

Periodic Spinodal Decomposition in Solid and Fluid Binary Mixtures

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Periodic spinodal decomposition can be realized by changing the reduced temperature periodically. Experimental predictions are made for solid and fluid binary mixtures. The scattered light (or neutron) intensity is shown to be much enhanced as a result of periodic formation of domains. A phase transition is also discussed, which occurs as the average temperature is lowered with a fixed size of the temperature vibration.

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In previous papers¹ nonlinear effects of strong sound waves were examined in the neighborhood of second-order phase transitions. There, the temperature difference $T - T_c$ is assumed to be oscillating with a frequency Ω as

$$T - T_c = \Delta T_0 + T_1 \cos(\Omega t - Kx), \quad (1)$$

where ΔT_0 is the average of $T - T_c$, T_1 is a positive constant, and T_c is the equilibrium critical temperature. Note that $T - T_c$ can be made oscillating by various other methods, for example, by application of periodic pressure or periodic magnetic field.

We are interested in the case $|\Delta T_0| < T_1$. Here the system is unstable periodically when $T - T_c$ becomes negative. This results in enhancement of the critical fluctuations with sizes greater than a characteristic length ξ_c defined by $\xi_c = \xi_0 (T_1/T_c)^{-\nu}$, where ξ_0 and ν are determined by the relation for the equilibrium correlation length $\xi = \xi_0 (\Delta T/T_c)^{-\nu}$. The fluctuations with wavelengths greater than ξ_c can be enhanced by the periodic quench, whereas those with wavelengths smaller than ξ_c are little affected. The degree of the enhancement is represented by the dimensionless number

$$\mu = \Gamma_c / \Omega = \gamma_0 \xi_c^{-z} / \Omega = \gamma_0 \xi_0^{-z} (T_1/T_c)^{\nu z} / \Omega, \quad (2)$$

where $\Gamma_c \equiv \Gamma(\xi_c^{-1})$, $\Gamma(k)$ being the order parameter decay rate with wave number k , z is the dynamic critical exponent, and γ_0 is a constant. This number is the ratio of the period of the quench to the time scale of the growing fluctuations. For $\mu > 1$ strong enhancement of the fluctuations occurs, while for $\mu \ll 1$ the period of the quench is too small to produce significant nonlinear effects. However, if μ is too large, the system reaches the final stage of the phase separation in a time interval with negative temperature. Then the process becomes rather macroscopic.

In our problem there are two characteristic processes, the formation and the decay of clus-

ters. The former process occurs while $T < T_c$ and the latter one while $T > T_c$. If the clusters are destroyed almost completely while $T > T_c$, the process of phase separation must be stopped and the system will tend to be in a periodic state. However, if the average temperature ΔT_0 is lowered gradually, the decay mechanism becomes ineffective and the clusters will be only partially destroyed. Then, the phase separation will proceed without limit.

In this Letter I propose experiments of periodic spinodal decomposition in solid and fluid binary mixtures.²⁻⁴ For solid mixtures the time scale of the phase separation is very slow and suitable experimental conditions will be simply realized by changing the temperature macroscopically. For fluid mixtures the critical temperature T_c can be made to oscillate by periodic pressure. Let us consider a critical binary mixture of isobutyric acid and water as an example. In this fluid T_c depends on the pressure as $dT_c/dp = -0.05 \text{ mK atm}^{-1}$. Here the changes in the temperature and the critical composition are negligible.² If p_1 is the magnitude of the pressure vibration, then

$$\mu = (k_B T / 16\bar{\eta}) \xi_0^{-3} (T_1/T_c)^{3\nu} / \Omega = C_\mu p_1^{3\nu} / \Omega,$$

where $\bar{\eta}$ is the shear viscosity, $T_1 \equiv |dT_c/dp| p_1$, and $C_\mu = 1.5 \times 10^2$ with p_1 in atmospheres and Ω in hertz. For example, if $p_1 = 0.2 \text{ atm}$ and $\Omega = 1 \text{ sec}^{-1}$, we obtain $T_1 = 10 \text{ mK}$ and $\mu = 7.2$.

I present some numerical results for the periodic quench at the critical composition. They have been obtained with a computational scheme of Langer, Bar-on, and Miller (LBM)⁵ for the solid case and that of Kawasaki and Ohta (KO)⁶ for the fluid case. The KO theory takes into account of the hydrodynamic interaction by grafting mode coupling onto the LBM scheme.

For the solid case the correlation function of the Fourier component of the concentration

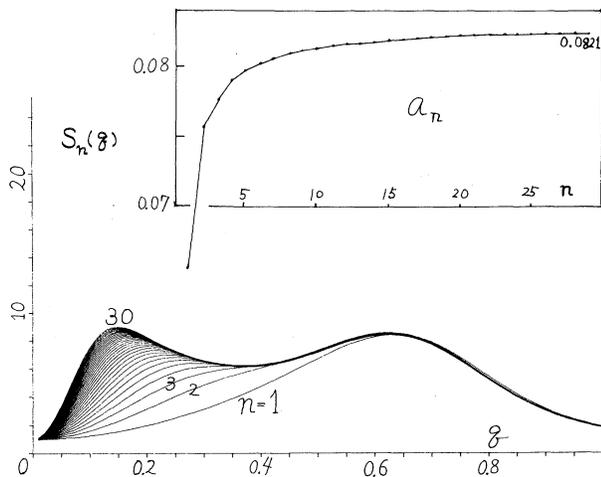


FIG. 1. $S_n(q)$ for solid mixtures at $\mu=20$ and $\sigma=-0.4$. In the inset $\{a_n\}$ are shown. They approach 0.0825.

$c(\vec{r}, t)$ obeys the equation⁵

$$\frac{\partial}{\partial t} \hat{S}(t) = -2Lk^2[k^2 + A(t)]\hat{S}_k(t) + 2Lk^2, \quad (3)$$

where L is the kinetic coefficient and $A(t)$ is given by

$$A(t) = r(t) + \frac{g}{6} \langle c(\vec{r}, t)^4 \rangle / \langle c(\vec{r}, t)^2 \rangle. \quad (4)$$

Here $r(t)$ represents $T - T_c$ and will be assumed to be undergoing a step-wise oscillation

$$r(t) = r_1[\sigma + F(t/t_p)], \quad (5)$$

where r_1 is the magnitude of the oscillation, $r_1\sigma$ is the average, and $F(x)$ is a step-wise periodic function defined as $F(x) = -1$ for $n < x \leq n + \frac{1}{2}$ and $F(x) = 1$ for $n + \frac{1}{2} < x \leq n + 1$ with n integral. Thus t_p is the period of the oscillation. In this case it is convenient to redefine μ as $\mu = Lr_1^2 t_p$. I assume that $c(\vec{r}, t)$ consists of Fourier components with wave numbers smaller than $k_{\max} = k_c \equiv r_1^{1/2}$ since the fluctuations with wave numbers greater than k_c are little affected by the oscillation. Note that k_c is roughly the inverse of ξ_c . The dimensionless coupling constant $g^* = g/k_c$ is assumed to be 21.8.^{5,6} The equation for the one-point distribution function $\rho_1(c_1, t) \equiv \langle \delta(c(\vec{r}, t) - c_1) \rangle$ is solved by approximating it as a sum of displaced Gaussians.

I introduce a dimensionless wave number $q = k/k_c$, a dimensionless time $\tau = 2Lk_c^4 t$, and a dimensionless structure factor $S(q, \tau) = \hat{S}_k(t)k_c^2$. The period of the oscillation is 2μ in the dimension-

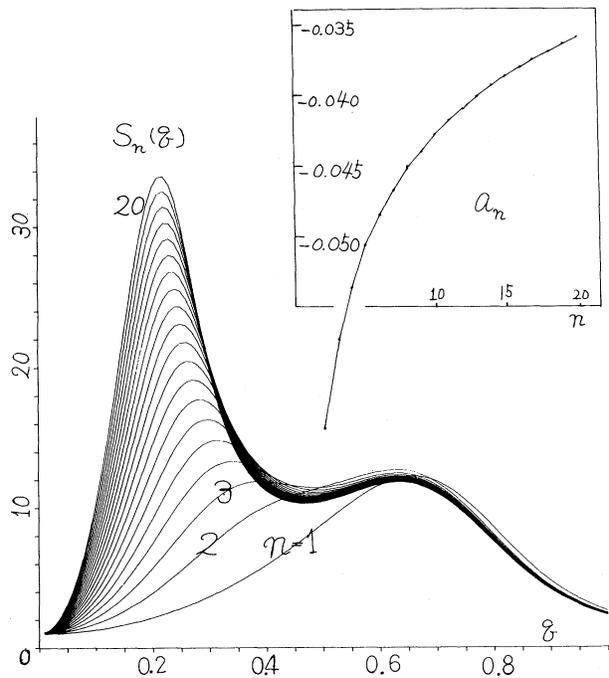


FIG. 2. $S_n(q)$ for solid mixtures at $\mu=20$ and $\sigma=0.7$. The $\{a_n\}$ remain negative.

less units. Then (3) becomes

$$\frac{\partial}{\partial \tau} S(q, \tau) = -q^2[q^2 + a(\tau)]S(q, \tau) + q^2, \quad (6)$$

where $a(\tau) = A(t)/k_c^2$. At $\tau=0$ I assume that $S(q, 0) = 1/(q^2 + 1)$.

Since $S(q, \tau)$ and $a(\tau)$ oscillate rapidly in each period, I plot in Figs. 1 and 2 the following av-

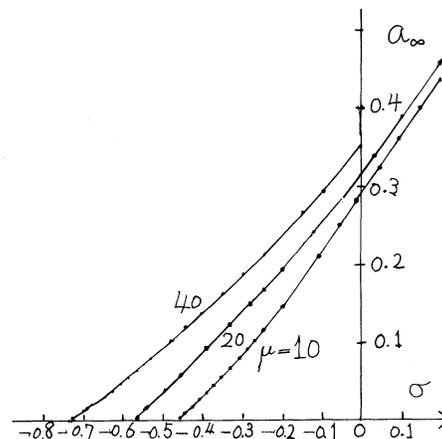


FIG. 3. a_∞ vs σ for solid mixtures.

eraged quantities up to $n = 30$:

$$S_n(q) = \frac{1}{2^\mu} \int_{2^{(n-1)\mu}}^{2^{n\mu}} d\tau S(q, \tau),$$

$$a_n = \frac{1}{2^\mu} \int_{2^{(n-1)\mu}}^{2^{n\mu}} d\tau a(\tau). \tag{7}$$

As a typical feature $S_n(q)$ has two peaks. This means that there are two types of clusters. The smaller ones are created and destroyed in each period, but a part of them survive to grow into the larger ones after several periods for negative σ . However, for shallow quenches (for σ

≥ 0.2) or for short-time quenches (for $\mu \leq 10$) the $S_n(q)$ have only one peak. When σ is greater than a critical value σ_c , $S_n(q)$ tend to a limit which assumes the Ornstein-Zernike form $(q^2 + a_\infty)^{-1}$ at small q , where $a_\infty = \lim_{n \rightarrow \infty} a_n$. At $\sigma = \sigma_c$, $a_\infty = 0$. This is because the long-wavelength fluctuations cannot change appreciably in one period and can see only the average of $a(\tau)$. $S(q, \tau)$ also tends to a periodic function as $\tau \rightarrow \infty$. For $\sigma < \sigma_c$, the $S_n(q)$ continue to grow. I display a_∞ versus σ in Fig. 3, which shows that $\sigma_c = -0.47, -0.57$, and -0.73 for $\mu = 10, 20$, and 40 , respectively. Note that $a(\tau)$ behaves almost periodically after several periods for $\sigma > \sigma_c$, so that a_∞ can be determined precisely.

For the fluid case $S(q, \tau)$ obeys the equation⁶

$$\frac{\partial}{\partial \tau} S(q, \tau) = -q^2 [q^2 + a(\tau)] S(q, \tau) + q^2 + \frac{3}{\pi} q^2 \int_0^1 dm Q(q/m) [S(m, \tau) - S(q, \tau) + (m^2 - q^2) S(m, \tau) S(q, \tau)], \tag{8}$$

where

$$Q(x) = \frac{1}{2}(x^{-1} + x^{-3}) \ln |(x+1)/(x-1)| - x^{-2}.$$

Here μ and τ should be redefined as $\mu = (k_B T / 12\pi\eta) k_c^3 t_p$ and $\tau = (k_B T / 6\pi\eta) k_c^3 t$. For $\sigma > \sigma_c$, the $S_n(q)$ tend to a limit which may be represented by $1/(q^2 + \kappa_\infty^2)$ at small q , as is shown in Fig. 4. Strikingly, κ_∞^2 is much smaller than a_∞ and appears to be of order a_∞^2 . For example, $\kappa_\infty^2 \cong 0.024$ and $a_\infty \cong 0.15$ at $\mu = 5$ and $\sigma = -0.2$. We

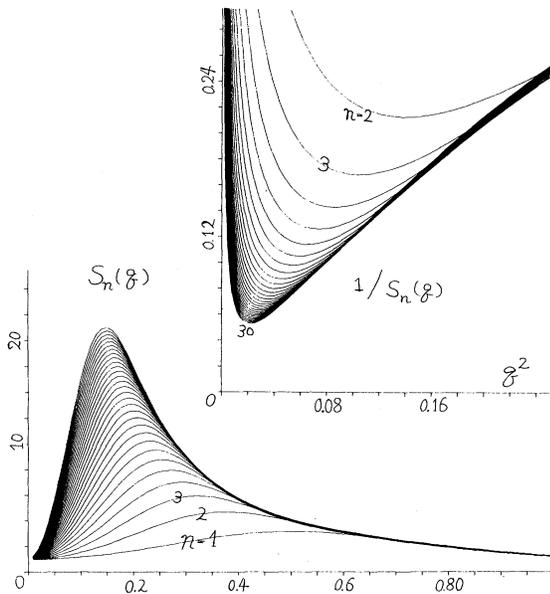


FIG. 4. $S_n(q)$ for fluid mixtures at $\mu = 5$ and $\sigma = -0.2$. In the inset $1/S_n(q)$ are displayed vs q^2 . In this case the system tends to a periodic state.

cannot find two peaks in $S_n(q)$ for $3 \leq \mu \leq 60$, although $S(q, \tau)$ has two peaks in some μ regions. This is probably because the hydrodynamic interaction gives rise to an anomalously large renormalization contribution to the transport coefficient,⁷ which may be expected to be of order κ_∞^{-1} . For $\sigma < \sigma_c$, the $S_n(q)$ continue to grow, as is shown in Fig. 5.

In this Letter I have found a new phase transition, which occurs when σ is lowered with μ fixed. For $\sigma > \sigma_c$ the clusters remain finite and the system is in the disordered phase. For $\sigma < \sigma_c$

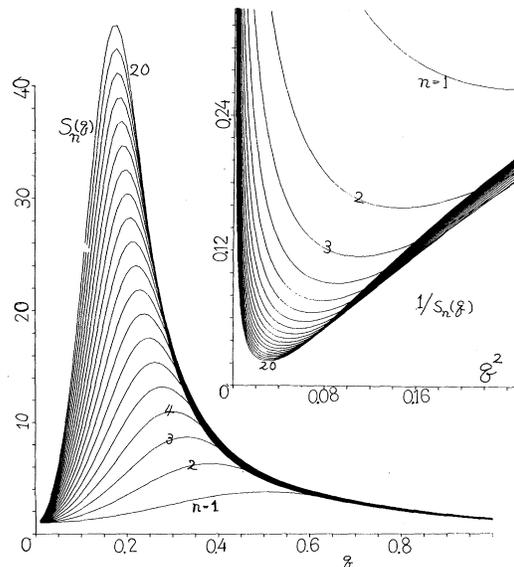


FIG. 5. $S_n(q)$ for fluid mixtures at $\mu = 5$ and $\sigma = -0.32$. In this case the intensity grows indefinitely.

the clusters grow and the system will be separated into two phases ultimately. However, we do not know the precise nature of the transition. It might be of first order. That is, the average concentration might jump discontinuously just below the transition. If this is true, the values of σ at which $\lim_{q \rightarrow 0} \lim_{\tau \rightarrow \infty} S(q, \tau)$ diverges should correspond to the limit of metastability, although these values have been regarded as the critical values in this Letter.

Finally it should be remarked that the results of this Letter are based on the LBM approximation and cannot be conclusive. Their verification (or modification) should be made in future theories or experiments.

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Second Zone in Ionic Solutions

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High-resolution incoherent neutron spectroscopy has, for the first time, been applied to aqueous solutions and has demonstrated unambiguously the existence of a second zone of weakly interacting water molecules around two divalent cations Ni^{2+} and Mg^{2+} .

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In an important paper published some 20 years ago, Frank and Wen¹ postulated that around ions in aqueous solutions two well-defined zones of water may exist. The first zone, the so-called primary hydration shell, is now established beyond any doubt.^{2,3} The dynamical behavior of weakly interacting water molecules like those in the second zone, however, is not amenable to conventional spectroscopic investigations.³ To use incoherent quasielastic neutron spectroscopy, for example, two stringent criteria must be met. First, k [(momentum transfer)/ \hbar] values must be such that

$$Dk^2\tau_\theta \ll 1,$$

where D is the translational diffusion coefficient and τ_θ is the correlation time for rotational mo-

tion of the hydrated ion; for $\tau_\theta \sim 10^{-11}$ sec,⁴ and $D \sim 10^{-9}$ m² sec⁻¹, $k \ll 1 \text{ \AA}^{-1}$. Secondly, the required observation time of the experiment τ_m (10^{-9} sec) implies an instrumental energy resolution of 1 μeV . Under these conditions the observed self-scattering law $S(k, \omega)$ will be Lorentzian in character and will, for ionic solutions in light water, be dominated by the hydrogen term, $S_H^S(k, \omega)$ given by

$$S_H^S(k, \omega) = (1/\pi) Dk^2 / [(Dk^2)^2 + \omega^2], \quad (1)$$

if on the time scale of the experiment there is just one population of water molecules (the so-called "fast-exchange" limit). The backscattering technique as exemplified by the instrument IN10 now available at the Institut Laue Langevin, Grenoble, allows data to be collected under the