ON SPINODAL DECOMPOSITION*

JOHN W. CAHN †

The stability of a solid solution to all infinitesimal composition fluctuations is considered, taking surface tension and elastic energy into account. It is found that for infinite isotropic solids, free from imperfections the spinodal marks the limit of metastability to such fluctuations only if there is no change in molar volume with composition. Otherwise the elastic energy due to a fluctuation stabilizes the solution and alters the criterion for the limit of metastability. For an unstable solution the kinetics of decomposition are discussed and the expected mean particle size or wavelength of the most rapidly growing fluctuation is derived.

SUR LA DECOMPOSITION SPINODALE

L'auteur considère la stabilité d'une solution solide en relation avec des fluctuations infinitésimales de la composition. En tenant compte de la tension superficielle et de l'énergie élastique, on trouve que pour des solides isotropes infinis et exempts d'imperfections, la décomposition spinodale indique la limite de métastabilité aux fluctuations considérées seulement dans le cas où il n'intervient pas de modification du volume molaire avec la composition. Autrement, l'énergie élastique résultant d'une fluctuation stabilise la solution e t modifie le critère de la limite de métastabilité. L'auteur discute de la cinétique de la décomposition dans le cas d'une solution instable et il en déduit la dimension moyenne de la particule ou de la longueur d'onde associée à la fluctuation la plus rapide.

ÜBER DIE UMSETZUNG AN DER SPINODALEN

Die Stabilität einer festen Lösung gegenüber allen infinitesimalen Schwankungen der Zusammensetzung wird betrachtet, dabei werden Oberflächenspannung und elastische Energie mit berücksichtigt. Es wird gezeigt, daß im unendlichen, isotropen und fehlerfreien Festkörper die Spinodale nur dann die Grenze der Metastabilität bezüglich solchen Schwankungen darstellt, wenn sich das molare Volumen mit der Zusammensetzung nicht ändert. Andernfalls stabilisiert die mit der Schwankung verknüpfte elastische Energie die Lösung und verändert die Bedingungen für die Grenze der Metastabilität. Für eine instabile Lösung wird die Kinetik der Umsetzung diskutiert und die zu erwartende mittlere Teilchengröße oder die Wellenlänge der am schnellsten wachsenden Schwankung abgeleitet.

1. INTRODUCTION

In his classic treatment of stability of phases, Gibbs[1] separated into two categories the infinitesimal changes to which a metastable phase must be resistant. One is a change that is infinitesimal in degree but large in extent, as exemplified by a small composition fluctuation spread over a large volume. If a phase is unstable to such a fluctuation, then there is no barrier (other than a diffusional one) to a continuous transformation to a more stable phase. Gibbs formulated the general conditions necessary for this type of instability. Specifically he showed that a necessary condition for stability for a fluid phase to such a fluctuation be that the chemical potential of each component increase with increasing density of that component. For a two component fluid this condition is equivalent to $\left(\dfrac{\partial^2 G}{\partial c^2}\right)_{T,P} \geqslant 0$ where G is the Gibbs free energy per mole of solution and c the composition. On a binary phase diagram the boundary of the unstable region is defined by the locus of $\left(\dfrac{\partial^2 G}{\partial c^2}\right)_{T,P} = 0$ and is usually but inappropriately called the spinodal. This condition for instability can be traced continuously to Gibbs' original work, and initially received much attention in Germany after a German translation by Ostwald of Gibbs' paper was published in 1891, although reference to Gibbs was rarely made.

In recent years there have been a number of workers who have extended Gibbs' concept of the spinodal to solid solutions[2–5] without clear proof that it continues to be valid. It is the purpose of the present paper to explore its validity.

The other changes considered by Gibbs are those which are large in degree but small in extent, an example being that of an infinitesimal droplet of material with properties approaching those of the more stable phase. This has given rise to the well-known classical nucleation theory. The two categories have apparently led to two irreconcilable schools, although they were clearly compatible to Gibbs. Recently it has been shown[6,7] that the mechanism of nucleation approaches the mechanism of spinodal decomposition continuously as the spinodal is approached.

The main controversy revolved around the apparent neglect of surface tension in the theories of spinodal decomposition. The answer to this controversy is in the fact that within the spinodal the solution is not unstable to fluctuations which form small droplets, but unstable to long range fluctuations, which are sufficiently large in extent that the surface tension contributions are always smaller than the volume energy contributions. In a recent paper Hillert,[7] in fact, considers the kinetics of decomposition within the spinodal of a regular solution with near neighbor interactions only, taking incipient surface tension into account, and in the present paper Hillert's treatment will be extended to three dimensional isotropic solids and generalized to any type of solution free from structural imperfections that give rise to long range elastic fields.

2. THE SPINODAL CONCEPT

(a) *Incompressible isotropic binary solution of constant molar volume*

It will be simpler first to consider an isotropic solid solution free from imperfections in which the molar volume is independent of both composition and pressure. For such a material it is possible[8] to write the total Helmholz free energy as

$$F = \int_V [f'(c) + \varkappa \, (\nabla c)^2] \, dV \,, \qquad (1)$$

where $f'(c)$ is the Helmholz free energy of a unit volume of homogeneous material of composition c and $\varkappa(\nabla c)^2$ is the first term of an expansion representing the increase in free energy due to introducing a gradient of composition. The second term gives rise to surface tension. Since we shall be concerned with testing the stability of an initially homogeneous solution to infinitesimal composition fluctuations the gradients will also be infinitesimal and the second

term will be completely sufficient to describe the contribution from the incipient "surfaces" (between regions differing in composition). Higher order gradient energy terms will be negligible, except at very large gradients.

We may also expand $f'(c)$ about the average composition c_0

$$f'(c) = f'(c_0) + (c - c_0) \left(\frac{\partial f'}{\partial c} \right)_{c \, = \, c_0}$$
$$+ \frac{1}{2} (c - c_0)^2 \left(\frac{\partial^2 f'}{\partial c^2} \right)_{c \, = \, c_0} . \qquad (2)$$

The difference in free energy per unit volume between the initial homogeneous solution and one with a composition given by

$$c - c_0 = A \cos \beta x \qquad (3)$$

is

$$\frac{\Delta F}{V} = \frac{A^2}{4} \left(\frac{\partial^2 f'}{\partial c^2} + 2\varkappa \beta^2 \right) . \qquad (4)$$

If this is negative, then the solution is unstable with respect to sinusoidal fluctuations of wavelength $2\pi/\beta$. Both terms are quadratic in the amplitude, so the stability criterion is initially independent of amplitude.

We shall assume $\varkappa$ to be positive; otherwise we would have negative surface tension, and no stability even outside the spinodal. With $\partial^2 f'/\partial c^2 > 0$ the solution is stable with respect to infinitesimal sinusoidal fluctuations of all wavelengths. With $\partial^2 f'/\partial c^2 < 0$ the solution is unstable with respect to infinitesimal sinusoidal fluctuations of wavelengths greater than $2\pi/\beta_c$ where

$$2\pi/\beta_c = [-8\pi^2\varkappa/(\partial^2 f'/\partial c^2)]^{\frac{1}{2}}. \qquad (5)$$

This concept was first given by Hillert[7], and shows that as the spinodal is approached the critical wavelength approaches infinity. The effect of incipient surface tension is to disallow the solution to decompose on too small a scale.

Now consider an arbitrary composition fluctuation. It can always be described by its Fourier components and, because of their orthogonality, the total change of free energy is the sum (or integral) of the free energy change accompanying each Fourier component. It is therefore sufficient to consider only the individual sinusoidal fluctuations in testing for stability to infinitesimal composition fluctuations;

if it is stable to all of these individually, it is stable to all infinitesimal fluctuations. If it is unstable to any of these it is obviously unstable, since we have taken surface tension into account.

For an infinite system, the limit of instability corresponds to the spinodal; for a finite system, neglecting changes in its exterior surface the spinodal curve is to be modified to take into account the fact that β can not be zero. Instability occurs approximately for a value of

$$(\partial^2 f'/\partial c^2) = -\frac{8\pi^2 \varkappa}{L^2}, \qquad (6)$$

where L is the largest linear dimension of the system. Since $\varkappa$ is of the order of $\varkappa T_c N_v^{1/3}$ where T_c is the critical temperature and N_v the number of atoms in a unit volume, this is a negligibly small correction except for very small systems.

It may be worthwhile to point out that equation (1) requires some sort of smoothing process and that for really short wavelength fluctuations its meaning would be doubtful. Happily in this application we have a short wavelength cut-off to the fluctuations of interest, because of the gradient energy term.

(b) Isotropic binary solid solution free from imperfections

In the previous section we considered a solution of constant molar volume. As a result, composition fluctuations were not accompanied by strains. In this section allowance for strain energy will be made. In order to do this we will require that $f'(c)$ be the Helmholz free energy of $1/V_0$ moles of stress free homogenous material where V_0 is the molar volume of material of composition c_0. It therefore is directly proportional to the free energy usually measured, except for a pressure term, which is negligible at one atmosphere. It is also the free energy needed to describe the equilibrium of two incoherent phases. If we consider a long range infinitesimal composition fluctuation in a perfect crystal there will be coherency strains if the molar volume is a function of composition. This will introduce additional energy. Because we are considering infinitesimal fluctuations only we may neglect the effect of spontaneously created dislocations in modifying the strain energy of the fluctuation, since such dislocations would require a finite energy.

Let us as before consider a fluctuation described by equation (3) in an isotropic material in which the stress free molar volume for small $(c-c_0)$ is given by

$$V(c) = V_0(1 + 3\eta(c-c_0)) = V_0(1 + 3A\eta \cos \beta x),$$

and the stress free strain is a pure dilatation, η being the linear expansion per unit composition change. The components of total strain resulting from this composition fluctuation are

$$\varepsilon_{xx}^T = A\,\eta\,\frac{1+\nu}{1-\nu}\cos \beta x$$

$$\varepsilon_{yy}^T = \varepsilon_{zz}^T = \varepsilon_{xy}^T = \varepsilon_{yz}^T = \varepsilon_{zx}^T = 0. \qquad (7)$$

The elastic strain is the difference between the total strain and the stress free strain and is

$$\varepsilon_{xx}^E = A\,\eta\,\frac{2\nu}{1-\nu}\cos \beta x$$

$$\varepsilon_{yy}^E = \varepsilon_{zz}^E = -A\eta \cos \beta x$$

$$\varepsilon_{xy}^E = \varepsilon_{yz}^E = \varepsilon_{zx}^E = 0, \qquad (8)$$

and the corresponding stress is

$$\sigma_{xx} = 0$$

$$\sigma_{yy} = \sigma_{zz} = -\frac{AE\eta}{1-\nu}\cos \beta x \qquad (9)$$

$$\sigma_{xy} = \sigma_{yz} = \sigma_{zx} = 0,$$

where E is Young's Modulus for the average composition. The variation of E with composition enters only in higher order terms. The local elastic strain energy per unit volume is thus

$$\frac{1}{2}\sum_{ij}\sigma_{ij}\,\varepsilon_{ij}^E = \frac{A^2\eta^2 E}{1-\nu}\cos^2 \beta x, \qquad (10)$$

and the average elastic energy per unit volume is

$$\frac{1}{V}\int \frac{1}{2}\sum_{ij}(\sigma_{ij}\,\varepsilon_{ij}^E)\,dV = \frac{A^2\eta^2 E}{2(1-\nu)}$$

which is independent of the wavelength.

It is possible to derive the elastic energy of an arbitrary composition fluctuation. By Fourier analysing the composition, finding the elastic energy of each Fourier component and noting that the components do not interact, one obtains that the total elastic energy of an infinite isotropic solid with an arbitrary composition fluctuation is

$$\frac{\alpha^2\eta^2 E}{1-\nu}, \qquad (11)$$

where

$$\alpha^2 = \int_V (c - c_0)^2 dV.$$

The elastic energy depends only on the integrated square deviation from the average composition and is independent of the other details of the fluctuation. Thus instead of equation (1) we have

$$F = \int_V \left[f'(c) + \frac{\eta^2 E}{1-\nu}(c - c_0)^2 + \varkappa(\nabla c)^2 \right] dV. \quad (12)$$

We have taken our co-ordinate system as imbedded in the original undistorted lattice. A unit volume in that co-ordinate system always contains $1/V_0$ moles. It was for this reason that the quantity f' was defined as it was. The difference in free energy per unit volume between the initially homogeneous solution and one with a composition fluctuation given by equation (3) is

$$\frac{\Delta F}{V} = \frac{1}{4} A^2 \left[\left(\frac{\partial^2 f'}{\partial c^2} \right) + \frac{2\eta^2 E}{1-\nu} + 2\varkappa \beta^2 \right]. \quad (13)$$

As before, if this is negative then the solution is unstable with respect to sinusoidal fluctuations of wavelength $2\pi/\beta$. Again all terms are quadratic in amplitude, so that the stability criterion is initially independent of amplitude. We find that the solution should remain stable to infinitesimal fluctuations inside the spinodal until

$$\frac{\partial^2 f'}{\partial c^2} < -\frac{2\eta^2 E}{1-\nu}.$$

The limit of stability is given by the locus of

$$\frac{\partial^2 f'}{\partial c^2} + \frac{2\eta^2 E}{1-\nu} = 0. \quad (14)$$

This condition reduces to the spinodal if $\eta = 0$. In order to estimate the magnitude of the change in the stability condition due to coherency strains, let us compute the distance on a phase diagram between the spinodal and the stability condition for several systems; Au–Ni for which η is large and Al–Zn and Au–Pt for which η is small. Let us express the difference as an undercooling below the critical point for a material of the critical composition. For this approximately

$$\left(\frac{\partial^2 f'}{\partial c^2} \right) = 4k(T - T_c)N_v.$$

The spinodal is at $T = T_c$; instability sets in at

$$T_c - T = \frac{\eta^2 E}{2(1 - \nu)kN_v}. \quad (15)$$

Thus coherency stress will stabilize a solid solution against infinitesimal composition fluctuations for

TABLE 1

System	η	$\dfrac{\eta^2 E(1 - \gamma) kN\nu}{°C}$
Al–Zn	0.0257	40
Au–Pt	0.038	200
Au–Ni	0.15	2000

a large undercooling below the spinodal. The phenomenon is clearly consistent with the great stability which Au–Ni exhibits to decomposition. Precipitation at higher temperatures is clearly cellular. For all compositions in the two phase field the solid solution remains unchanged until the cell front passes,[9] which is not what is expected if the solution were unstable.

(c) *The effect of the free surface*

In the infinite solid the total strain normal to the sinusoidal fluctuations has to be zero. In the vicinity of a free surface this need not be and some reduction of the elastic energy is to be expected. In addition a certain amount of interaction between Fourier components will occur. The extreme of this is for a finite solid with a constant composition gradient across it. For such a solid there is no elastic energy whatsoever. Thus a finite solid free from imperfections becomes unstable at the spinodal to such a composition fluctuation involving the whole crystal if we neglect gradient energy and changes in surface tension due to composition changes at the free surfaces.

(d) *The effect of imperfections*

The effect on the stress field of various imperfections will be such as to give rise to "atmospheres" in which the composition is so altered as to reduce the elastic energy. At certain critical compositions some imperfections give rise to atmospheres which will grow without limit, and it is highly unlikely that these compositions will be closely related to the spinodal.

3. KINETICS OF DECOMPOSITION WITHIN THE SPINODAL

Hillert[7] has treated the kinetics of spinodal decomposition by considering a diffusion equation in which the thermodynamic factors are included. Because the chemical potential decreases with increasing concentration of that component within the spinodal, the direction of the diffusive flux must correspond to a negative diffusion coefficient. In addition the diffusion equation must contain a higher order term reflecting the thermodynamic contributions of the gradient energy term. This will, for example, express the fact that in an equilibrium two phase mixture, composition gradients can exist at interfaces without a corresponding flux.

Because of the complexity of his formulation, Hillert had to constrain his composition fluctuation to those in which all composition gradients were along a given crystallographic direction, that is, normal to lattice planes of constant composition. In this paper, this artificial constraint on the gradients will be removed, and elastic energy introduced. By limiting ourselves to the initial stages of decomposition, it will be possible to get an analytic expression for the rate of growth and form of the composition fluctuation, which was not possible in Hillert's method. On the other hand the present treatment does not lend itself as readily to the consideration of the later stages of spinodal decomposition. In a homogeneous alloy the quantity $(\partial f'/\partial c)$ is proportional to the difference in the chemical potential of the two components, since it is the change in free energy when we replace some of one component by another. In the presence of a gradient, if we make a local change in composition we also change the local gradient. The quantity, corresponding to $(\partial f'/\partial c)$ and proportional to the chemical potential difference, is called the variational derivative. Consider a variation in composition

$$\delta F = \int_V \left\{ \left[\frac{\partial f'}{\partial c} + \frac{2\eta^2 E}{1 - \nu} (c - c_0) + \frac{\partial \varkappa}{\partial c} (\nabla c)^2 \right] \delta c + 2\varkappa \nabla c \, \delta(\nabla c) \right\} dV .$$

(16)

After integrating the last term by parts this becomes

$$\delta F = \int_V \left[\frac{\partial f'}{\partial c} + \frac{2\eta^2 E}{1 - \nu} (c - c_0) - \frac{\partial \varkappa}{\partial c} (\nabla c)^2 \right.$$

$$\left. - 2\varkappa \nabla^2 c \right] \delta c \, dV .$$

(17)

The quantity in brackets is the change in free energy due to a local change of composition δc. We may now define a positive quantity M such that the net flux of B atoms is given by

$$J = -M \, \mathrm{grad} \left[\frac{\partial f'}{\partial c} + \frac{2\eta^2 E}{1 - \nu} (c - c_0) \right.$$

$$\left. - \frac{\partial \varkappa}{\partial c} (\nabla c)^2 - 2\bar{\bar{x}} \nabla^2 c \right],$$

and

$$-\mathrm{div} \, J = \frac{\partial c}{\partial t} = \mathrm{div} \left\{ M \, \mathrm{grad} \left[\frac{\partial f'}{\partial c} + \frac{2\eta^2 E}{1 - \nu} (c - c_0) \right. \right.$$

$$\left. \left. - \frac{\partial \varkappa}{\partial c} (\nabla c)^2 - 2\varkappa \nabla^2 c \right] \right\} .$$

If we confine our interest to the initial stages of spinodal decomposition we may neglect all terms not linear in c and obtain

$$\frac{\partial c}{\partial t} = M \left(\frac{\partial^2 f'}{\partial c^2} + \frac{2\eta^2 E}{1 - \nu} \right) \nabla^2 c - 2M\varkappa \nabla^4 c .$$

(18)

The quantity $M[(\partial^2 f'/\partial c^2) + (2\eta^2 E/1 - \nu)]$ is now identified with the interdiffusion coefficient and $(-M\varkappa)$ is the thermodynamic correction factor for incipient surfaces. Note that the coherency strains have altered the usual thermodynamic factor appearing in the diffusion coefficient.

Equation (18) has one serious fault for small fluctuations, and that is that it can not possibly describe nucleation. It describes a system whose free energy decreases monotomically by a diffusion process, and therefore does not permit the small but finite excursions necessary for nucleation.

Equation (18) has a general solution of the form

$$c - c_0 = A(\beta, t) \cos \beta \cdot r,$$

(19)

where $A(\beta, t)$ obeys the differential equation

$$\frac{\partial A}{\partial t} = -M \left(\frac{\partial^2 f'}{\partial c^2} + \frac{2\eta^2 E}{1 - \nu} \right) \beta^2 A - 2M\varkappa \beta^4 A ,$$

and therefore

$$A(\beta, t) = A(\beta, 0) \exp [R(\beta)t],$$

where

$$R(\beta) = -M\beta^2 \left(\frac{\partial^2 f'}{\partial c^2} + 2\beta^2 \varkappa + \frac{2\eta^2 E}{1 - \nu} \right).$$

(20)

Comparison with equation (13) shows that the kinetic amplification factor R is negative when the solution is stable to that fluctuation. It is zero for β_c and positive for longer wavelengths and has a maximum at exactly $\sqrt{2}$ times the critical wavelength.

Consider an homogeneous solution within the spinodal. It will have initially a certain amount of fluctuation from the average composition which may be written as a Fourier integral

$$c(\mathbf{r},0) - c_0 = \int_\beta A(\beta,0) \exp (i\beta \cdot r) \, d\beta.$$

Each Fourier component of that fluctuation will grow or diminish according to its wavelength and at any later stage

$$c(\mathbf{r},t) - c_0 = \int_\beta A(\beta,0) \exp [R(\beta) \, t + i\beta \cdot r] \, d\beta. \quad (21)$$

Because of the maximum in R as a function of wavelength, those components of the fluctuation with $\sqrt{2}$ times the critical wavelength will grow fastest and will dominate. This principle of selective amplification depends on the initial presence of these wavelengths but does not critically depend on their exact amplitude relative to other wavelengths if the time t is large compared with $1/R(\beta_c/\sqrt{2})$. It does not depend on any additional assumptions, since different wavelengths can coexist and do not interfere with one another.

We can not say much about the actual rate of spinodal decomposition, except to place an upper limit on it.

$$\frac{d\ln\alpha}{dt} \leqq 2R(\beta_c/\sqrt{2}) = \frac{M}{4\varkappa}\left(\frac{\partial^2 f'}{\partial c^2} + \frac{2\eta^2 E}{1-\nu}\right)^2, \quad (22)$$

where α is defined in equation (10). The quantity $d\ln\alpha/dt$ will be greatest when the fluctuation is sinusoidal with wavelength $2\sqrt{2\pi/\beta c}$. Since it will approach zero as the limit of metastability is reached, it is unlikely that this mechanism of spinodal decomposition will be observed near the limit of metastability; for it is too slow there, and long before it will have a chance, ordinary nucleation and growth resulting from finite fluctuations not permitted by equation (18) will have taken over. However, well inside the unstable region when the critical wavelength has become small, this spinodal mechanism may be the observed one.

4. DISCUSSION

We have seen that the concept of a region in the phase diagram in which the solution is unstable to infinitesimal fluctuations is unaltered by the introduction of surface tension and elastic energy. However, the details are altered. Surface tension prevents decomposition of the solution on too fine a scale, without altering the criterion for stability. Elastic energy alters the criterion itself.

We have examined only infinitesimal fluctuations. For these, the treatment of the elastic energy and incipient surface free energy is exact. By considering the rate of growth of the fluctuations it was possible to make some prediction about the nature of the finite fluctuations resulting from the infinitesimal ones. To treat the problem more fully requires the introduction of higher order terms, particularly in the free energy expansion, so that the fluctuation will cease growing when equilibrium is reached. This was done in one dimension by Hillert.[7] It is hoped that the interparticle distance or wavelength expected from considering the initial stages of decomposition will persist at least until the stage of coalescence when larger particles will grow at the expense of smaller ones.

There is no nucleation barrier when the solution is unstable to infinitesimal fluctuations, but that does not mean that decomposition will proceed by a spinodal mechanism. Within the unstable part of the phase diagram, sufficiently near the limit of metastability such a mechanism will be slower than a nucleation and growth mechanism whose rate need not vanish at the limit. Thus the expected change of mechanism will not be observed at the spinodal in solids for two reasons:

(1) Elastic energy will change the criterion for the limit of metastability.

(2) The rate of the spinodal mechanism is initially too slow to compete with a nucleation and growth mechanism.

These two factors are most serious near the critical temperature, and spinodal decomposition should not be observed there. At lower temperatures the spinodal curve is not sufficiently well known to permit a clear test of the shift, except when the predicted shift is very large as it is in the Au–Ni system. In fact nothing which could possibly be interpreted as spinodal decomposition has been reported at high temperatures for Au–Ni. Even for Al–Zn it

has been reported that the solid solution undercools by about 10°C in the vicinity of the critical temperature.[10] Presumably at only 10°C undercooling it decomposes by a nucleation and growth mechanism.

How does one experimentally distinguish between a spinodal and a nucleation and growth mechanism? For much of the decomposition attributed to the spinodal it has been possible to show that it was clearly nucleation and growth since decomposition started at a few nucleation centers and spread from there.[11] The problem is much more subtle when there is apparently easy and copious volume nucleation, especially to phases intermediate in composition. True spinodal decomposition should possess the following properties.

(1) It should occur everywhere within a sample, except that near a structural imperfection the rate or mechanism may be different.

(2) The amplitude of composition fluctuations should grow continuously until a metastable equilibrium is reached with a preferential amplification of certain wavelength components. The investigations on spinodal decomposition[3–5] in systems in which side bands appear, have shown these criteria are satisfied. Whether there are other mechanisms which give rise to similar behaviour but which do not rely on instability to infinitesimal composition fluctuations remains to be seen.

ACKNOWLEDGMENTS

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