Chapter 12

Spinodal Decomposition

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The first intimation of what is now regarded as a structure possibly produced by spinodal decomposition came in the early 1940's. At that time Bradley was reported (1) to have observed sidebands (or satellites) around the Bragg peaks of the x-ray diffraction pattern from a Cu–Ni–Fe alloy that had been quenched and then annealed inside the miscibility gap. Further observations on the same alloy were made by Daniel and Lipson (2, 3), who demonstrated that the sidebands could be explained by a periodic modulation of composition in the ⟨100⟩ directions. From the spacing of the sidebands they were able to determine the wavelength of the modulation, which was of the order of 100 Å.

The growth of a composition modulation in an initially homogeneous alloy implies uphill diffusion or, equivalently, a negative diffusion coefficient. Becker (4) and Dehlinger (5) had already predicted a negative diffusivity inside the spinodal region of a binary system. But their treatments could not account for the growth of a modulation of a particular wavelength, such as was observed in the Cu-Ni-Fe alloy. And, in fact, as we will see later, any model based on Fick's law yields a physically unacceptable solution when the diffusion coefficient is negative.

The first explanation of the periodicity was given by Hillert (6, 7). Starting with a regular solution model, he derived a flux equation for one-dimensional diffusion on a discrete lattice. This equation differed from the usual one by the inclusion of a term that allowed for the effect on the driving force of the interfacial energy between adjacent atomic planes that differed in composition. Hillert solved the flux equation numerically and found that inside the spinodal it yielded a periodic variation of composition with distance. Furthermore, the wavelength of the modulation was of the same order as that observed in the Cu-Ni-Fe alloys. A more flexible continuum model was subsequently developed by Cahn (8, 9) (who, incidentally, was apparently the first to use the term "spinodal decomposition"). In addition to using an interfacial

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Table I. List of Symbols

A	Cross-sectional area of system
$A(\beta,t)$	Amplitude of Fourier component of wavenumber β at time t
B	Function of wavenumber defined by Eq 55
$\tilde{D}$	Interdiffusion coefficient
D_i^*	Tracer diffusivity for component i
$\tilde{D}_i$	Effective interdiffusivity defined by Eq 97
F	Integral molar Helmholtz free energy
F_T	Integral Helmholtz free energy of specimen
F_i^E	Excess partial molar Helmholtz free energy of component i
G	Integral molar Gibbs free energy
J_i	Flux of component i
K	Gradient-energy coefficient
M	Mobility
N_v	Number of atoms per unit volume
P	Pressure
$R(\beta)$	Amplification factor for Fourier component of wavenumber β
S	Integral molar entropy
S_i^E	Excess partial molar entropy of component i
T	Temperature (°K)
T_c^0	Homogenizing temperature (°K)
T_s	Temperature on the chemical spinodal (°K)
T_c	Temperature on the coherent spinodal (°K)
V	Molar volume
Y	Function of the elastic constants defined by Eq 36
a	Lattice parameter
c	Atomic fraction of component 2
c_e	Equilibrium composition
c_0	Average composition
c_s	Composition on the spinodal
c_{ij}	Elastic constants
d	Interplanar spacing
f	Helmholtz free energy per unit volume
f''	$\equiv \partial^2 f/\partial c^2$
k	Boltzmann's constant
l,m,n	Direction cosines
s	Entropy per unit volume or diffraction vector
t	Time
x,y,z	Spatial coordinates
β	Wavenumber ($= 2\pi/\lambda$)
β_c	Critical wavenumber ($= 2\pi/\lambda_c$)
β_m	Wavenumber of Fourier component receiving maximum amplification ($=2\pi/\lambda_m$)
ε	Strain
η_i	$\equiv (\partial \ln a/\partial c)_0$
λ	Wavelength ($= 2\pi/\beta$)
λ_c	Critical wavelength ($=2\pi/\beta_c$)
λ_m	Wavelength of Fourier component receiving maximum amplification ($=2\pi/\beta_m$)
μ_i	Chemical potential of component i per atom
σ	Stress
ω	Interaction energy per unit volume of a regular solution

energy term, Cahn also introduced a term for the effect of coherenc strains. The latter term is important because it determines the morph ology of the decomposition in elastically anisotropic materials. Also, i is because of coherency strains that spinodal decomposition does no occur in certain systems where it would otherwise be expected.

Spinodal decomposition is of interest on two counts. First, it is on of the few solid-state transformations for which there is any plausibl quantitative theory. The reason for this is the inherent simplicity of th reaction. It can be treated purely as a diffusional problem and, moreover many of the characteristics of the decomposition can be described b an approximate analytic solution to the diffusion equation. In contrast theories for nucleation and growth have to invoke the thermodynamic of fluctuations, and the diffusional problem involved in the growth o the nucleus is far more difficult to solve because it is unrealistic t linearize the diffusion equation. Second, from the practical viewpoin spinodal decomposition is of interest because it affords a means o producing a very finely dispersed structure that can enhance th properties of a material.

In the review that follows of the theoretical and experimental worl on spinodal decomposition, primary emphasis has been placed on th basic elements developed by Cahn in his first two papers (8, 9) on th subject. Derivations of the important expressions are given in full, o the premise that it is easier for a reader to skip a step than it is fo another to bridge the algebraic gap between "it is easily shown that' and the ensuing equation. The presentation of the theory is based o experience gained in teaching this material several times in a graduat course at Northwestern University. In some cases the derivations diffe from those originally given by Cahn, but the principals involved an the results are, of course, identical. Later developments are dealt wit more briefly and discussion of certain peripheral topics, such as strength ening due to spinodal decomposition, is omitted entirely. Also, where possible, duplication is avoided of material (historical aspects, fo example) covered by Cahn in his excellent 1967 Institute of Metals Lecture (10). A list of symbols is given in Table I.

Theory

Definition of the Spinodal for a Binary System

Consider a system containing a simple miscibility gap as shown in Fig. 1. At any temperature inside the gap, say T_0, we can expect that the free energy of an undecomposed solid solution will vary with composi-

tion as depicted by the top curve. The points of common tangency to this curve define, of course, the composition of the coexisting phases at T_0. In addition, there are two inflection points at which

$$f'' = 0 \qquad (1)$$

where $f'' \equiv (\partial^2 f/\partial c^2)_{T,V}$, f being the Helmholtz free energy, c the atomic fraction of the second component, and V the volume*. The locus of points satisfying this equation is the spinodal and is depicted by the dashed curve on the phase diagram (Fig. 1). Inside the spinodal, f'' is negative, and outside it is positive. For solid solutions an additional term, which will be considered later, has to be added to Eq 1 to allow for the effect of coherency strains.

It is apparent that the spinodal is usually associated with a positive deviation from ideality. In addition to miscibility-gap systems, a spinodal can occur in other systems, such as a eutectic in which there is a two-phase region. However, in order to ensure a continuous free-energy

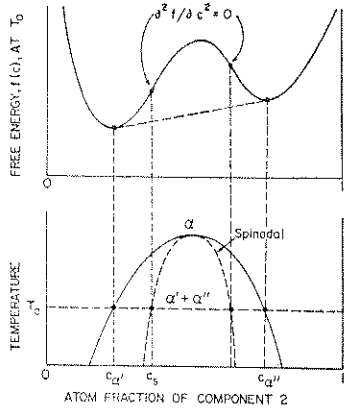

Fig. 1. The chemical spinodal is defined by the locus of temperatures (such as T_0*) on the phase diagram at which* $(\partial^2 f/\partial c^2) = 0$*. Inside the spinodal* $(\partial^2 f/\partial c^2)$ *is negative and outside it is positive.*

* Normally the spinodal is defined in terms of $(\partial^2 g/\partial c^2)_{T,P}$, where g is the Gibbs free energy. Cahn's use of f is a carry-over from a treatment (11) of nucleation where it is essential to use f (or the PV potential). This is because the work of nucleation is *not* given by the change in the Gibbs free energy, since the pressure is not constant throughout the system after nucleation. With one exception, we will be considering condensed systems at atmospheric pressure. In this case the difference between f and g is negligible and can be ignored.

function from one phase to another, the coexisting phases must either have the same crystal structure or there must exist a metastable phase of the same structure as one of the equilibrium phases.

The physical significance of the spinodal is that it is the boundary between the unstable and metastable parts of a two-phase region. This can be demonstrated by determining the sign of the change in free energy for a small composition fluctuation. Since the derivation that follows is valid for a change in any extensive property, we will use the general symbol X in place of f.

Let us suppose that the property X has the composition dependence shown in Fig. 2. We wish to determine the change ΔX in X for the system when one mole of composition c' is formed from a solution of composition c_0. It will be assumed that the amount of solution is large enough for its compositional change to be negligible. At first sight it might appear that ΔX is given by $X(c') - X(c_0)$. But this would be true only for an open system in which material could be exchanged with an external source. For a closed system we have to allow for the change in X due to exchange of material with the solution. We therefore have to work in terms of the partial molar properties $\bar{X}_1$ and $\bar{X}_2$ of the two

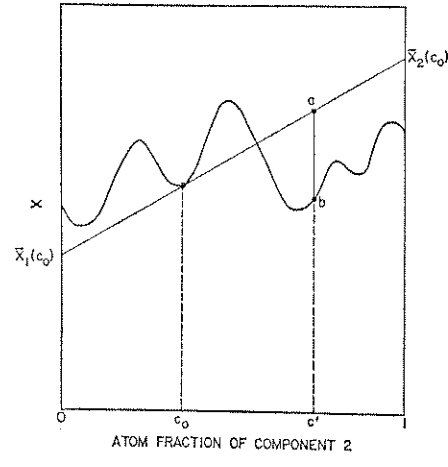

Fig. 2. The change ΔX *in an extensive molar property* X *accompanying the formation of 1 mole of solution of composition* c' *from an infinite reservoir of composition* c_0 *is given by the distance* ab*. If, as shown, point* b *lies below the tangent,* ΔX *is negative.*

components. The change in X for the transfer of c' mole of component 2 from material of composition c_0 to that of c' is $[\bar{X}_2(c') - \bar{X}_2(c_0)]c'$. Allowing for the analogous change for the transfer of component 1, we obtain

$$\Delta X = [\bar{X}_2(c') - \bar{X}_2(c_0)]c' + [\bar{X}_1(c') - \bar{X}_1(c_0)](1 - c')$$

This can be rewritten as

$$\begin{aligned}\Delta X &= c'\bar{X}_2(c') + (1-c')\bar{X}_1(c') - c_0\bar{X}_2(c_0) - (1-c_0)\bar{X}_1(c_0) \\ &\quad + (c_0 - c')[\bar{X}_2(c_0) - \bar{X}_1(c_0)] \\ &= X(c') - X(c_0) - (c' - c_0)(dX/dc)_{c_0}\end{aligned} \tag{2}$$

From this equation it is apparent that ΔX is numerically equal to the distance ab in Fig. 2 and is negative if the curve at c' lies below the tangent.

The result given by Eq 2 holds for any value of $(c' - c_0)$. Let us now consider the special case of an infinitesimal fluctuation $\delta c = (c' - c_0)$ from the initial composition. Expanding X in a Taylor's series about c_0, we obtain:

$$X(c') = X(c_0) + \delta c X'(c_0) + (1/2)(\delta c)^2 X''(c_0) + \ldots$$

in which primes on the X's denote derivatives with respect to c. Substituting in Eq 2 we obtain

$$\Delta X = (1/2)(\delta c)^2 X''(c_0) + \ldots$$

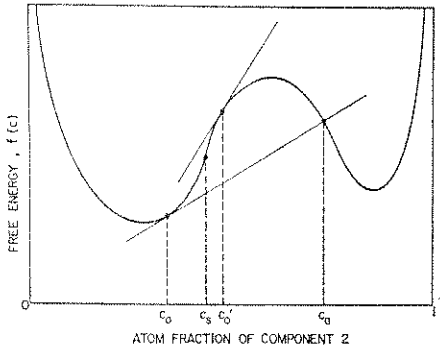

Fig. 3. Following the construction shown in Fig. 2, any fluctuation, no matter how small, from an initial composition (say c_0') lying inside the spinodal decreases the free energy. However, for an initial composition (c_0) lying outside the spinodal, the composition of the fluctuation has to exceed c_s for there to be a decrease in the free energy.

or, if X is the Helmholtz free energy f

$$\Delta f = (1/2)(\delta c)^2 f''(c_0) + \ldots \tag{3}$$

Thus, as shown in Fig. 3, if the initial composition c_0 lies outside the spinodal $[f''(c_0) > 0]$, an infinitesimal fluctuation increases the free energy and the system is therefore metastable. However, inside the spinodal $[f''(c_0) < 0]$ any fluctuation, no matter how small in degree, decreases the free energy and the system is unstable. An apt mechanical analog of these two cases has been given by Cahn (10).

Since there is no thermodynamic barrier inside the spinodal, the decomposition is determined solely by diffusion.

Classical Diffusion Equation

We will first derive the customary diffusion equation in terms of the mobility and free-energy gradient and then show why this has to be modified for diffusion inside the spinodal (or, for that matter, outside the spinodal if diffusion is occurring over very short distances). For mathematical simplicity we will throughout restrict the treatment to one-dimensional diffusion. This limitation is justified because in the early stages of spinodal decomposition (which will be our primary concern) there is no interaction between composition modulations in different directions.

As a starting point we assume that in a binary system the fluxes, J_1 and J_2, of the components are proportional to the gradient in chemical potentials with respect to some fixed reference plane. Thus

$$J_1 = -N_V(1 - c)v_1(\partial\mu_1/\partial x) \tag{4}$$

and

$$J_2 = -N_V c v_2(\partial\mu_2/\partial x) \tag{5}$$

in which the v's are the atomic velocities under a unit potential gradient, the μ's are the chemical potentials per atom and N_V is the number of atoms per unit volume. With respect to a moving reference plane for which the total flux is zero (the Matano interface), the flux of component 2 is

$$J = J_2 - c(J_1 + J_2) = -N_V c(1 - c)[v_2(\partial\mu_2/\partial x) - v_1(\partial\mu_1/\partial x)] \tag{6}$$

For reasons that will be apparent in the next step, we will rewrite this in the form

$$\begin{aligned}J = -N_V c(1 - c)\{&[(1 - c)v_2 + cv_1][(\partial\mu_2/\partial x) - (\partial\mu_1/\partial x)] \\ &+ (v_2 - v_1)[c(\partial\mu_2/\partial x) + (1 - c)(\partial\mu_1/\partial x)]\}\end{aligned} \tag{7}$$

The last term of Eq 7 in square brackets is zero because of the Gibbs–Duhem relationship,

$$(1 - c)\partial\mu_1 + c\partial\mu_2 = 0$$

Equation 7 thus reduces to

$$J = -N_V M[(\partial\mu_2/\partial x) - (\partial\mu_1/\partial x)] \tag{8}$$

where M is a mobility* defined by

$$M \equiv c(1 - c)[(1 - c)v_2 + cv_1] \tag{9}$$

Since

$$N_V(\mu_2 - \mu_1) = df/dc$$

(the factor of N_V appears because the μ's are the chemical potentials per atom while f is the free energy per unit volume), the flux equation can be written

$$J = -M(d/dx)(df/dc) \tag{10}$$

For a system in equilibrium, the chemical potentials, and hence their difference, are constant throughout the system. Thus Eq 10 satisfies the physical requirement that the net flux should go to zero as equilibrium is approached. For the time dependence of the composition we obtain on differentiating Eq 10 (assuming M and f'' to be constants)

$$\partial c/\partial t = -(1/N_V)(\partial J/\partial x) = (M/N_V)f''(\partial^2 c/\partial x^2) \tag{11}$$

in which the factor of N_V reappears because the derivative has to be taken with respect to the concentration (in atoms per unit volume) of component 2. Comparing Eq 11 with the usual statement of Fick's second law

$$\partial c/\partial t = \tilde{D}(\partial^2 c/\partial x^2) \tag{12}$$

it is seen that the mobility is related to the interdiffusion coefficient by

$$M = \tilde{D}N_V/f'' \tag{13}$$

It follows from the solution to be derived later for a more general equation that a particular solution to Eq 12 is

$$c - c_0 = A(\beta, t) \exp(i\beta x) \tag{14}$$

in which c_0 is the average composition and $A(\beta,t)$ is the amplitude of

* Some authors [for example, Hillert (6, 7)] exclude the factor of $c(1 - c)$ in the definition of M. We are following Cahn's usage here.

the Fourier component of wavenumber β at time t ($\beta = 2\pi/\lambda$, where λ is the wavelength). In terms of the initial amplitude at time zero

$$A(\beta, t) = A(\beta, 0) \exp[R(\beta)t] \tag{15}$$

where $R(\beta)$ is an "amplification factor" given by

$$R(\beta) = -(M/N_V)\beta^2 f'' \tag{16}$$

All sums of solutions of the form of Eq 14 are also solutions to Eq 10 and the Fourier components behave independently of one another. This is a consequence of the linearization of Eq 10 and is not true unless M and f'' are assumed to be independent of c.

Let us now examine the properties of the solution. Since M is inherently positive (10), the sign of $R(\beta)$ is determined by that of f''. In a one-phase region or metastable part of a two-phase region of the phase diagram, $f'' > 0$. Thus $R(\beta) < 0$ and Eq 15 predicts that any existing composition fluctuations will decay out. This is to be expected in the one-phase region, since the equilibrium state is a homogeneous solid solution. It is also the result we should expect for the metastable region because, in deriving the flux equation, no provision was made for thermal fluctuations. The equation cannot, therefore, predict nucleation.

Inside the spinodal $f'' < 0$ and $R(\beta) > 0$ for all values of β. Therefore,

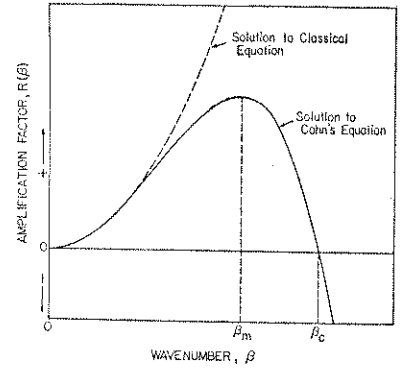

Fig. 4. Dependence of the amplification factor on wavenumber. Dashed curve is solution (Eq 15 and 16) to the classical diffusion equation (Eq 11). Full curve is solution (Eq 51 and 52) to Cahn's equation (Eq 46). The wavenumber receiving maximum amplification is β_m, and β_c is the critical wavenumber.

according to Eq 15 any modulation will grow. The dependence of $R(\beta)$ on wavenumber β or wavelength λ ($=2\pi/\beta$) is shown schematically by the dashed curves in Fig. 4 and 5. The amplification factor (and thus the growth rate) approaches infinity as $\lambda \to 0$ (or $\beta \to \infty$). This result holds, of course, only for a continuum. For a bcc lattice it can be shown (12) that the fastest growing modulation in the ⟨100⟩ will have a wavelength equal to the lattice parameter. This will lead to the formation of an $ABAB\ldots$ type of structure associated with an ordering reaction. But this is in conflict with experimental facts since the observed wavelengths in the Cu-Ni-Fe alloys were of the order of 100 Å. We must therefore conclude that Eq 11 is not applicable inside the spinodal.

Modified Diffusion Equation

As we have seen, when $f'' < 0$ (or, equivalently, with a negative interdiffusion coefficient) the classical diffusion equation yields a $1/\lambda^2$ dependence for the amplification factor. This is merely the familiar $(Dt)^{1/2}$ law in another form. If we are to account for the experimental results inside the spinodal, we require an additional term in the diffusion equation that inhibits the growth of very short wavelength modulations. The nature of this term is not difficult to see. The composition variation between the maxima and minima of the modulations is comparable with a diffuse interface between two phases, and we know that there is an excess free energy associated with such an interface. Since this "interfacial" energy is positive it will decrease the driving force available for diffusion and, the shorter the wavelength, the greater will be the decrease. This was not allowed for in deriving the classical equation since it was

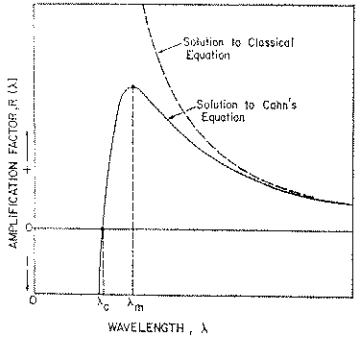

Fig. 5. Same curve as in Fig. 4 but plotted versus wavelength λ ($= 2\pi/\beta$) instead of the wavenumber β

tacitly assumed that the driving force was independent of wavelength.

In order to estimate quantitatively the interfacial term, Cahn (8) utilized a treatment (13) that assumed that the free energy of a nonhomogeneous system could be expressed by a multivariable Taylor's expansion:

$$f(y,z,\ldots) = y(\partial f/\partial y) + z(\partial f/\partial z) + \ldots + (1/2)[y^2(\partial^2 f/\partial y^2) + z^2(\partial^2 f/\partial z^2) + 2yz(\partial^2 f/\partial y \partial z) + \ldots] + \ldots$$

in which the variables, y, z, ... are the spatial composition derivatives (dc/dx, d^2c/dx^2, etc). For the free energy of a small volume element containing a one-dimensional composition variation we thus have (neglecting third and high-order terms)

$$f = f(c) + L(dc/dx) + K_1(d^2c/dx^2) + K_2(dc/dx)^2 \qquad (17)$$

in which

$$L = \partial f/\partial(dc/dx)$$
$$K_1 = \partial f/\partial(d^2c/dx^2)$$
$$K_2 = (1/2)\partial^2 f/\partial(dc/dx)^2$$

(evaluated at zero gradients) and $f(c)$ is the free energy that a volume element of composition c would have if it were homogeneous. [It would have been possible to include c as a variable in the expansion, but it is more convenient to use the function $f(c)$.] For crystals with a center of symmetry the free energy must be invariant with respect to a change in sign of the axis. Thus the coefficient L in Eq 17 must be zero. Integrating Eq 17 we obtain for the total free energy of the system of cross-sectional area A

$$F_T = A\int [f(c) + K_1(d^2c/dx^2) + K_2(dc/dx)^2]dx \qquad (18)$$

Integrating the second term by parts

$$\int K_1(d^2c/dx^2)dx = [K_1(dc/dx)]_S - \int (dK_1/dc)(dc/dx)^2 dx$$

Assuming that the system is homogeneous at the surface the first term on the right-hand side vanishes. (For a macroscopic system this term is negligible even if dc/dx is not zero at the surface.) We can therefore rewrite Eq 18 in the form:

$$F_T = A\int [f(c) + K(dc/dx)^2]dx \qquad (19)$$

where

$$K = K_2 - (dK_1/dc)$$

and is termed the "gradient-energy coefficient". Considering only

nearest-neighbor interactions and neglecting the effect of coherency strains, it has been shown (13) that

$$K = (2/3)h^M_{0.5} r_0^2 \tag{20}$$

in which $h^M_{0.5}$ is the heat of mixing per unit volume at $c = 0.5$ and r_0 is the nearest-neighbor distance. Since the presence of a spinodal is associated with a positive deviation from ideality, it follows that for such systems $K > 0$. (A negative K is in any case not allowable in a continuum model.) In the absence of coherency strains, K is a second-rank tensor and is thus isotropic in cubic crystals.

In deriving the classical flux equation, the potential for diffusion was found to be df/dc. We now have to determine the corresponding quantity when the free energy of the system is given by Eq 19. The potential has to satisfy two requirements. First, it must reduce to the classical one, df/dc, when the gradient-energy coefficient is set equal to zero. Secondly, at equilibrium the potential should be constant throughout the system. This second requirement suggests that we examine the condition for equilibrium in a nonhomogeneous system.

For a system in equilibrium the free energy will be a minimum, thus we have to determine the variation of c with x that minimizes the integral in Eq 19 subject to the condition that the average composition remains constant; that is,

$$\int (c - c_0)dx = 0 \tag{21}$$

It can be shown (for example, see reference 14) that for $y(x)$ to maximize or minimize the integral

$$\int P(x, y, y')dx$$

where $y' \equiv (dy/dx)$] subject to the constraint

$$\int Q(x, y, y')dx = \text{const}$$

it must satisfy the Euler equation

$$\frac{d}{dx}\left(\frac{\partial U}{\partial y'}\right) - \frac{\partial U}{\partial y} = 0 \tag{22}$$

where

$$U = P - \alpha Q$$

in which α is a Lagrangian multiplier.

With reference to our problem it is apparent that $y \equiv c$, $x \equiv x$, $y' \equiv (dc/dx)$ and $U \equiv f(c) + K(dc/dx)^2 - \alpha(c - c_0)$.

Substituting in Eq 22 we obtain as the condition for a stationary value (which it can be shown is, in fact, a minimum)

$$df/dc - 2K(d^2c/dx^2) = \alpha \tag{23}$$

This then is the differential equation that the composition dependence has to obey when the system is in equilibrium. The analogous equation for the classical case is:

$$df/dc = N_V(\mu_2 - \mu_1) = \text{const} \tag{24}$$

It is apparent that α, as defined by Eq 23, has the properties of the potential we are seeking. It reduces to the classical case, Eq 24, with a zero gradient-energy coefficient and it is constant throughout the system when it is in equilibrium.

Substituting α for (df/dc) in Eq 10 we obtain the modified flux equation

$$J = -M(d/dx)[(df/dc) - 2K(d^2c/dx^2)] \tag{25}$$

Performing the differentiation assuming K a constant we obtain

$$J = -M[f''(dc/dx) - 2K(d^3c/dx^3)] \tag{26}$$

Finally,

$$\begin{aligned} \partial c/\partial t &= -(1/N_V)(dJ/dx) \\ &= (M/N_V)[f''(d^2c/dx^2) - 2K(d^4c/dx^4)] \end{aligned} \tag{27}$$

in which we have assumed M and f'' to be independent of composition—assumptions that will in any case be necessary when we come to solve the equation. The implication of these assumptions will be discussed later.

It will be seen that Eq 27 differs from the classical Eq 11 by the inclusion of the term $-(M/N_V)[2K(d^4c/dx^4)]$. As will be shown when the solution to Eq 27 is obtained, it is this term that inhibits the growth of very short wavelength modulations. However, before solving the equation we will consider the correction that has to be applied for coherency strains.

Coherency Strain Energy

For most crystalline solid solutions there is a variation of lattice parameter with composition. If the lattice of such a solution is to remain coherent in the presence of a composition modulation, work has to be performed in straining the lattice. The maintenance of coherency thus affects the driving force for diffusion.

Consider a crystal (Fig. 6) containing a one-dimensional composition modulation along the x direction. The composition will be uniform

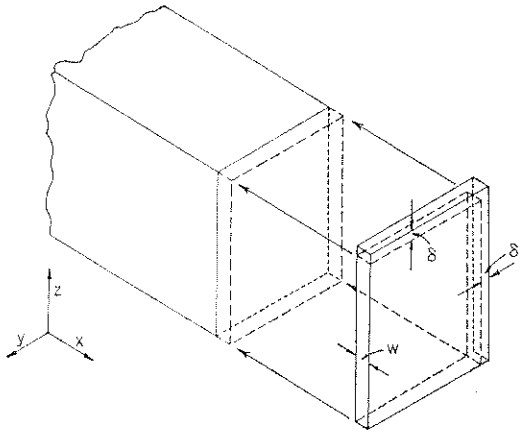

Fig. 6. A slice of material of lattice parameter a *has to be subjected to strains* $\delta = (a - a_0)/a_0$ *in the* z *and* y *directions if it is to be coherent with a section with unit edge lengths and with a lattice parameter* a_0 *in the zy plane. (Hilliard, reference 15)*

across any zy plane and we would therefore expect no variation of atom spacing within the plane. But, because of the composition variation in the x direction we might expect a variation of the spacing within a zy plane as it is moved along the x axis. However, it is the basic premise of Cahn's calculation (9) that no such variation is allowable if the lattice is to remain coherent.* The reasoning is as follows. Let us assume that there is a difference in the internal spacing between two adjacent zy planes. As we move from a region where there is an exact matching of atoms across the two planes, there will be an increasing relative displacement of the atoms. Eventually, this displacement will have reached half an atomic spacing. At this point, or before, coherency has been lost between the planes. We thus come back to the requirement that for a coherent lattice the lattice spacing in the plane of the modulation is independent of the location of the plane.

Starting from this premise we will calculate (15) the elastic strain energy for a cubic crystal. This will be done by estimating the work required to deform a slice of material so that it can be added coherently

* Strictly speaking, this condition holds only for a specimen of infinite cross-sectional area since the stress is relaxed at a free surface. However, an unpublished calculation by H. E. Cook has shown, as one would intuitively expect, that the effect of this relaxation is only significant if the lateral dimensions of the specimen are of the order of the wavelength of the composition modulation.

to an existing slab (Fig. 6) of unit cross-sectional area. As before, we will assume that the composition modulation is along the x' direction and, as indicated, a prime will be used to distinguish the reference axes from the standard axes of a cubic system (that is, along the ⟨100⟩). Let the lattice spacing in the plane of the slab be a_0 and that of the undeformed slice a. If the slice is to be coherent after addition to the slab it must be subjected to a strain of

$$\delta = (a - a_0)/a_0 \tag{28}$$

in the z' and y' directions. The straightforward method of calculating the work of deformation would be to evaluate the unknown stresses and strains resulting from this deformation. However, we would then be faced with the task of transforming three elastic constants from the primed to the standard axes; this is algebraically very messy. Instead, therefore, the work will be expressed in terms of the linear compressibility (which is independent of direction) and one direction-dependent elastic constant. In order to do this we will suppose that the deformation required to achieve coherency is accomplished in two steps. First, the slice is deformed hydrostatically to produce the required strains in the z' and y' directions. In the second step, the sides of the slice parallel to the x' direction are clamped and the stress in this direction is relaxed reversibly.

The linear compressibility (16) of a cubic system is $1/(c_{11} + 2c_{12})$, where the c's are the elastic constants. The stresses required to produce a hydrostatic strain of δ are therefore

$$\sigma_{x'} = \sigma_{y'} = \sigma_{z'} = \delta(c_{11} + 2c_{12}) \tag{29}$$

The elastic work per unit volume is given by

$$W_E = (1/2)\Sigma_i \sigma_i \varepsilon_i \tag{30}$$

where the ε_i are the strains. The work performed per unit volume of the slice during the first step is therefore

$$W_E(1) = (3/2)(c_{11} + 2c_{12})\delta^2 \tag{31}$$

During the second step in which the stress along x' is relaxed, the sides of the slice are clamped. Hence $\varepsilon_{z'} = \varepsilon_{y'} = 0$. Thus, the standard elastic equation

$$\sigma_{x'} = c_{1'1'}\varepsilon_{x'} + c_{1'2'}\varepsilon_{y'} + c_{1'3'}\varepsilon_{z'}$$

yields

$$\varepsilon_{x'} = \sigma_{x'}/c_{1'1'}$$

and thus

$$W_E(2) = \delta^2(c_{11} + 2c_{12})^2/2c_{1'1'} \tag{32}$$

after substitution from Eq 29. The net work performed on the slice in order to achieve coherency is

$$W_E = W_E(1) - W_E(2)$$

and, hence, from Eq 31 and 32

$$W_E = (\delta^2/2)(c_{11} + 2c_{12})\{3 - [(c_{11} + 2c_{12})/c_{1'1'}]\} \quad (33)$$

The final step is to express $c_{1'1'}$ in terms of the constants referred to the standard axes. Following the usual prescription for rotation of axes (see, for example, reference 17) we obtain

$$c_{1'1'} = c_{11} + 2(2c_{44} - c_{11} + c_{12})(l^2m^2 + m^2n^2 + l^2n^2) \quad (34)$$

in which l, m, n, are the direction cosines of the x' axis and, therefore of the direction of the composition modulation. Combining Eq 33 and 34 we obtain

$$W_E = Y\delta^2 \quad (35)$$

where

$$Y = (1/2)(c_{11} + 2c_{12}) \times \left[3 - \frac{c_{11} + 2c_{12}}{c_{11} + 2(2c_{44} - c_{11} + c_{12})(l^2m^2 + m^2n^2 + l^2n^2)}\right] \quad (36)$$

This is the expression given by Cahn (9). In its derivation we have tacitly assumed that the composition modulation does not produce any shear strains. Cahn considered this question and concluded that shear would be absent for modulations along ⟨100⟩, ⟨110⟩, ⟨111⟩ and that for other directions the effect of shear strains would be small. (An exact expression for Y is given in the Appendix.) It follows from Eq 35 that the total elastic strain energy of a slab of cross-sectional area A is

$$W_E = A\int Y\delta^2 dx \quad (37)$$

We next have to relate the strain δ to the composition variation. Let a_0 be the lattice parameter of the unstrained solid* of the average composition c_0. Then a Taylor's expansion about c_0 yields

$$a = a_0[1 + \eta(c - c_0) + \ldots]$$

in which

$$\eta = (1/a_0)(da/dc) = d\ln a/dc \quad (38)$$

* We are assuming at this point that the lattice spacing in the plane of the modulation will be that corresponding to the average composition c_0. This seems intuitively obvious and, in fact, it can be shown that it is the value which minimizes the total strain energy.

where the derivatives are evaluated at c_0. Thus, neglecting higher-order terms

$$\delta = (a - a_0)/a_0 = \eta(c - c_0) \quad (39)$$

Substituting this in Eq 37, we obtain

$$W_E = A\int \eta^2 Y(c - c_0)^2 dx \quad (40)$$

This simple result indicates that the strain energy of a modulation depends only on the amplitude and is independent of the wavelength. For a given amplitude the strain energy W_E is proportional to Y. We will now consider values of this quantity for various special cases.

For an isotropic material

$$2c_{44} - c_{11} + c_{12} = 0 \quad (41)$$

and Eq 36 reduces to

$$Y[\text{iso}] = c_{11} + c_{12} - 2(c_{12}^2/c_{11}) \quad (42)$$

This equation can also be written in terms of Young's modulus E and Poisson's ratio ν using the standard relationships

$$c_{11} = E(1 - \nu)/(1 - 2\nu)(1 + \nu)$$

and

$$c_{12} = E\nu/(1 - 2\nu)(1 + \nu)$$

Substituting in Eq 42 we obtain

$$Y[\text{iso}] = E/(1 - \nu) \quad (43)$$

For most metals the left-hand side of Eq 41 is positive. The elastic energy will thus be a minimum for those directions that minimize $(l^2m^2 + m^2n^2 + l^2n^2)$. By inspection these are seen to be ⟨100⟩. For this case

$$Y[100] = c_{11} + c_{12} - 2(c_{12}^2/c_{11}) \quad (44)$$

the same as for an isotropic material. At least one metal, molybdenum, has an anisotropy of opposite sign. In this case, the directions for minimum W_E will be those that maximize the directional cosine function. These directions are ⟨111⟩, and

$$Y[111] = 6c_{44}(c_{11} + 2c_{12})/(c_{11} + 2c_{12} + 4c_{44}) \quad (45)$$

As will be shown later, the growth rate of the modulations will be a maximum in the directions that minimize Y. These directions therefore determine the morphology of the decomposition in cubic solid solutions.

The calculation of the elastic strain energy that we have just considered is based on a continuum model and it must therefore break down as the wavelength of the modulation approaches the atomic spacing. Recently, Cook and de Fontaine (18) have derived the elastic energy of a composition modulation in a Bravais lattice and their results are applicable to modulations of all wavelengths. They find that the elastic energy is dependent on the wavelength as well as the direction of the modulation (whereas, in the continuum model it is independent of wavelength). Furthermore, a macroscopically isotropic crystal is anisotropic on an atomic scale. These results are illustrated by a plot (Fig. 7) they made of Y in reciprocal space for the h_1h_20 section of the first Brillouin zone of a bcc crystal. The values used for the elastic moduli were $c_{11} = 4$, $c_{12} = 2$ and $c_{44} = 1$ (in arbitrary units) which satisfy the condition, Eq 41, for isotropy in the continuum model. It will be seen from Fig. 7 that at the origin (for an infinite wavelength) $Y = 4$ which, as one would expect, is the value given by Eq 42 for the continuum model. There is a saddle point at the origin; Y increases along ⟨110⟩ and decreases along ⟨100⟩, becoming zero at the 100 superlattice positions.

Cook and de Fontaine pointed out that it is possible, within the framework of the continuum model, to make a first-order correction for the wavelength dependence of Y by using an expansion about the origin. Since the wavelengths of interest in spinodal decomposition are

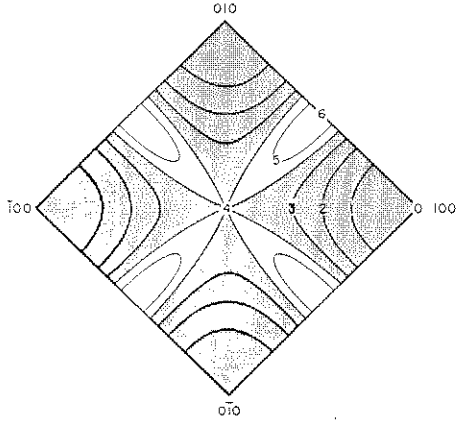

Fig. 7. Variation of the effective modulus Y *in the* h_1h_20 *section of the first Brillouin zone of a macroscopically isotropic bcc crystal (Cook and de Fontaine, reference 18)*

typically $10a$ to $20a$ (where a is the lattice parameter) this is a satisfactory approximation. The first term in the expansion is the value of Y given by the continuum calculation. The next term is proportional to the second derivative since the first derivative vanishes at the origin. The second term is algebraically of the same form as the chemical gradient energy term already introduced. The coefficient of the elastic gradient energy can therefore be incorporated into K. Unlike the chemical contribution, the elastic contribution to K is anisotropic even in cubic crystals. For the example shown in Fig. 7, it will be positive for wavevectors along ⟨110⟩ and negative for those along ⟨100⟩. This is another factor in addition to Y that may influence the morphology of the decomposition.

It now only remains to incorporate the elastic energy into the diffusion equation. It follows from Eq 19 and 40 that the free energy of a solution including the elastic energy is

$$F_T = A\int [f(c) + \eta^2 Y(c - c_0)^2 + K(dc/dx)^2]dx$$

Following the same steps to derive Eq 27 and assuming $\eta^2 Y$ to be independent of c, we obtain

$$\partial c/\partial t = (M/N\nu)\{[f'' + 2\eta^2 Y](d^2c/dx^2) - 2K(d^4c/dx^4)\} \quad (46)$$

which is the equation* given by Cahn. Using Eq 13 it can also be written in terms of $\tilde{D}$:

$$\partial c/\partial t = \tilde{D}\{[1 + (2\eta^2 Y/f'')](d^2c/dx^2) - (2K/f'')(d^4c/dx^4)\} \quad (47)$$

Solution of Diffusion Equation

If the coefficients of Eq 46 are assumed to be independent of c, it can be solved either by a separation of variables or by a Fourier transform method. We will use the latter since it is quicker. If $A(\beta)$ is the amplitude of a Fourier component of wavenumber β ($=2\pi/\lambda$, where λ is the wavelength) the spatial composition variation can be expressed by the Fourier integral

$$c - c_0 = \int A(\beta) \exp(i\beta x)d\beta \quad (48)$$

in which the coefficients are defined by the inverse relationship

$$A(\beta) = (1/2\pi)\int (c - c_0) \exp(-i\beta x)dx \quad (49)$$

* Apart from a factor of $N\nu$ which is missing from Cahn's equation; its absence is not noticed until a numerical calculation comes out in error by some 23 orders of magnitude.

Substituting Eq 48 in 46 and noting that

$$d^n c/dx^n = \int (i\beta)^n A(\beta) \exp(i\beta x) d\beta$$

we obtain on equating coefficients

$$dA(\beta)/dt = -(M/N_V)\{f'' + 2\eta^2 Y + 2K\beta^2\}\beta^2 A(\beta) \quad (50)$$

This is an ordinary differential equation that has the solution:

$$A(\beta, t) = A(\beta, 0) \exp[R(\beta)t] \quad (51)$$

in which $A(\beta, 0)$ is the initial amplitude of the Fourier component of wavenumber β and $R(\beta)$ is an amplification factor defined by

$$R(\beta) = -(M/N_V)\{f'' + 2\eta^2 Y + 2K\beta^2\}\beta^2 \quad (52)$$

or, in terms of $\tilde{D}$,

$$R(\beta) = -\tilde{D}\{1 + (2\eta^2 Y/f'') + (2K/f'')\beta^2\}\beta^2 \quad (53)$$

If the solid solution has undergone a perfect quench from the single-phase region into the spinodal, the initial amplitudes $A(\beta, 0)$ will be those of the thermal fluctuations that are in equilibrium at the quenching temperature T_q. These are given by (19, 20)

$$\langle A^2(\beta)\rangle = [kT_q/V_T(f'' + 2\eta^2 Y + 2K\beta^2)] \quad (54)$$

where V_T is the volume of the specimen. It will be seen that the amplitudes decrease monotonically with increasing β, but that the dependence is fairly weak. Usually, some decomposition will occur during the quench. In this case $A(\beta, 0)$ will be the spectrum at the end of the quench.

Comparing Eq 16 and 52 it will be seen that the amplification factor differs from that for the classical equation by terms in $2\eta^2 Y\beta^2/f''$ and $2K\beta^4/f''$. The first comes from the elastic strains and will be absent if the temperature is high enough for the strains to be relieved by plastic deformation. The second term involving the gradient energy becomes increasingly important with increasing β, that is, with decreasing wavelength, λ. For values of K normally encountered, the gradient term is significant only for $\lambda \gtrsim 100$ Å. Thus, as has been shown by experience, the classical equation is satisfactory for the interpretation of the usual diffusion measurements, since these are made at high temperatures with micron or greater penetration distances.

As was the case with the calculation of the elastic strain energy, we must expect that Eq 46 will break down at large wavenumbers because of the continuum approximation. This limitation has recently been eliminated by the derivation (12) of an analogous equation for a discrete lattice. For diffusion along ⟨100⟩ or ⟨110⟩ in bcc or along ⟨100⟩ or ⟨111⟩ in fcc, the solution to the discrete equation is given by Eq 51 and 52 if β^2 is replaced by the function

$$B^2 = (2/d^2)[1 - \cos(\beta d)] \quad (55)$$

in which d is the interplanar spacing. Expanding the cosine term we obtain

$$B^2 = \beta^2[1 - (\beta^2 d^2/12) + \ldots] \quad (56)$$

The fractional error in using the continuum approximation is therefore approximately $(\beta^2 d^2/12)$. As previously noted, the wavelengths of interest in spinodal decomposition are typically greater than $10a \approx 20d$. For this wavelength, $(\beta^2 d^2/12) = 0.8\%$, so that the error in using the continuum approximation is negligible.

The Early Stages of Spinodal Decomposition

We have just demonstrated that the continuum approximation will be a satisfactory one in the treatment of spinodal decomposition. Let us now consider the effect of the other approximations that have been introduced.

In deriving and solving the diffusion equation it was assumed that K, $\eta^2 Y$, M and f'' were independent of composition. These assumptions can be eliminated from the derivation of the equation—it is merely a matter of carrying along the higher derivatives. However, the equation cannot be solved analytically unless it is linearized. There is theoretical (13) and experimental (21) evidence that to a first approximation K is

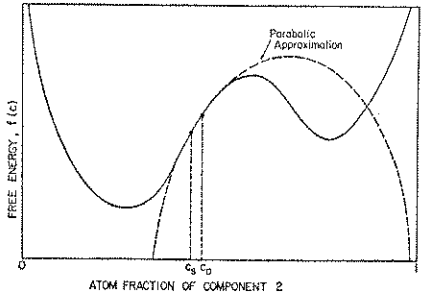

Fig. 8. The assumption that $(\partial^2 f/\partial c^2)$ is independent of composition is equivalent to fitting the free-energy function (full curve) by a parabola (dashed curve)

independent of composition. But the assumption that the other coefficients are constant is not very satisfactory, and it is particularly bad for f''. As shown in Fig. 8, the use of a constant f'' is equivalent to fitting the free-energy curve by a parabola. It is apparent that this approximation becomes progressively worse as the average composition c_0 approaches that, c_s, of the spinodal. Because of the linearization of the diffusion equation, the solution is only valid for small composition amplitudes—for the early stages of the decomposition. However, this limitation is not as severe as it might seem since the most important characteristic of the transformation, namely the morphology, is established in the early stages and thereafter changes only slowly with time.

Let us now examine the properties of the solution to the diffusion equation inside the spinodal. It will be seen from Eq 51 that in order for growth of a component to occur, the amplification factor $R(\beta)$ has to be positive. Since M in Eq 52 is inherently positive, $R(\beta)$ is positive if

$$f'' + 2\eta^2 Y + 2K\beta^2 \leq 0 \tag{57}$$

For a system with a spinodal, K is expected to be positive. The inequality 57 can thus be satisfied only in the region for which

$$f'' + 2\eta^2 Y \leq 0 \tag{58}$$

This expression, taken as an equality, defines the *coherent* spinodal (as distinguished from the *chemical* spinodal defined by Eq 1). Since Y is a function of direction in a crystalline material, it follows that the coherent spinodal temperature will also vary with the direction of the wavevector. The temperature will be a maximum for those directions that minimize $2\eta^2 Y$.

The difference between the temperature T_s of the chemical and that T_s^* of the coherent spinodal can be estimated by expanding f'' about T_s and substituting in Eq 58. Noting that $f'' = 0$ at T_s, we obtain

$$T_s^* - T_s \approx -2\eta^2 Y/(\partial f''/\partial T)_{T_s} \approx 2\eta^2 Y/s'' \tag{59}$$

in which $s'' = (\partial^2 s/\partial c^2)$ where s is the entropy per unit volume. Equation 59 is a good approximation because the entropy of mixing is only weakly temperature dependent. Since we can expect* $s'' < 0$, Eq 59 indicates that $T_s^* < T_s$, thus the coherent spinodal lies inside the chemical spinodal. The coherency strains therefore tend to stabilize the solid

* The condition $s'' < 0$ is not required thermodynamically. However, the only exceptions found in the examination by the author of the data compiled for many systems by Hultgren, Orr, Anderson and Kelley (22) were for systems exhibiting a tendency to ordering—systems having a negative deviation from ideality.

solution. If the entropy of mixing is assumed to be ideal, then

$$s'' = -Nvk/c(1 - c) \tag{60}$$

and Eq 59 becomes

$$T_s^* - T_s \approx -2\eta^2 Yc(1 - c)/kNv \tag{61}$$

Variations in the depression of the spinodal in different systems are determined primarily by η because this has a much larger possible variation than does Y. For systems, such as Al–Zn, where there is only a small variation of lattice parameter with composition, the difference between the two spinodals is only a few degrees, whereas in others, such as Au–Ni, it is several hundred degrees.

For any particular temperature and composition within the spinodal there will be a critical wavenumber β_c (and a corresponding wavelength, $\lambda_c = 2\pi/\beta_c$) satisfying

$$f'' + 2\eta^2 Y + 2K\beta_c^2 = 0 \tag{62}$$

for which $R(\beta)$ is zero. Fourier components for which $\beta < \beta_c$ will grow. Existing components with $\beta > \beta_c$ will decay. It follows from Eq 58 and 62 that the coherent spinodal corresponds to the locus of $\beta_c = 0$.

It is convenient to rewrite Eq 52 in terms of β_c. Substituting from Eq 62 we obtain

$$R(\beta) = (2KM/Nv)(\beta_c^2 - \beta^2)\beta^2 \tag{63}$$

This function is shown by the full curve in Fig. 4. There is a maximum at

$$\beta_m = \beta_c/\sqrt{2} \tag{64}$$

(found by equating the derivative of Eq 63 to zero). The variation of the amplification factor on β or, as is more easily visualized, on λ (full curve, Fig. 5) is easily explained physically. Starting from a long wavelength, $R(\lambda)$ increases as $1/\lambda^2$ because of the decrease in diffusion distance. In this region the classical diffusion equation (dashed curve) is a satisfactory approximation. But, with decreasing wavelength, the composition gradients increase and more energy is tied up in the incipient interfaces. This reduces the driving force and eventually it more than offsets the reduction in diffusion distance and thus leads to a maximum in $R(\lambda)$ at λ_m. For $\lambda < \lambda_m$ the gradient effect dominates and $R(\lambda)$ eventually becomes negative.

Substituting from Eq 64 into 63 we obtain for the maximum value of $R(\beta)$:

$$R(\beta_m) = (2KM/Nv)\beta_m^4 \tag{65}$$

$$= (KM/2Nv)\beta_c^4 \tag{66}$$

Thus, $R(\beta_m)$ is strongly dependent on β_m. It follows from Eq 62 and 64 that

$$\beta_m^2 = -(f'' + 2\eta^2 Y)/4K \tag{67}$$

and, since

$$f''(T) \approx (T - T_s)(\partial f''/\partial T) = -(T - T_s)s'' \tag{68}$$

we have

$$\beta_m^2 \approx [(T - T_s)s'' - 2\eta^2 Y]/4K \tag{69}$$

where T_s is the temperature of the chemical spinodal. Since $s'' < 0$, it follows from Eq 69 that β_m increases with decreasing values of $2\eta^2 Y$. Thus, by Eq 65, $R(\beta_m)$ will be a maximum for wavevectors in the direction that minimize Y (assuming that the anisotropy in the elastic contribution to K does not predominate).

Combining Eq 59 and 69 we obtain for β_m^2 in terms of the temperature T_s^* of the coherent spinodal

$$\beta_m^2 \approx (T - T_s^*)s''/4K \tag{70}$$

from which it follows that β_m increases with decreasing temperature. Combining this result with Eq 65 we see that starting from zero at $T = T_s^*$, $R(\beta_m)$ initially increases with decreasing temperature. However, the increase in $R(\beta_m)$ will eventually be offset by the decrease in mobility. The isothermal-time-transformation curves for the decomposition will therefore be of the familiar C shape, as shown in Fig. 9.

The results for the early stages of the decomposition can be summarized as follows:

1 There will be one wavelength, λ_m, of the initial Fourier spectrum that will have the maximum growth rate. Any Fourier components having wavelengths less than a critical value λ_c (where $\lambda_c = \lambda_m/\sqrt{2}$) will decay.
2 λ_m (and therefore λ_c) decreases with: (*a*) decreasing temperature; (*b*) decreasing values of K; and (*c*) the shift of the average composition c_0 towards the center of the spinodal.
3 In cubic materials, preferential growth will occur along those directions (usually ⟨100⟩) that minimize the coherency strain energy.
4 The rate of decomposition is zero at the temperature of the spinodal and passes through a maximum with decreasing temperature.

Morphology of the Decomposition

As we have seen there exists a Fourier component of wavenumber β_m for which the amplification factor $R(\beta)$ is a maximum. Because of the exponential dependence (Eq. 51) of the amplitude on $R(\beta)$ we would expect that components with wavenumbers clustered about β_m would,

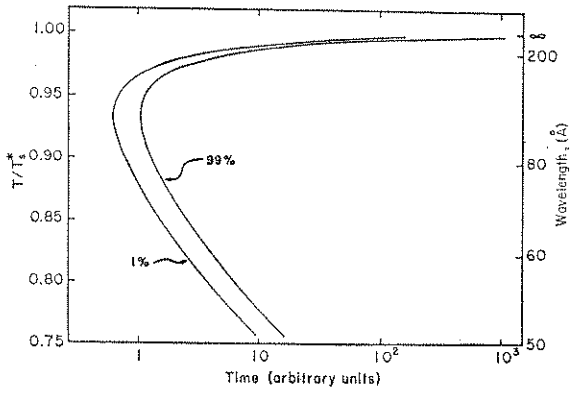

Fig. 9. Isothermal-transformation diagram for spinodal decomposition. The curves are for a hypothetical but not unrealistic set of parameters. The right-hand scale gives the characteristic wavelength corresponding to the reduced temperature on the left-hand scale. (Huston, Cahn and Hilliard, reference 20)

after a very short time, dominate the decomposition. In determining the structure produced by spinodal decomposition we shall assume that the composition variation can be described by sinusoidal modulations of a constant wavenumber β_m. (However, when reviewing the experimental results, we shall see that the Fourier spectrum never becomes as sharp as one would anticipate from the theory.)

Let us first consider decomposition in a material which is either isotropic or for which there is no significant elastic-energy contribution. In this case there will be no preferred directions for the Fourier components. These will therefore have random directions and phase angles. Cahn (23) has simulated this condition on a computer, using a Gaussian distribution for the amplitudes. Figure 10 shows the cross section of the structure (for $c_0 = 0.5$) resulting from the superposition of 100 random sine waves with the wavelength λ indicated at the bottom of the figure. The points in the plot depict regions where the composition is greater than c_0. In contrast to what is normally thought of as a "spinodal structure" the figure does not display a highly developed periodicity. This is because the components are random in direction.

From a study of a sequence of cross sections for different volume fractions of the two phases in the final structure Cahn demonstrated that connectivity of the phases is maintained over a very wide range of volume fractions (approximately 0.15 to 0.85). He suggested that this

factor (which has important technical consequences) was one which distinguished spinodal decomposition from nucleation and growth in an isotropic material. The latter reaction results in the formation of discrete particles that are likely to become interconnected only when the two phases have approximately the same volume fractions. However, Seward, Uhlmann and Turnbull (24) have shown that discrete particles can become interconnected by coalescence. They therefore claimed that interconnectivity (at least during the late stages of the transformation) is not proof of spinodal decomposition.*

We will next consider decomposition in cubic materials, where there is a significant contribution from the elastic strain energy. In Cahn's treatment the only anisotropic term in the solution of the diffusion equation was Y. But since then, as we have seen, the results of Cook and de Fontaine (18) indicate that there is a strain contribution that renders the gradient-energy coefficient anisotropic. However, the effect of this on the morphology has not yet been fully explored and we will therefore have to neglect it or, at least, assume that the anisotropy in Y is the dominant factor.

Let us first treat the most common case in which the ⟨100⟩ are the

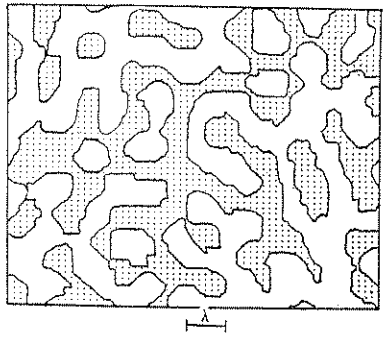

Fig. 10. Cross section of a spinodal structure in an isotropic material simulated by Cahn (23) on the computer by adding 100 random sine waves of wavelength λ. The points define regions where the concentration is greater than the average. Note the high degree of connectivity and the absence of regular periodicity.

*** Note added in proof:** However, J. W. Cahn in a private communication has pointed out that if the mobility is strongly composition dependent (as is the case for the $BaO\text{-}SiO_2$ system studied by Seward, Uhlmann and Turnbull) one would expect the formation of a discontinuous structure in the early stages of spinodal decomposition. The observations on $BaO\text{-}SiO_2$ are not therefore inconsistent with a spinodal mechanism.

preferred directions of growth because of the minimum in Y. The structure will then be given by the superposition of composition modulations whose wavefronts are parallel to the three equivalent {100} planes. Assuming, as in the isotropic case, that the modulations are sinusoidal and are of equal amplitude A and wavelength λ, the composition at a point defined by the Cartesian coordinates (x, y, z) referred to axes along ⟨100⟩ is

$$c - c_0 = A[\sin(2\pi x/\lambda) + \sin(2\pi y/\lambda) + \sin(2\pi z/\lambda)] \qquad (71)$$

By inspection it is seen that maxima occur at

$$x = \lambda[(1/4) + p],\ y = \lambda[(1/4) + q],\ z = \lambda[(1/4) + r]$$

where p, q and r are integers. The minima are at

$$x = \lambda[(3/4) + p],\ y = \lambda[(3/4) + q],\ z = \lambda[(3/4) + r]$$

These points define a CsCl-type structure in which the maxima and minima lie at the sites of the two atoms in the structure. Expanding the sine terms in Eq 71 about the maxima in $(c - c_0)$ we find

$$c - c_0 = A[3 - (4\pi^2/\lambda^2)(x^2 + y^2 + z^2) + \ldots] \qquad (72)$$

for x, y and $z \ll \lambda$. The contour surfaces of equal composition will thus be spherical in the vicinity of the maxima. The same holds for the contours around the minima. The loci of points for which $c = c_0$ are those satisfying

$$\sin(2\pi x/\lambda) + \sin(2\pi y/\lambda) + \sin(2\pi z/\lambda) = 0 \qquad (73)$$

This defines the surfaces of a truncated octahedron (tetrakaidecahedron) around each maxima and minima. If the volume fractions of the phases are approximately equal, the final structure will consist of tetrakaidecahedral particles arrayed on a CsCl structure with a lattice parameter of λ. As the volume fraction of one of the phases is diminished it will appear as octahedral particles whose corners are aligned along ⟨100⟩ and which occupy a simple cubic lattice, again with a spacing of λ.

The case of decomposition along ⟨111⟩ is somewhat more complicated. There are now four equivalent habit planes: (111), $(\bar{1}11)$, $(1\bar{1}1)$ and $(11\bar{1})$. A change in phase of one of the modulations will cause a change in the form of the structure. (In the {100} case a phase change produces only a displacement of the structure.) Following Cahn (25) the structure developed by {111} modulations can be described as follows. A pair of the modulations, say $(1\bar{1}1)$ and $(\bar{1}11)$, will reinforce to produce a regular array of rods along [110]. The remaining two modulations produce a periodic variation along these rods. Altogether,