Decay of a shell on the surface of a small spherical particle

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The redistribution of atoms on the surface of a small particle is investigated in systems with limited solubility. It is shown that three types of density profile are possible. First is the density distribution in the critical nucleus, second the distribution corresponding to formation of an equilibrium new-phase region on the particle surface, and third the formation of metastable density distributions similar in form to a network of tesseral spherical harmonics. In all three types of distribution, size effects are found, due to correlation of the particle radius with the characteristic dimension of the separated new phase. A unique type of size "quantization" is observed, manifested in the fact that periodic distributions are produced only for definite particle sizes. It is established that decay on the surface is forbidden below a certain limiting size.

Both experimental and theoretical attempts to study the decay of a solid solution on a flat surface of a crystal are known. In particular, a thermodynamic analysis of phase transitions on the surface of a massive sample is reported in Ref. 1. It is noted in Ref. 2, however, that different crystalline modifications cannot coexist on a flat surface, since the specific volumes of the phases are unequal. Yet phase transitions on surfaces, with formation of islands of a new phase, were observed in experiment,[3] with dimensions exceeding the interatomic distance.

A phase transition on the surface of a small particle should exhibit substantial differences from a phase transition on a flat surface, since the two-dimensional region in question has no boundary. In addition, noticeable size effects can be expected if the characteristic lengths are found to be of the order of the particle size. Investigation of phase transitions on surfaces of minute particles is therefore undoubtedly of interest.

EULER-LAGRANGE EQUATION OF A DECAYING SHELL

Two-dimensional concentration distributions in the surface layer of a spherical particle were investigated in a radially stepwise approximation. It was assumed that the interior of the particle is frozen, and atom exchange with the shell is forbidden. This statement of the problem makes sense, since the surface-diffusion coefficients exceed the bulk coefficients susbstantially (by several decades). The most difficult to account for is the elastic interaction between a two-dimensional tangential irregularity and the particle core, since the elastic energy does not reduce to a surface energy and a three-dimensional asymmetric problem must be solved. It should be noted that in this situation the elastic interaction has two causes: first, the Laplace-tension change due to the change of the particle surface energy and second, the dilatational interaction due to the difference between the atomic radii of the components when the atoms are redistributed in the shell.

Let us estimate the contribution of the first of these causes. A change of the particle surface energy by $\delta F_s = \Sigma\delta\alpha$ leads to a change of the elastic energy by $\delta F_\sigma = VKu_{ll}\delta u_{ll}$, where Σ is the surface area of the particle, V its volume, K the isotropic compression modulus, α the specific surface energy, and u_{ll} the isotropic-compression strain. Typical values of the constants for metals are $\alpha \sim 1$ N/m and $K \sim 5\cdot 10^{10}$ N/m^2. Assuming that $\alpha + \partial\alpha/\partial u_{ll} \approx \alpha$, in order of magnitude, we have $\delta F_\sigma/\delta F_s \sim \alpha/KR \approx 10^{-3}$, for particles of radius $R = 10$ nm. Consequently, the elastic-energy change due to the curvature is small compared to the inducing surface-energy change. The difference between the atomic radii of the components leads to a considerably larger effect. The latter can be estimated from a general solution of the elastic problem for a spherical region.[4] Confining ourselves to a spherically symmetric contribution to the displacement field, we can readily show[5] that when the atomic fraction one of the components is changed from c to $c + \delta c$ in a surface layer of thickness $\varepsilon \ll R$ the change of the particle elastic energy is equal to

$$\delta F_\sigma = [\varepsilon\Sigma E/(1-\sigma)]\delta(\omega c)^2, \tag{1}$$

where $\omega \equiv (r_B - r_A)/r_A$, r_A and r_B are the atomic radii of the components, E is Young's modulus, and σ is the Poisson coefficient. By comparing this value with the surface-energy change corresponding to the same density increment we can estimate the ratio of the atomic radii at which the elastic-energy contribution is small:

$$\omega^2 \ll |\alpha_A - \alpha_B|(1-\sigma)/2c\varepsilon E, \tag{2}$$

where α_A and α_B are the specific surface energies of the pure components.

The condition obtained is quite stringent. In particular, $\omega^2 \leqslant 10^{-2}$ if $c \sim 0.5$, $\sigma \sim 0.25$, $E = 10^{11}$ N/m^2, $|\alpha_A - \alpha_B| \sim 0.5$ N/m, and $\varepsilon = 0.5$ nm. The condition is actually met, however, in unstable solid solutions, whose decay is due according to the Hume-Rothery criterion not to a size factor but to an electronic one.[6] No account is taken of the elastic contribution in our present investigation of the thermodynamics of a surface solution.

The analysis of the restructuring of the shell is based on an investigation of a free-energy functional. Since the characteristic dimensions of the produced new phase are usually noticeably larger than the interatomic distance, we confined ourselves in the gradient expansion of the free-energy density to the second derivatives with respect to the coordinates, i.e., the concentrations $c(\theta,\varphi)$ were assumed from the outset to be smooth functions. With the foregoing taken into account, the change of the free energy upon formation of the new phase was written in the form[7]

$$\Delta F(c)=\varepsilon R^2\oiint_\Sigma \{f(c)-f(\bar{c})+\beta_1(\nabla c)^2+\beta_2\nabla^2 c\}\,d\Omega, \tag{3}$$

where c is the atomic fraction of the second component in the two-component particle, β_1 and β_2 are the expansion constants, $f(c)$ is the free-energy density averaged over a layer of thickness ε. The Green formula

$$\oiint_\Sigma (U_1\Delta_{\theta,\varphi}U_2-U_2\Delta_{\theta,\varphi}U_1)\,d\Omega=0, \tag{4}$$

where $\Delta_{\theta,\varphi}$ is the Laplace operator and U_1 and U_2 are arbitrary functions, is valid on the surface of the sphere.

The term proportional to β_2 in (1) can therefore be omitted. The parameter β_1, in turn, should be positive, otherwise any deviation of the concentration from the mean value would decrease the free energy and cause loss of stability regardless of the form of the function $f(c)$. In order of magnitude $\beta_1 \approx za^2W$, where W is the two-particle interaction energy, a is the lattice constant, and z is the coordination number.[8]

Since there is no exchange of atoms between the shell and the frozen interior of the particle, the average concentration of the component on the surface is conserved:

$$\oiint_\Sigma c\,d\Omega=4\pi\bar{c}. \tag{5}$$

By varying the functional (3) and taking relation (4) and (5) into account, we obtain the Lagrange equation of our problem

$$\Delta_{\theta,\varphi}c+\frac{R^2}{2\beta_1}\{\overline{f_c'}-f_c'\}=0, \qquad \overline{f_c'}\equiv\frac{1}{4\pi}\oiint_\Sigma f_c'\,d\Omega \tag{6}$$

with periodic boundary conditions. The quantity $\bar{f}'_c$ actually assumes the role of the chemical potential. Let us analyze Eq. (6) for the case of a parabolic dependence of the free-energy density on the concentration. The Lagrange equation is then linearized and can be rewritten in the form

$$\Delta_{\theta,\varphi}\delta c=(R^2/2\beta_1)f_c''\delta c, \qquad \delta c\equiv c-\bar{c}. \tag{7}$$

This is the equation for the eigenvalues of the Laplace operator. It has nontrivial bounded solutions $Y_{lm}(\theta,\varphi)$ only at definite values of the coefficients, viz.,

$$R^2 f_c''/2\beta_1=-l(l+1). \tag{8}$$

where l is an integer. It is clear that if $f_c''>0$ there are no nonzero solutions at all, and the particle surface remains stable to decay. If, however, $f_c''<0$, solutions are possible. This can be easily understood by investigating the second variation of the functional (3)

$$\delta^2\Delta F\sim\oiint_\Sigma (f_c''\eta^2+\beta_1(\nabla\eta)^2)\,d\Omega, \tag{9}$$

where η is an arbitrary deviation from the specified concentration profile. If $f_c''>0$, the quadratic form under the integral sign in (9) is positive-definite, meaning a minimum on the free-energy hypersurface. If, however, $f_c''<0$, the quadratic form considered is negative at certain values of η and the solution becomes unstable to decay. A unique size "quantization" takes place in the case. Loss of stability notwithstanding, decay is possible not on all particles, but only on this whose size satisfies condition (8). The concentration distribution corresponding to this size is similar in form to a tesseral spherical harmonic (Fig. 1).

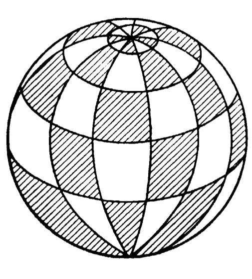

FIG. 1. Periodic distribution of concentration on the surface of a small particle.

Note that a distribution of this type can be produced on the surface of a small particle as a result of relaxation stresses due to structural tension,[9] i.e., lowering of the elastic energy is apparently an additional stimulus to the formation of such concentration profiles.

AXISYMMETRIC EXTREMAL DISTRIBUTIONS OF THE CONCENTRATION

Let us investigate in greater detail the axisymmetric distribution of the concentration of the components on the surface of a sphere. We attempt first to classify the types of possible concentration profiles. Multiplying both halves of Eq. (6) by ∇c and taking the equality $\nabla(\nabla c)^2=2(\nabla c)\nabla^2 c$, into account, we get

$$\nabla(f-c\bar{f}_c'-\beta_1(\nabla c)^2)=0. \tag{10}$$

Consequently, the quantity

$$E=f-c\bar{f}_c'-\beta_1(\nabla c)^2 \tag{11}$$

is the first integral of the Lagrange equation. The existence of the first integral (11) follows directly from the absence of an explicit coordinate dependence of the kernel of the functional (3). For the axisymmetric distribution $c(\theta)$, the relation obtained can be solved with respect to the derivative and permits separation of the variables

$$\frac{1}{R}\frac{dc}{d\theta}=[(f-c\bar{f}_c'-E)/\beta_1]^{1/2}. \tag{12}$$

Integrating this equation, we have

$$R(\theta-\theta_0)=\beta_1\int dc[\beta_1(f-c\bar{f}_c'-E)]^{-1/2}. \tag{13}$$

The character of the solution is obviously determined both by the form of the function $f(c)$ and by the value of the parameter E. In real situations the phase diagrams of decaying solid solutions have, besides a two-phase region, a certain region of homogeneity. The free-energy density is usually approximated by two parabolas[10]:

$$f(c)=\alpha(c-c_{01})^2,\quad c\leqslant c^*,$$
$$f(c)=\alpha(c-c_{02})^2,\quad c>c^*. \tag{14}$$

In this case $c^* = (c_{01}+c_{02})/2$.

It can be easily shown that an equation of type (13) with a two-parabola approximation of the free-energy density describes three concentration-profile forms.[8] The smallest possible value $E = E_0 > 0$ corresponds under phase-equilibrium conditions to a two-domain state. The case $E > E_0$ describes a nonequilibrium or a metastable distribution. There are thus three qualitatively different solutions. First, an equilibrium region of the new phase on the particle surface; second, a concentration distribution in the critical nucleus; third, formation of metastable periodic distributions. In contrast to the case of an unbounded region, Eq. (13) may have no solutions at all. Moreover, since the particle dimensions are close to the characteristic dimension of the emerging segregation, size effects manifest themselves in all three types of concentration profile. For example, the periphery of the central section through the particle must span an integer number of the periods λ of the metastable concentration distributions. The quantization of the period imposes an additional restriction on the possibility of their realization, and prevents in particular the existence of oscillating distributions on particles of size smaller than λ.

The distribution of the components in the critical nucleus is described by a system of equations that can be easily obtained from relations (6)–(14):

$$\frac{d}{dt}\left[(1-t^2)\frac{d}{dt}u_j\right]+p(p+1)u_i=0,$$
$$u_j\equiv c-c_{0j}-\frac{\bar{f}_c'}{2\alpha},\qquad p=-\frac{1}{2}\pm\frac{i}{2}(4R^2\alpha/\beta_1-1)^{1/2}, \tag{15}$$

where $t\equiv\cos\theta$, and the index j assumes two values, $j=1$ for $c\leqslant c^*$ and $j=2$ for $c>c^*$.

The differential equations (15) are Legendre equations. The character of solutions of equations of this type depends on the value of the parameter p, and is therefore determined by the ratio of the particle size to the correlation length $(\beta_1/\alpha)^{1/2}$. Thus, if $2R>(\beta_1/\alpha)^{1/2}$, the solutions are the conics $\tilde{P}_p(t)$ and $\tilde{Q}_p(t)$ of the first and second kind, respectively. If $2R=(\beta_1/\alpha)^{1/2}$ the solutions of Eqs. (15) are complete elliptic integrals. If, however, $2R<(\beta_1/\alpha)^{1/2}$, the concentration distribution is described by Legendre functions.[11] Note that the maximum area of the critical nucleus is equal to half the area of a spherical particle, since further growth of the region occupied by the new phase is accompanied by a decrease of the phase-separation boundary.

Let us study in greater detail the situation in which the concentration distribution constitutes two regions separated by a boundary zone. In this case, in Eq. (3), the integral of a term that contains derivatives with respect to the coordinates differs from zero only in the transition zone. Therefore, to simplify the qualitative analysis of the behavior of the equilibrium region of the new phase on the particle boundary as a function of its size, we replace the transition zone between the phases by a line of energy γ per unit length. Obviously, at equilibrium the phase-separation boundary is a circle, and the component distribution is symmetric about an axis perpendicular to the plane of this circle and passing through its center. Let us find the minimum of the free energy is the class of θ functions. In this case ΔF becomes a function of two variables, viz., the area of the surface occupied on the sphere by phase 1, and the concentration of one of the components in it. We put $c_1<c^*<c_2$, and then

$$\Delta F=[f(c_1)-f(\bar{c})]\Sigma_1+[f(c_2)-f(\bar{c})]\Sigma_2+\gamma L,$$
$$\Sigma_1+\Sigma_2=\Sigma,\quad c_1\Sigma_1+c_2\Sigma_2=\bar{c}\Sigma, \tag{16}$$

where Σ_1 and Σ_2 are the areas occupied by the first and second phases, and L is the length of the separation boundary. Minimization of ΔF with respect to the concentration leads to the standard condition that the chemical potential be constant, $f'(c_1)=f'(c_2)$. The concentration corresponding to this equation is described by the relations

$$c_1=\bar{c}+(c_{01}-c_{02})\Sigma_2/\Sigma,\quad c_2=\bar{c}-(c_{01}-c_{02})\Sigma_1/\Sigma. \tag{17}$$

Putting $\xi\equiv\Sigma_1/\Sigma$, we have $L=(\Sigma/R)[\xi(1-\xi)]^{1/2}$.

We investigate the behavior of the function $\Sigma F(\xi)$ on the segment $\xi\in[0,1]$. Its extremal points satisfy the equation $\Delta F'=0$ In view of the condition (17), we have

$$b(\xi-\xi^*)=(2\xi-1)/4[\xi(1-\xi)]^{1/2},$$
$$b\equiv(c_{01}-c_{02})^2\alpha\varepsilon R/\gamma,\quad \xi^*\equiv(\bar{c}-c_{02})/(c_{01}-c_{02}). \tag{18}$$

According to this equation, the extrema are determined by the point where the straight line $y=b(\xi-\xi^*)$ intersects the curve $y=(2\xi-1)/4[\xi(1-\xi)]^{1/2}$ (see Fig. 2). Depending on the position of the point ξ^* on the ξ axis, two qualitatively different situations are encountered. Thus, if $\xi^*\notin(0,1)$, i.e., $\bar{c}\notin(c_{01},c_{02})$, there exists only one intersection of the lines in question. In the opposite case $\xi^*\in(0,1)$ one can have one, two, or three intersections. Assume that Eq. (18) has at a certain dimension R a single solution. Variation of the particle radius leads to rotation of the straight line

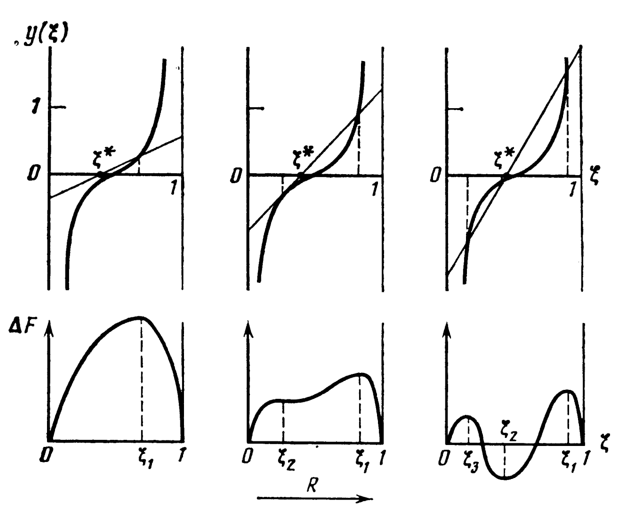

FIG. 2. Dependence of the change of the free energy on the area of the new phase. The arrow marks the direction in which the particle size increases.

around the point ξ^*. If $\bar{c}\in(c_{01},c_{02})$, the line is tangent to the curve at a parameter value $b=b_0$ determined by the conditions $\Delta F'(\xi)=0$ and $\Delta F''(\xi)=0$, and an inflection point appears on the $\Delta F(\xi)$ plot. Three intersections are realized with further rotation of the line, corresponding to an increase of the particle size (see Fig. 2). The extremal state is a minimum of the function $\Delta F(\xi)$ if the condition $\Delta F''(\xi)>0$ is met. Graphically it means a large slope of the straight line compared with the curve at the extremal point. The situation with one intersection corresponds therefore to a maximum of $\Delta F(\xi)$. In the case of a triple intersection the outer points correspond to maxima, and the middle one to a minimum of the free energy. The maxima are barriers preventing nucleation of a new phase, and the minimum describes a stable or metastable two-phase state, and occurs only in particles whose radius exceeds $\gamma b_0/(c_{01}-c_{02})^2\alpha\varepsilon$. The change of the character of $\Delta F(\xi)$ with decreasing particle size is shown in Fig. 2. A decrease of the size causes an increase of the barrier to nucleation of the new phase, and weakening of the thermodynamic stimulus to the transformation, and even its prevention.

Note that the parameters c_{01}, c_{02}, and α, which specify the form of the $f(c)$ curve, are temperature dependent. The two-phase region expands when the temperature is lowered. This is tantamount to increasing the difference $|c_{01}-c_{02}|$, and hence also of the slope of the line $y(\xi)$. In contrast to the size dependence, however, the temperature variation on the free-energy extremum not only changes the slope of the line but also displaces the point ξ^*.

The anomalies in the formation of a new phase on a particle surface are size-dependent. These anomalies are due, on the one hand, to the fact that the particle surface is closed, and on the other, to the proximity of its size to the characteristic decay length. The first of these factors leads to a unique quantization effect, and the second is manifested in a reconstruction of the thermodynamic stimulus to the phase transition.

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