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John W. Cahn

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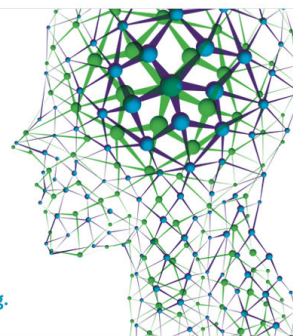
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Phase Separation by Spinodal Decomposition in Isotropic Systems

JOHN W. CAHN*

General Electric Research Laboratory, Schenectady, New York

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The theory of phase separation from a single phase fluid by a spinodal mechanism is given. The predicted structure may be described in terms of a superpositioning of sinusoidal composition modulations of a fixed wavelength, but random in amplitude, orientation, and phase. Sections through a calculated structure are shown. These show that the structure has many of the geometrical features found in phase separable glasses, in particular the high degree of connectivity among particles of each phase.

BY various thermal treatments, most commonly by cooling or heating, a stable single phase can be made unstable with respect to a mixture of two phases. The thermodynamics, kinetics, and resultant morphology of such phase separation have been widely investigated. In many cases it is found that the original phase has a considerable range of metastability; that is, it can exist for long times as a single phase.

In his classic treatment of heterogeneous equilibrium, Gibbs¹ derived a necessary condition for the stability or metastability of a fluid phase, namely, that the chemical potential of a component must increase with increasing density of that component. For two components this reduces to $(\partial^2 G / \partial c^2)_{T,P} > 0$. If this condition is not met, the solution is unstable with respect to continuous composition changes. The limit of metastability, that is, where $\partial^2 G / \partial c^2 = 0$, is called the spinodal.

In the metastable region on a phase diagram, which is between the spinodal and the phase boundary, a finite fluctuation is required to render the solution unstable. This fluctuation is called a nucleus, and the work of forming such a nucleus is a measure of the metastability of the phase. Theoretical calculations of this work of formation show that it approaches zero at the spinodal.²

If one wishes to study phase separation in the unstable region, one must carefully choose systems in which it is possible to bring a homogeneous solution through the metastable region without significant phase separation. Thus one should choose a system in which phase separation is slow compared with the time it takes to change the temperature of the sample. The speed of phase separation is related, among other things, to the diffusion coefficient, which is small for solids and viscous liquids, such as glass forming solutions. The rate of temperature change is high for metals and thin samples. Solid metallic solutions can be successfully quenched into the unstable region without any difficulty, often in large samples. The theory of phase separation of cubic solid solutions³ predicts that the

instability results in composition modulations in certain crystallographic directions, the directions being dictated by elastic anisotropy, and that the amplitude of the modulations changes with time but that, initially at least, the wavelength (or spacing between peaks in the modulations) remains constant. For a range of compositions that will give approximately equal volume fractions the two phases form an interconnected lattice-work aligned along the crystallographic direction. Such types of phase separation have in fact been observed⁴⁻⁶ and they differ distinctly from what one would expect in nucleation and growth.

For isotropic solid solutions or for fluid solutions the theory predicts similar modulations in composition.⁷ Because there are now no crystallographic limitations on direction, it becomes worthwhile to examine the geometrical aspects of the resultant two-phase morphology. In particular the connectivity of the two phases is of interest. We begin with the theory of spinodal decomposition.

THEORY

Consider an inhomogeneous solution whose composition everywhere differs only slightly from the average composition, and with small composition gradients. Its free energy is given by⁸

$$F = \int [f(c) + \kappa(\nabla c)^2] dV. \quad (1)$$

Here $f(c)$ is the free-energy density of homogeneous material of composition c , $\kappa(\nabla c)^2$ is the additional free-energy density if the material is in a gradient in composition. Let us assume that the molar volume is independent of composition. If we expand $f(c)$ about the average composition c_0 .

$$f(c) = f(c_0) + (c - c_0) \left(\frac{\partial f}{\partial c} \right) + \frac{1}{2} (c - c_0)^2 \left(\frac{\partial^2 f}{\partial c^2} \right) + \dots, \quad (2)$$

* Present address: Department of Metallurgy, MIT, Cambridge, Massachusetts.

¹ J. W. Gibbs, *Collected Works* (Yale University Press, New Haven, Connecticut, 1948), Vol. 1, pp. 105-115.

² J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **31**, 688 (1959).

³ J. W. Cahn, *Acta Met.* **10**, 179 (1962).

⁴ P. J. Tufon and R. B. Nicholson (to be published).

⁵ D. P. Seraphim, N. R. Stemple, and D. T. Novick, *J. Appl. Phys.* **33**, 136, 1962.

⁶ J. W. Cahn, *J. Appl. Phys.* **34**, 3581 (1963).

⁷ J. W. Cahn, *Acta Met.* **9**, 795 (1961).

⁸ J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).

and bear in mind that

$$\int (c - c_0) dV = 0, \quad (3)$$

we may express the free-energy difference between the initially homogeneous solution and the inhomogeneous solution as

$$\Delta F = \int \left[\frac{1}{2} \left(\frac{\partial^2 f}{\partial c^2} \right) (c - c_0)^2 + \kappa (\nabla c)^2 \right] dV, \quad (4)$$

We assume κ positive; κ negative would be another kind of instability. Then we see that the solution is stable to all infinitesimal fluctuations if $\partial^2 f / \partial c^2 > 0$. If on the other hand $\partial^2 f / \partial c^2$ is negative, the solution is unstable to such a fluctuation for which the first term dominates. By choosing a large enough distance scale, such a fluctuation can always be found.

In the development of the theory it becomes convenient to consider the Fourier components of the composition rather than the composition. Because of the orthogonality of the Fourier components, ΔF is the sum of contributions from each Fourier component separately. Consider one such component, $A \cos \beta x$. It contributes to ΔF the quantity

$$\frac{1}{4} V A^2 \left[\left(\partial^2 f / \partial c^2 \right) + 2\kappa \beta^2 \right]. \quad (5)$$

Thus Fourier components of sufficiently large wavelength, or sufficiently small wavenumber β , result in decreasing free energy if the solution is in the unstable region. The maximum wavenumber β_c is given by

$$\beta_c = \left(\frac{-\partial^2 f / \partial c^2}{2\kappa} \right)^{\frac{1}{2}}. \quad (6)$$

The kinetics of the initial stages of phase separation can be obtained by simply solving the diffusion equation. We define a mobility M which is (minus) the ratio of diffusional flux to the gradient in chemical potential

$$J_B = -J_A = M \nabla (\mu_A - \mu_B). \quad (7)$$

Simple thermodynamic considerations show that M must be positive if the diffusion which results spontaneously from the chemical potential gradient is to result in a decrease in free energy. We obtain $\mu_A - \mu_B$ from the variational derivative of F in Eq. (1),

$$\mu_A - \mu_B = (\delta F / \delta c_A) = (\partial f / \partial c_A) - 2\kappa \nabla^2 c_A$$

$$+ \text{terms higher in order and degree.} \quad (8)$$

We may discard the higher order terms if we are only interested in the initial stages. By substituting Eq. (8) into Eq. (7) and taking the divergence, and keeping only first degree terms, we obtain the following diffusion equation:

$$\partial c / \partial t = M \left(\partial^2 f / \partial c^2 \right) \nabla^2 c - 2M\kappa \nabla^4 c. \quad (9)$$

Since the coefficient of $\nabla^2 c$ may be identified with a diffusion coefficient we see that at the spinodal the diffusion coefficient changes sign. The solution to Eq.

(9) is

$$c - c_0 = \exp[R(\beta)t] \cos(\beta \cdot \mathbf{r}), \quad (10)$$

where $R(\beta)$ is given by

$$R(\beta) = -M \left(\partial^2 f / \partial c^2 \right) \beta^2 - 2M\kappa \beta^4, \quad (11)$$

and is, as expected, negative for all β in the metastable region and positive for $\beta < \beta_c$ in the unstable region.

Because the equation is homogeneous and linear in c , all sums of solutions are possible solutions:

$$c - c_0 = \sum_{\text{all } \beta} \exp[R(\beta)t] \times [A(\beta) \cos(\beta \cdot \mathbf{r}) + B(\beta) \sin(\beta \cdot \mathbf{r})]. \quad (12)$$

The A and B are to be evaluated at $t=0$ by Fourier analysing the fluctuations in the initial solution.

The amplification factor $R(\beta)$ is shown in Fig. 1 to have a rather sharp maximum at

$$\beta_m = \beta_c / \sqrt{2} = \frac{1}{2} \left[- \left(\partial^2 f / \partial c^2 \right) / \kappa \right]^{\frac{1}{2}}. \quad (13)$$

Because the amplitude of a sine wave at time t has $R(\beta)$ in an exponent, we can ignore all Fourier components but those which have a wavenumber β_m for which $R(\beta)$ is a maximum. Thus,

$$c - c_0 \cong \exp[R_m t] \sum_{\beta_m} [A(\beta) \cos(\beta \cdot \mathbf{r}) + B(\beta) \sin(\beta \cdot \mathbf{r})], \quad (14)$$

where R_m is given by several equivalent expressions,

$$R_m = \begin{cases} M \left(\partial^2 f / \partial c^2 \right)^2 / 8\kappa \\ 2M\kappa \beta_m^4 \\ -\frac{1}{2} M \left(\partial^2 f / \partial c^2 \right) \beta_m^2, \end{cases} \quad (15)$$

obtained by substituting Eq. (13) into Eq. (11), and the summation is only over waves for which the magnitude of β is β_m .

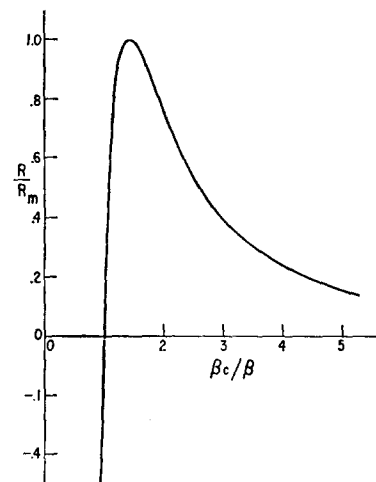


FIG. 1. The exponential amplification factor [Eq. (12)] as a function of wavelength [Eq. (14)]. The critical wavelength $2\pi/\beta_c$ is related to thermodynamic parameters alone [Eq. (6)]; the peak amplification factor also depends on the diffusional mobility [Eq. (15)].

Thus, at some time after phase separation starts, a description of the composition in the solution will be a superposition of sine waves of fixed wavelength, but random in orientation, phase, and amplitude. That such a description corresponds to phase separation may be verified by examining the integrated square of the deviation from the average composition.

$$\int (c - c_0)^2 dV = \frac{1}{2} V \exp[R_m t] \sum_{\beta_m} [A^2(\beta) + B^2(\beta)]. \quad (16)$$

For anisotropic solids only wavevectors in certain crystallographic directions need be considered. For instance for β along $\langle 100 \rangle$ in a cubic crystal, the maxima and minima in the composition form a large CsCl structure (two intertwined simple cubic structures with $\langle 100 \rangle$ rods of high and low concentrations connecting the respective extremes).

For the isotropic case, the Fourier inversion is not so easy to visualize. Therefore a computer was used to generate random numbers with a Gaussian distribution for amplitudes and to generate random numbers with a flat distribution in the interval 0 to π for phase angles. Directional cosines were computed from three random numbers chosen from a set with a flat distribution in the interval -1 to 1 . If the sum of their squares did not exceed 1 , they were normalized to 1 and used as directional cosines. The Fourier series was then summed and printed on a three-dimensional grid. For comparison 20, 50, and 100 sine terms were summed to see how the various aspects of the concentration distribution depends on the number of terms. Figure 2 shows a plane from each of these structures. If the concentration is below c_0 , the space is left blank; if it exceeds c_0 , an asterisk is printed. Therefore the blanks and stars represent points in what will become one phase or the other. The wavelength $2\pi/\beta_m$ is indicated. There appear to be no essential differences among the structure, and it may be assumed that even 20 waves is a sufficiently large number for our purpose. In Fig. 3 a succession of closely spaced sections of the 100-term structure is given.

DISCUSSION

We have derived the initial stages of phase separation in a solution which is unstable with respect to continuous composition change. The resultant two-phase morphology is shown in Figs. 2 and 3. For comparison Fig. 4 shows replica micrographs of two glasses rapidly cooled from a single phase region into a two-phase region⁹ and maintained there. Such a replica would correspond to a section. Figure 5 shows an electron micrograph by transmission of a Vycor in which one phase has been leached out and the voids

⁹ J. J. Hammel and H. Golob, "Experimental Evidence for Spinodal Decomposition in Glasses of the $\text{Na}_2\text{O}-\text{SiO}_2$ System," paper presented at the Fall 1964 Meeting of the American Ceramic Society at Bedford, Pennsylvania.

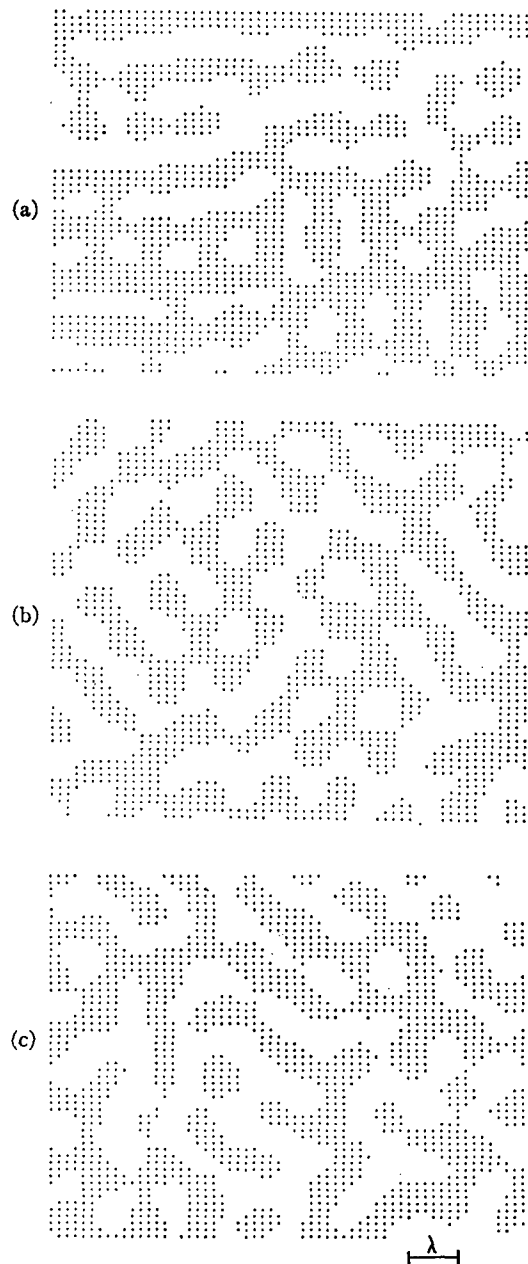


FIG. 2. Computed sections through the two-phase structure for (a) 20, (b) 50, and (c) 100 random sine waves (50:50 volume fraction).

filled with lead.¹⁰ The very striking interconnectivity of the two phases is thereby illustrated. That this connectivity is predicted by the theory can be verified by examining Fig. 3.

The initial stages of phase separation are symmetric about c_0 . It is possible to show that, as the phase separation continues, higher-order terms in Eqs. (7)–(9) will bring in harmonics which will distort the composition so that the structure will become a mixture of two

¹⁰ W. G. Schmidt and R. J. Charles "Metal Impregnation of Porous Glasses," J. Appl. Phys. (to be published).

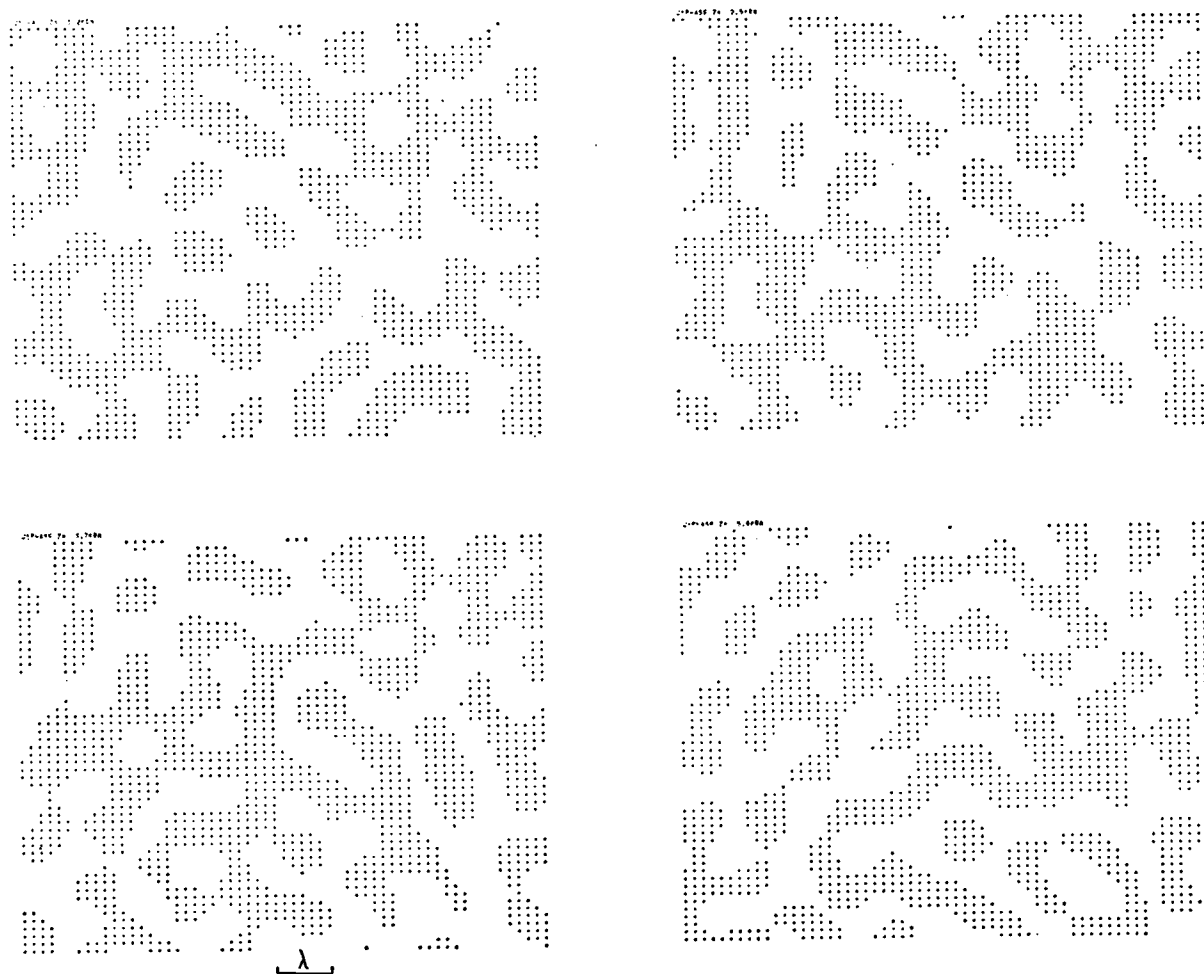


FIG. 3. A succession of computed sections through the 50:50 two-phase structure for 100 random sine waves. Note that all particles are interconnected. The spacing between sections is $1.25/\beta_m$. Top: $Z=1.25/\beta_m$ and $Z=2.5/\beta_m$; bottom: $Z=3.75/\beta_m$ and $Z=5/\beta_m$.

phases, each of which is homogeneous except for the vicinity of the interfaces. As this structure is approached, interface tension will cause agglomeration into larger particles and the breakup of connectivity. These later stages are beyond the scope of this paper except that we make some qualitative observations.

The formulation of the theory contains the surface free energy implicitly. For example, Eq. (1) may be used to calculate surface free energy. Thus it is somewhat surprising that Eq. (14) predicts that the geometrical arrangement of the composition modulation does not change with time during the early stage of the reaction. Only the amplitudes of the modulations change. Thus it seems plausible to suggest that the geometric shapes of the interfaces that are forming may be close to being metastable to rearrangements caused by surface tension. For example, the curvature of the isoconcentration surface at $c=c_0$ is zero, when averaged over the entire surface. It may well be a surface that nowhere has large curvature and thus is highly metastable.

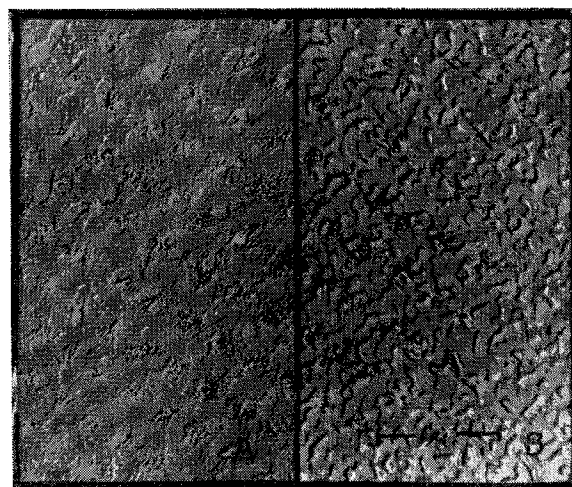


FIG. 4. Thermally treated glasses in the $\text{Na}_2\text{O}-\text{SiO}_2$ system. This system is believed to have a metastable liquid miscibility gap below the liquidus. (A) 11.6-mole% Na_2O after 90 min at 800°C , (B) 6.8-mole% Na_2O after 18 h at 696°C . Platinum preshadowed replicas of fresh fractures (after Hammel and Golob⁹).

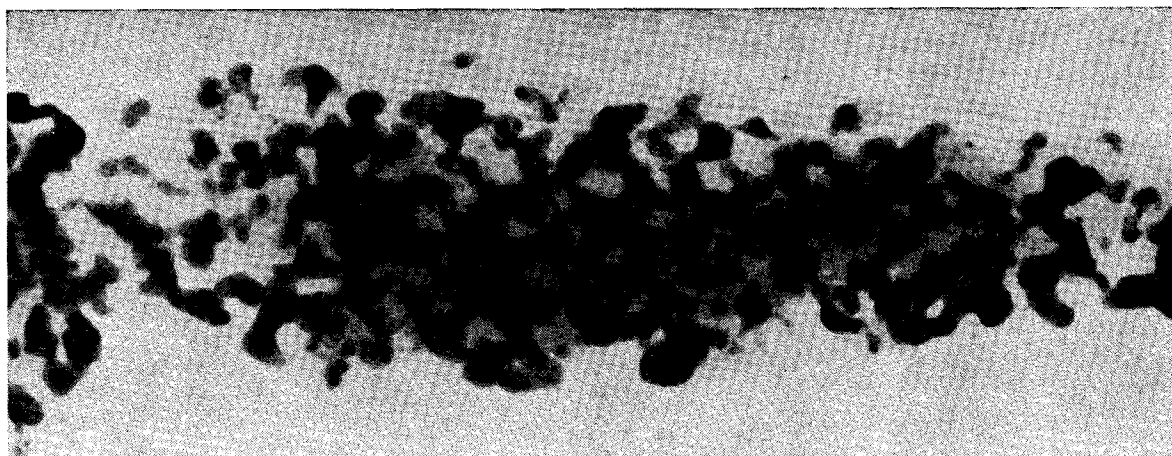


FIG. 5. Unsintered Vycor, with one phase replaced by lead, $\times 200\,000$ (after Schmidt and Charles¹⁰).

An important parameter of the two-phase structure is the relative volume fraction of the two phases. When these are equal we may assume that the isoconcentration surface at c_0 is representative of the two-phase morphology. Here everything that increased in composition eventually becomes one phase and vice versa. The two phases are completely interconnected.

If the volume fraction of one phase is less than the other, let us assume that if we select an isoconcentration surface which encloses that volume fraction, it will outline the phase distribution for us. Figure 6 shows such a structure for a 76:24 distribution of phases. Connectivity is still maintained. The transition from a connected minor phase to isolated particles seems to occur in the volume fraction range of $15 \pm 3\%$.

It becomes worthwhile to examine the essential difference between this mechanism and nucleation and growth. In the latter mechanism the new phase starts from small regions, the nuclei, which then proceed to grow in extent. At any time the structure is clearly two phase, and, except for interface regions, the compositions are those of either one phase or the other.

In the spinodal mechanism the composition changes gradually in both directions from the average. In the early stages at least the entire composition range between the composition extremes exists within the sample, and with time the spread in composition increases. Thus growth is not in extent but in amplitude. This kind of growth, as can be seen from Eq. (4), is thermodynamically impossible except in the unstable region. Only in the unstable region does such a change lead to decrease in free energy. This not only implies that such fluctuations will occur, but conversely once they have occurred they will not spontaneously disappear. Furthermore, the observation of such fluctuations implies that the spinodal has been crossed.

While observation of such continuous composition change in both directions from the average is proof that the spinodal has been crossed, the peculiar phase

distribution with its very high degree of connectivity is also a good indication that a spinodal mechanism is involved. This feature applies only to the region where the volume fraction of the minor phase exceeds about 15%. For small volume fractions of one phase the resultant morphology is not too different from nucleation and growth, except that the particles have a tendency to be a wavelength apart.

For nucleation and growth, the number of particles depends on the nucleation rate, which is a very sensitive function of composition, temperature, and number and kind of second phase heterogeneities. In the spinodal mechanism, nucleation catalysts play a role only within a wavelength, and then only as perturbations. If a second-phase particle has nucleated and begun to grow while the sample was passing through the metastable region, it will cease growing in the normal fashion but will become a center from which a composition modulation is expected to spread.¹¹ The particle becomes in effect a wave packet to be used as the boundary condition for the A and B in Eq. (12). In polycrystalline samples, the spinodal morphology is observed⁴ to extend unchanged right up to grain boundaries, which should be nucleation catalysts. Because the number of particles depends on the wavelength and volume fraction and because these are not very sensitive to small changes in composition or temperature, the structure resulting from the spinodal mechanism should be quite reproducible.

In simple solution models, the region enclosed by the spinodal is most of the two-phase region. Figure 7 shows this for a regular solution model. Because there is metastability with respect to short-wavelength fluctuations, solution models which implicitly assume long range homogeneity can be used for such estimates of the unstable region. All of these indicate a very large unstable region.

¹¹ M. Hillert, *Acta Met.* **9**, 525 (1961).



FIG. 6. A succession of computed sections through a 76:24 two-phase structure showing that connectivity of the minor phase (the asterisks) is maintained. The spacing between sections is $3.75/\beta_m$. Top: $Z=0$ and $Z=3.75/\beta_m$; bottom: $Z=7.5/\beta_m$ and $Z=11.25/\beta_m$.

Systems with phase diagrams of the form shown in Fig. 7 (i.e., having a consolute temperature) are most likely to have a spinodal. However it is possible to have a spinodal in systems that do not have a consolute temperature in the equilibrium phase diagram. In many of these systems it is possible to observe experimentally the equilibrium between the two related metastable phases, that form from the spinodal mechanism and determine a portion of the metastable phase diagram. For example, in some of the glass-forming systems, liquid phase separation occurs in the equilibrium phase diagram above the crystallization temperature (e.g., SiO_2 with either TiO_2 , MgO , FeO , ZnO , CaO , or SrO)¹²; in others (e.g., $\text{Li}_2\text{O}-\text{SiO}_2$, $\text{BaO}-\text{SiO}_2$ and Vycor)¹³⁻¹⁵ the liquid phase separation occurs only

metastably below the equilibrium crystallization temperature. Such metastable phase diagrams have a metastable upper consolute temperature, that should be detectable. At present little is known about the metastable phase diagrams, except that at high temperatures there is a single-phase fluid region and that at lower temperatures there is phase separation into two fluids. This information suggests that an upper consolute temperature exists in such systems.

There are also systems exhibiting a spinodal in which it will not be possible to observe a metastable equilibrium between related phases, because some entirely different phase nucleates and grows from one or both of the composition extremes in the spinodal structure. In these systems the spinodal mechanism may be observed as a clustering reaction preceding the formation of the new phases and it is likely that the geometrical shape of the new phase will be dictated by the geometry of the spinodal clustering reaction.

The kinetics of the initial stages and resulting morphology are given entirely by the magnitude of κ , $\partial^2 f / \partial c^2$, and M . The first two establish a wavenumber

¹² E. M. Levin, H. F. McMurdie, and R. P. Hall, *Phase Diagrams for Ceramists* (The American Ceramic Society, 1956), Figs. 128 and 130.

¹³ R. Roy, *Symposium on Nucleation and Crystallization in Glasses and Melts* (The American Ceramic Society, 1962), p. 39.

¹⁴ R. J. Charles, *J. Am. Ceram. Soc.* **46**, 235 (1963).

¹⁵ N. B. Volf, *Technical Glasses* (Sir Isaac Pitman and Sons, Ltd., London, 1961), Chap. X.

of wavelength, and this together with M describes the kinetics. No other parameter enters. From statistical mechanical considerations,⁸ κ has been shown to be slowly varying with temperature and composition; the temperature dependence of $\partial^2 f / \partial c^2$ is given by $-\partial^2 s / \partial c^2$, where s is the entropy per unit volume. Thus, the square of the observed wavenumber should be proportional to the undercooling ΔT below the spinodal:

$$\beta_m^2 = [(\partial^2 s / \partial c^2) / 2\kappa] \Delta T, \quad (17)$$

and a plot of β_m^2 vs T could be used to obtain a measurement of the quantity enclosed in brackets and the position of the spinodal. For a regular solution

$$\frac{\partial^2 s}{\partial c^2} = \frac{RT}{V_m} \left[\frac{(1/c) + 1}{1-c} \right],$$

where V_m is the molar volume. The mobility could be extrapolated from the single-phase region or might even be estimated from quick viscosity measurements at temperature.

In summary the theory of spinodal decomposition has been shown to predict a two-phase structure, which resembles that found in glass systems. A particular striking feature of this structure is the connectivity of the two phases which is expected when the volume fraction of the minor phase exceeds about 15%. While such morphologies are strong indications that phase separation occurred by a spinodal mechanism, they are not proof that the spinodal mechanism has occurred. To establish that the composition of the phases change continuously during phase separation would be direct proof. Once it has been established that spinodal decomposition is going on, the kinetics of the initial stages of phase separation and the resulting morphology are fully described by the theory.

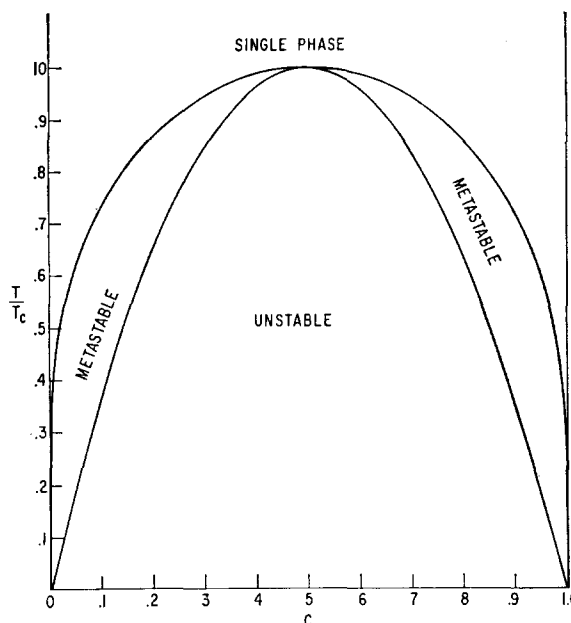


FIG. 7. Phase diagram of a regular solution showing the equilibrium phase boundary and the spinodal.

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