximation [6].

Thus for a homogeneous bulk phase of an A_cB_{1-c} alloy with N atoms at temperature T, the free energy of mixing is given by

$$G_{mix}^{hom}(c, T) = N(h_{mix}(c) - Ts_{mix}(c)) = Ng(c, T) \tag{1}$$

where the mixing enthalpy per atom is given by

$$h_{mix}(c) = \omega c(1 - c) \tag{2}$$

and the mixing entropy per atom is

$$s_{mix}(c) = -k[c \ln c + (1 - c)\ln(1 - c)]. \tag{3}$$

Here ω is the regular solution parameter, describing the intermetallic cohesive properties. One notices that the variable transformation $c \to \frac{1}{2}(1 + s)$ takes equation (1) into the mean-field free energy of Ising systems. Alloys with $\omega > 0$ (corresponding to ferromagnetic systems) have a positive mixing enthalpy and thus a miscibility gap in the phase diagram, while alloys with $\omega < 0$ (corresponding to antiferromagnetic systems) tend to form ordered alloys. Our interest is in the size dependence of the miscibility gap in phase diagrams.

For our model alloy Ag–Cu in the considered temperature range considered we use $\omega = 0.276$ eV/atom, estimated on the basis of effective-medium theory [7]. This value is consistent with the experimentally observed heat of solution [8]. In the following c refers to the Ag concentration. Using the Ising mean-field solution [1] one finds a bulk

phase diagram corresponding to equation (1) as shown in figure 2 with $T_c = \frac{1}{2}\omega/k$. For our specific model system Ag–Cu, only the lowest part of this phase diagram is actually relevant, because melting occurs experimentally at $1053 \text{ K} = 0.66T_c$.

If an alloy cluster with a finite number of atoms N separates into two phases with N_1 and N_2 atoms and concentrations c_1 and c_2 respectively, an interface free energy must be included:

$$G_{\text{mix}}^{\text{sep}}(c, T, N) = N_1 g(c_1, T) + N_2 g(c_2, T) + A\sigma(c_1, c_2, T) \qquad (4)$$

where A is the interface area and $\sigma(c_1, c_2, T)$ is the positive interface free energy. At this level we do not include a surface correction term in the free energy of mixing explicitly (here it may be taken as a temperature-dependent constant). Explicit inclusion of a more reasonable surface free-energy term introduces many uncertain parameters, thus blurring the characteristics of the model. The influence of the surface free energy is discussed qualitatively later. To quantify the relationship between N_1, N_2 and A, we consider a spherical cluster model for simplicity.
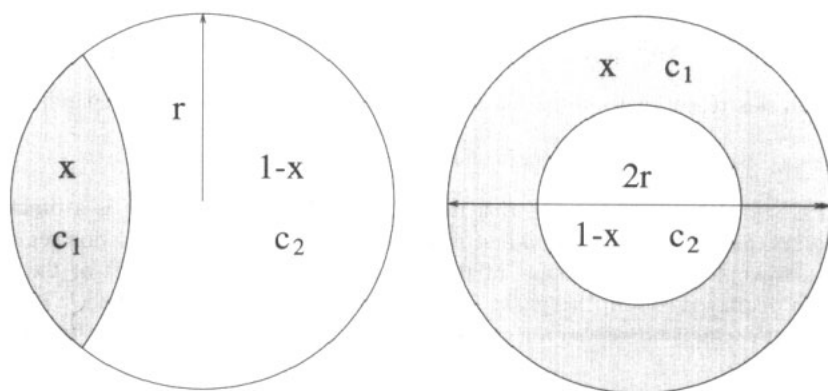

Figure 1. Sketch of the two most probable phase separation configurations for a spherical cluster.

The two most obvious separation geometries are sketched in figure 1. On the left the sphere is sectioned by the interface of least area, a spherical cap. Neglecting the differences in surface energy corresponds to fixing the wetting angle at 90°. On the right one spherical phase is encapsulated within the other. Although the left-hand option has smaller total interface area than the right-hand one, relative differences in interface tensions, cluster size or temperature may favour the right-hand option over parts of or the entire concentration range. For simplicity we consider in the following the left-hand option, which also turns out to be the most relevant for our model system Ag–Cu, but analogous results may readily be found for the right option. Substantial improvement in the notational clarity is obtained neglecting volume changes and differences in alloying—thus characterizing the alloy by a single cubic lattice constant a. Simple algebraic and geometric considerations now reduce equation (4) to the scaled equation

$$g^{\text{sep}}(c, T, \rho) = xg(c_1, T) + (1 - x)g(c_2, T) + \frac{3}{16}\frac{\alpha(x)\gamma(c_1, c_2, T)}{\rho} \qquad (5)$$

$$c = xc_1 + (1 - x)c_2$$

with

$$x = \frac{N_1}{N} \qquad \alpha(x) = \frac{A(x)}{\pi r^2} \qquad \rho = \frac{r}{a}. \qquad (6)$$

We have taken the atomic density to be $n_{FCC} = 4/a^3$, and thus $N = \frac{16}{3}\pi\rho^3$, and introduced the free interface energy per a^2, $\gamma(c_1, c_2, T)$. A trigonometric relation determining the scaled area function $\alpha(x)$ corresponding to the above assumptions can be found, but it turns out that the exact form of $\alpha(x)$ is of minor importance (giving small variations in the width of the model phase diagram). Thus for computational convenience we use the parametrization

$$\alpha(x) = \pi 32^{1/3}(x^{2/3} - 2^{-1/3}x^{4/3}) \qquad 0 \leqslant x \leqslant \frac{1}{2} \qquad (7)$$

having the correct asymptotic behaviour in the limits $x \to 0$ and $x \to \frac{1}{2}$.

The thermodynamic equilibrium free energy and configuration are determined by minimizing equation (5) with respect to the internal variables (x, c_1), which generally has to be done numerically. (We use a conjugate gradient algorithm.) To make further progress, assumptions about $\gamma(c_1, c_2, T)$ have to be made. The simplest approximation is to neglect the concentration dependence and take

$$\gamma(c_1, c_2, T) = h_0 - T s_0. \qquad (8)$$

With this representation the cluster is expected to undergo phase separation whenever

$$g^{sep}(c, T, \rho)\langle g(c, T). \qquad (9)$$

It is seen from equation (5), that the shape of the phase diagram is a function only of the form parameters $z_1 = h_0/\omega\rho$ and $z_2 = s_0/\rho$. In figure 2 the separation region of the model is shown for selected values of these parameters. The downshift of the critical point is also displayed. From the phase diagrams one notices, as anticipated, a lower critical size, beneath which no separation occurs. From equation (5) it can be shown that the critical size is

$$N_0 = N_c(0) = \frac{9\pi}{4}\left(\frac{h_0}{\omega}\right)^3. \qquad (10)$$

Using perturbation theory in the bulk limit of equation (5) one can derive an asymptotic expression for the repression of T_c:

$$\frac{T_c(N)}{T_c} = 1 - \left(\frac{2\pi}{3}\right)^{1/6}\left(\frac{h_0}{\omega} - \frac{s_0}{2}\right)^{1/2} N^{-1/6}. \qquad (11)$$

Although the size exponent $-\frac{1}{6}$ may reflect the inherent shortcomings of the mean-field approximation, the expression indicates that the decay to bulk behaviour is rather slow, the prefactor being of order unity.

In equation (5) we neglected a surface correction term in the free energy of mixing. This has two important consequences. Often atoms of the substance with the lowest surface energy segregate to the surface to form a monolayer with higher concentration than in the bulk. This surface-enrichment factor may be estimated semi-empirically [9]. The total surface segregation is, to a first approximation, independent of whether phase separation occurs in the bulk or not, but, due to the large ratio of the number of surface atoms to that of bulk atoms, surface segregation strongly influences the bulk alloy composition. Thus, in the simplest approximation, the surface coupling may be treated as a shift of the surface tensions and bulk concentrations. We include for simplicity only the latter effect, when comparing with the Monte Carlo simulation results.
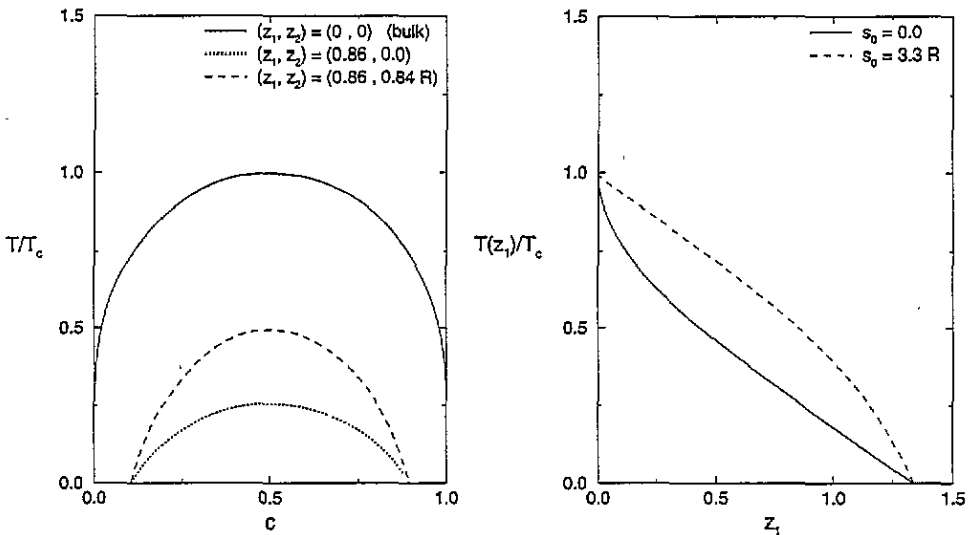
Figure 2. Model phase diagram curves enclosing regions where phase separation is thermodynamically stable (left) and the downshift of the critical point (right) for the thermodynamic model for selected values of the form parameters $z_1 = h_0/\omega\rho$ and $z_2 = s_0/\rho$. With the values for h_0 and s_0 derived later, the phase diagrams shown above correspond to the bulk and $N = 1000$ atoms, with and without interface entropy included. Our model system -Ag–Cu corresponds to $T_c = \frac{1}{2}\omega/k = 1605$ K.

3. Description of the simulations

Our Monte Carlo simulation study interatomic interactions are calculated using the effective-medium theory [7]. This calculation scheme offers a compromise between accurate total energies and computational speed, and has been used in a large variety of contexts [7]. All simulations are performed with (N, c, T) constant, N in the range [55; 1205] atoms and T in the primary range [280; 700] K.

We focus attention on clusters with approximately equiatomic bulk composition, where separation effects should be most pronounced for large clusters. Due to the surface segregation of Ag, see figure 4, in our model system we take $c = 0.75$ which implies that the bulk concentration $c_b \in [0.4; 0.65]$ for $N \in [55; 1205]$ and $T \in [280; 700]$ K. The overall trend in the variations of surface segregation with cluster size and temperature is caused by competition between entropy and segregation enthalpy, that is, the surface segregation process saturates with decreasing temperature and increasing cluster size. This means that c_b increases slightly when temperature and cluster size increases.

Initially, the simulation lattice is chosen as a spherical truncated FCC crystallite, centred at a lattice point. The lattice constant a is determined assuming a linear concentration dependence. To provoke a possible phase separation, the cluster is nucleated in the following way: the cluster lattice is sectioned by a (111) interface in two parts with volume fractions of approximately $\frac{1}{3}$ and $\frac{2}{3}$. In the smallest cluster fraction, Ag atoms are placed in a pure Ag FCC phase, while the rest of the atoms are distributed in a random FCC phase in the largest cluster fraction. We check later that the initial interface orientation is unimportant for our results. The lattice constant is now relaxed by minimizing the energy with respect to the lattice constant. Also local and surface relaxation effects are included by performing 25 steepest-descent steps.

For each nucleated initial cluster, 500 Monte Carlo steps are performed. Only swaps of atoms are included. To exclude artificial strain effects, each proposed Monte Carlo step is combined with a steepest-descent step to relax the local environment before the energy difference is evaluated. Thus our simulations do not suffer some of the problems of fixed-lattice simulations. Inspecting the simulation output, one notices that the structures are relaxed FCC although surface reconstructions are frequently encountered. At $N = 55$ total reconstruction to a Mackay icosahedron is observed.

To quantify the degree of phase separation we define a global and a local measure. As long-range-order parameter we use the scaled difference vector between the centres of mass for the two species:

$$d = \frac{1}{D} \left(\frac{1}{N_{Ag}} \sum_{Ag \; atoms} R_i \; - \; \frac{1}{N_{Cu}} \sum_{Cu \; atoms} R_j \right) \tag{12}$$

where D is the average diameter of the cluster. One notices that d is insensitive to phase separation configurations with inversion symmetry, such as the right-hand one in figure 1. We also define the short-range-order parameter

$$z = \frac{Z_{Ag(bulk)\to Ag}}{Z_{Cu(bulk)\to Ag}} - 1 \tag{13}$$

where $Z_{Ag(bulk)\to Ag}$ and $Z_{Cu(bulk)\to Ag}$ are the average numbers of Ag nearest neighbours for Ag and Cu atoms in the bulk, respectively. We focus on bulk coordination relations because we want to distinguish bulk phase separation from surface segregation, which occurs rather independently of bulk chemical structure. For random alloys $\langle z \rangle = 0$.

First we scanned for size dependence of the phase separation at four different temperatures, as shown in figure 3. One notices irregularity of the size dependence. Whereas the continuum model predicts a sharp size limit, $N_c(T)$, the transition to a phase-separated equilibrium state is seen to occur over a finite size range of the order of 100–300 atoms in the temperature range considered. Also one sees that the relative stability of the degree of phase separation with respect to temperature variations depends on cluster size and that the peaks in $\langle |d| \rangle$ and $\langle z \rangle$ are correlated.

We investigated the peak at $N = 321$ atoms for different initial orientations of the interface separating the nucleated and homogeneous phases (two random and the two other principal orientations) but found essentially the same averages of $|d|$ and z (with a standard deviation of 1.3% although the resulting interfaces seemed to belong to two different interfaces, (110) and (221)). Similar results were found for other selected cluster sizes. All averages of derived variables characterizing the cluster seem to have converged after a few hundred Monte Carlo steps. However, we cannot exclude the possibility that some results may belong to highly stable local minima in configuration space.

Browsing through the simulation output, one also notices that phase separation is associated with different interface orientations with respect to the underlying FCC lattice. In figure 4 we have shown examples of sliced clusters of different sizes at different temperatures with various degrees of phase separation.

The large fluctuations in $\langle |d| \rangle$ and $\langle z \rangle$ in the threshold size region are intelligible because the free energies of the phase-separated and homogeneous cluster are almost equal, and thus microstructural conditions (e.g. surface structure) have a large influence on the resulting chemical structure of the cluster.

Inspecting the simulation output we notice that the fluctuations in $\langle |d| \rangle$ above the separation threshold are largely driven by the symmetry properties of the separation geometry, e.g. the deep peak at $N = 429$ almost displays inversion symmetry, as shown in
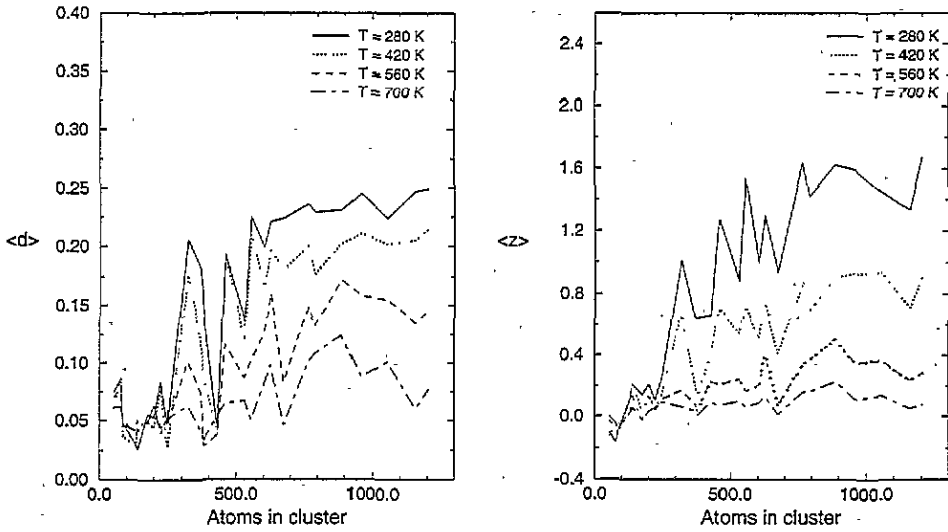
Figure 3. The average scaled difference vector $\langle|d|\rangle$ (left) and the average SRO parameter $\langle z\rangle$ (right) for clusters with $c = 0.75$ at 26 different sizes N at $T = 280$ K, 420 K, 560 K and 700 K. The lines connecting data points are for visual convenience.
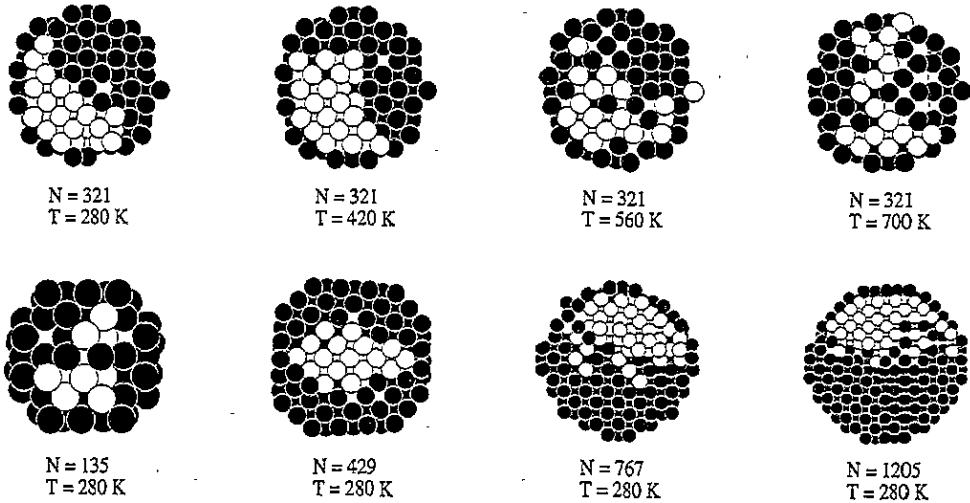

| N = 321 | N = 321 | N = 321 | N = 321 |
| T = 280 K | T = 420 K | T = 560 K | T = 700 K |

| N = 135 | N = 429 | N = 767 | N = 1205 |
| T = 280 K | T = 280 K | T = 280 K | T = 280 K |

Figure 4. Eight clusters at different sizes and temperatures, sliced through the centre perpendicular to the (100) direction. Ag atoms are black, Cu atoms are white. One notices the high Ag concentration in the surface layer.

figure 4. Using $N = \frac{16}{3}\pi(r/a)^3$ we cannot associate the fluctuations in figure 3 with one or a set of length scales (e.g. critical interfacial diameters). Although using more data points will reduce the noise level, such length scales should appear in figure 3, using the estimate

$$\Delta N \sim \frac{\partial N}{\partial r}\frac{a}{2} \sim 4N^{2/3} \tag{14}$$

giving $50 < \Delta N < 450$ for the cluster sizes investigated. Also stress analysis does not reveal the mechanisms governing the fluctuations in figure 3. One merely finds that von Mises' shear stress is distributed over the entire cluster, and that the hydrostatic pressure is

distributed according to the atomic size difference.

Our simulations also show that the peaks in $\langle|d|\rangle$ and $\langle z \rangle$ are uncorrelated with the peaks in the compactness of the cluster surfaces. The compactness of a cluster is defined as the Monte Carlo average of the ratio of surface atoms to bulk atoms in the cluster.

To extract the average properties, we draw a smooth Fermi curve through the data points for each simulation temperature:

$$\bar{d}(N) = d_0 + \frac{d_\infty - d_0}{1 + \exp[\tau(n_c - N)]} \tag{15}$$

with the form parameters d_0, d_∞, τ, n_c given by a least-squares fit, thereby estimating an average lower critical size n_c at four temperatures, as shown in figure 5 (right) as dots. The estimated critical size at the highest temperature (700 K) is somewhat uncertain, because the transition region seems to be rather close to the largest cluster sizes investigated. A more precise estimate would require more data points in the range 1200–2000 atoms, due to the noise level. Also shown in figure 5 is a fit to the simulation result (for the three lowest temperatures) of the simple thermodynamic cluster model with interface enthalpy $h_0 = 930$ mJ m^{-2} and interface entropy $s_0 = 3.3R$. The interface enthalpy is in reasonable agreement with a crude semi-empirical estimate for a high-angle grain boundary [10] $h_0 \sim 600$ mJ m^{-2} although the interface entropy is somewhat higher than the generally assumed experimental range $s_0 \sim 1 - 2R$ [6, 10], but consistent with the roughness of the interfaces—see figure 4. The reasonable agreement of the interfacial model parameters with semi-empirical and experimental values is promising, because the model curve $T_c(N)$ is rather sensitive to variations in the interfacial model parameters. We estimate the average absolute suppression size for the Ag–Cu system to be $N_0 \sim 270$.

One should note that the relative accuracy of the temperature scale for the comparison is determined by the accuracy of the regular solution approximation.
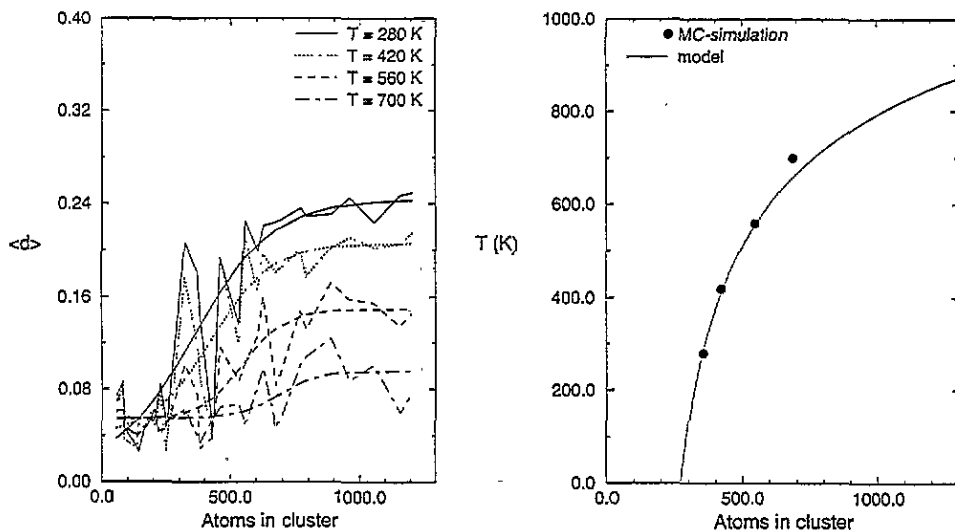

Figure 5. Left: smooth curves, $\bar{d}(N)$, drawn through $\langle d \rangle(N)$ giving average estimates for $N_c(T)$ as shown to the right as dots. Also shown to the right: the model prediction (solid curve) with $h_0 = 930$ mJ m^{-2} and $s_0 = 3.3R$, giving an estimate at the average absolute suppression size for the Ag–Cu system of $N_0 \sim 270$.
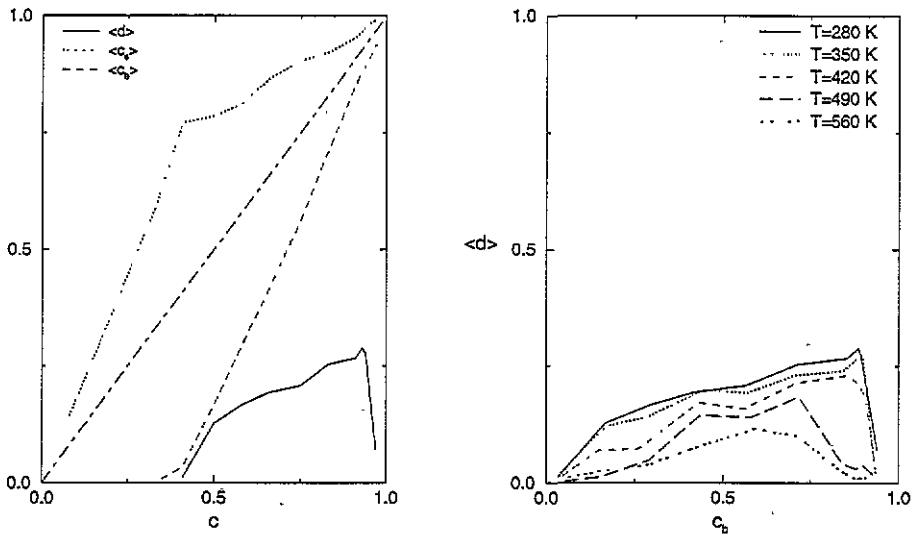
Figure 6. The effect of varying concentration and temperature on average phase separation for $N = 321$. To the left $\langle d \rangle$ and the surface and bulk concentration of Ag are plotted against total Ag concentration at $T = 280$ K. To the right $\langle d \rangle$ is plotted against bulk Ag concentration at different temperatures.

Further evidence against special lengths being associated with separation fluctuations is found by varying the average concentration. We studied the peak at $N = 321$ at $T = 280$ K by varying c in the interval [0.08; 0.97], as shown in figure 6. One notices the pronounced surface segregation of Ag. According to the simple cluster model one expects the scaled difference vector $d(c_b)$ to be maximal at and symmetric around $c_b = \frac{1}{2}$. The asymmetry is mainly induced by coupling to surface segregation: the interfacial energy at nucleation scales as $V^{2/3}$, where V is the volume of the nucleus, that is with infinite initial slope. Ag has the alternative of adhering to the segregated surface monolayer. This adhesion scales linearly with V (via some chemical potential). Thus nucleation of Ag is deferred until inwards growth of Ag is energetically unfavourable. Cu, on the other hand, does not have the possibility of growing inwards and must nucleate. The influence of this effect is size dependent and the asymmetry decreases with temperature, as the surface segregation becomes less prominent. For other systems excess enthalpy effects might also cause such asymmetries.

4. Conclusion and discussion

On the basis of our Monte Carlo simulation study and a simple thermodynamic model for the model system Ag–Cu we have extrapolated a size limit for small clusters—in an average sense—beneath which the equilibrium state is unlikely to be phase separated at any temperature.

However—due to the large ratio of the number of surface atoms to that of bulk atoms—the surface induces interesting effects and complications, e.g. how the degree of phase separation varies with chemical composition and temperature; but our results indicate, that surface compactness is uncorrelated with bulk phase separation.

We find that some statistical properties of the size dependence, e.g. the temperature

Table 1. Critical sizes for different alloy systems.

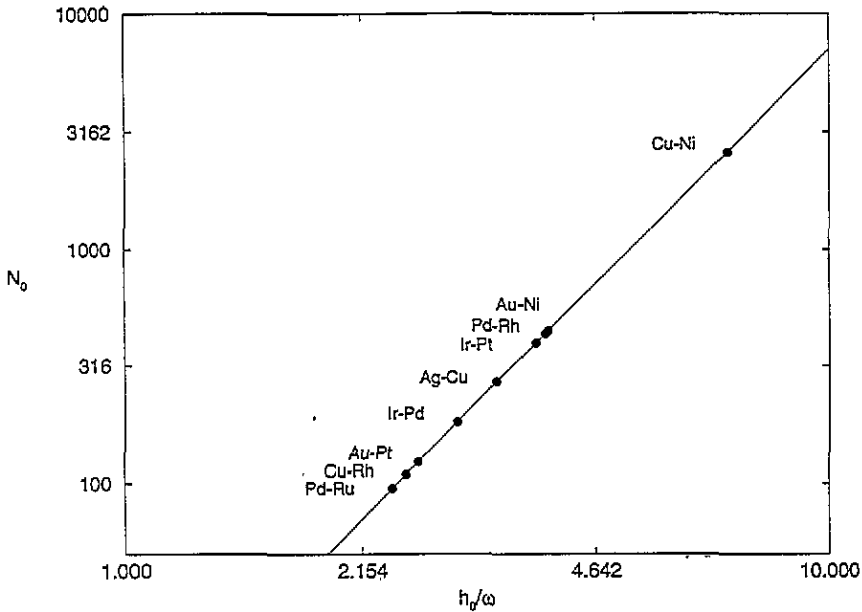| System	N_0	r_0
Pd–Ru	95	7.7
Cu–Rh	109	6.9
Au–Pt	123	7.7
Ir–Pd	182	8.6
Ag–Cu	270	9.7
Ir–Pt	394	11.1
Pd–Rh	433	11.4
Au–Ni	445	11.3
Cu–Ni	2590	19.2

Figure 7. N_0 versus h_0/ω shown with logarithmic axes for the representative model systems displayed in table 1.

dependence, can be understood in terms of a simple thermodynamic model based on the competition between stabilizing phase-separation free energy and destabilizing interface free energy.

Although our study has been limited to one alloy system, we expect our basic results to extend to a wider range of alloy combinations with similar properties, due to the generality of the driving mechanisms governing the size dependence.

We have used the simple model to predict the critical size r_0 of other alloy systems with a miscibility gap, using equation (10) as shown in table 1. A crude estimate is obtained with the interface enthalpy h_0 estimated via semi-empirical theory [10] and the regular solution parameter ω estimated from the experimental measured heats of solution [8] and the experimental phase diagrams [11]. For simplicity, neglecting excess enthalpy and entropy effects and volume changes on alloying beyond Vegard's law, we arrive at table 1 for the critical size r_0, assuming the alloy cluster to be approximately spherical.

All values are tabulated for equiatomic bulk composition (i.e. the overall chemical composition c of the cluster may be somewhat different, due to surface segregation). The structures of the alloy cluster are assumed to be FCC. For simplicity the clusters are assumed to be phase separated as shown on the left in figure 1.

Acknowledgment

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