

Hydrodynamic singularity in the spinodal decomposition of a binary liquid

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(Received 27 April 1981)

The long-wavelength diffusion involved in spinodal decomposition in the critical region depends upon transport of the concentration fluctuations by the hydrodynamic shear modes. As spinodal decomposition advances the concentration fluctuations become peaked at some wave number k_0 . We demonstrate here that the Onsager coefficient for such a fluid is also strongly wave-number dependent and develops a logarithmic singularity at k_0 . This will tend to enhance and speed up the spinodal decomposition and will significantly affect the comparison of theory with experiment.

Recent experimental work^{1,2} has demonstrated how the metallurgically important phenomenon of spinodal decomposition can also be observed in a binary liquid. This is accomplished by abruptly changing the temperature of the liquid so as to bring it past its critical, or consolute, point. The purpose of this paper is to point out that the theory that has been developed for solids³⁻⁵ cannot be applied without modification to spinodal decomposition in liquids. This is because of the essential role played by the hydrodynamic shear modes in the latter case. We discuss this complication and give explicit results for the special cases of greatest interest—the initial^{6,7} and the well-advanced phases of spinodal decomposition. In the latter case we find that the phenomenon is enhanced by a singular contribution from the long-wavelength hydrodynamic modes.

In the very first stages of spinodal decomposition the growth has just started and the concentration fluctuations are still described by the equilibrium Ornstein-Zernike (OZ) correlation function⁸

$$g(k, \kappa) = \frac{C}{k^2 + \kappa^2}, \quad (1)$$

where k is the wave number, κ^{-1} the correlation length, and C a constant proportional to the isothermal derivative of the concentration with respect to osmotic pressure. The flow in response to a thermodynamic force tending to change the concentration fluctuation of wave number k has been calculated from mode coupling by Kawasaki⁹ and from the equivalent decoupled-mode approximation by the present author.¹⁰ It is described by the nonlocal Onsager coefficient (neglecting the noncritical background contribution)

$$\lambda(k, \kappa) = \frac{C}{8\pi\eta\kappa} L\left(\frac{k}{\kappa}\right), \quad (2)$$

where the relatively small effects produced by the critical variation of the shear viscosity¹¹ η are neglected here. The Kawasaki function of the dimensionless momentum ratio $z = k/\kappa$ is

$$L(z) = \frac{1}{z^2} + \left(\frac{1}{z} - \frac{1}{z^3}\right) \tan^{-1}z \\ = \begin{cases} \frac{4}{3}, & z = 0 \\ \pi/(2z), & z \gg 1. \end{cases} \quad (3)$$

The regression of the fluctuations at equilibrium is described by the nonlocal diffusion coefficient

$$D(k, \kappa) = T \frac{\lambda(k, \kappa)}{g(k, \kappa)}. \quad (4)$$

Substitution from Eqs. (1)–(3) gives the familiar results^{9,10} $D(0, \kappa) = T\kappa/6\pi\eta$ and $D(k, 0) = Tk/16\eta$ for the hydrodynamic and extreme nonhydrodynamic limits, respectively. (The temperature T is measured in units such that Boltzmann's constant equals one.)

When the fluid is brought out of equilibrium and spinodal decomposition starts, Eq. (4) can no longer be used. Instead, the factor Tg^{-1} is replaced by a k -dependent function which is negative over a range of small k values and which contrasts with the positive definiteness of Tg^{-1} (a property also of nonequilibrium distributions). This change describes qualitatively the thermodynamic forces which tend to produce growth rather than regression of the fluctuations. The resulting negative diffusion coefficient is, however, also strongly affected by the k dependence of $\lambda(k, \kappa)$. This is the additional feature which is lacking in the spinodal decomposition of solids, where λ can be assumed to be a constant. The full variation of $\lambda(k, \kappa)$ is shown by the plot of $L(z)$ in Fig. 1 (curve labeled OZ). In comparisons of theory with ex-

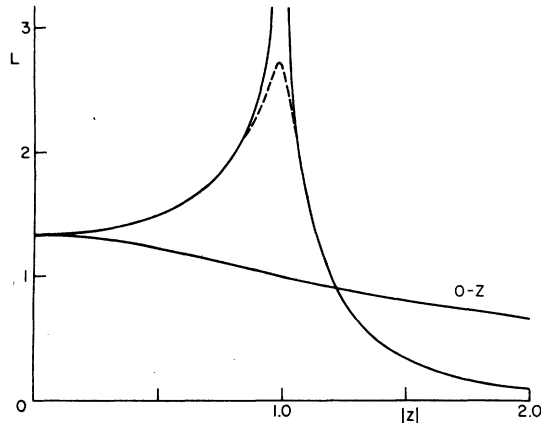


FIG. 1. $L(z)$ vs $|z|$ for real and imaginary z , representing the nonlocal Onsager coefficient for equilibrium (OZ) and advanced spinodal decomposition, respectively. $|z|$ is the wave number in dimensionless units. The diverging curve represents the extreme case of an isotropic δ -function distribution of fluctuations concentrated at $|z|=1$. The logarithmic singularity results from the diverging contribution of the long-wavelength hydrodynamic shear modes and is cut off for a " δ function" of finite width. The dashed curve is drawn for a distribution twice as sharp as that shown in Fig. 2. Because of linearity, the functions can be superposed.

perimental data on the initial stages of spinodal decomposition it is essential to take this variation into account.

The purpose of this paper is to demonstrate the effect of the hydrodynamics on the Onsager coefficient. For this reason we limit our attention to the numerator of Eq. (4). In fact, we will no longer have reference to Eq. (4), which has served primarily to introduce the important role played by the Onsager coefficient. We do not attempt a full description of the spinodal decomposition process. It is not in general possible to follow the course of the spinodal decomposition by means of a simple equation such as Eq. (4). It is instead necessary to join the theory of the Onsager coefficient, which we present here, to some theory of the thermodynamic forces (including the Brownian motion effects) such as that of Langer and Bar-on.⁵ Our goal is the more modest one of describing the hydrodynamic modification that has to be taken into account at any given stage of the process. The calculation of the actual amount of the modification depends upon the size of the fluctuations that have accumulated since the moment that the system was brought out of equilibrium and the spinodal decomposition started. At any given stage of the spinodal decomposition the accumulated fluctuations are described quantitatively by the correlation function g .

The k dependence of λ becomes even more pronounced in the later stages of the spinodal decomposition of a fluid. The growth occurs in a restricted k range, leading to the formation of a peak in g centered at some value k_0 . This can reasonably be represented by a more-or-less sharp δ function, as shown in Fig. 2. For comparison, the initial OZ form for g is also shown, rescaled by setting $\kappa = k_0$. The k dependence of λ corresponding to an arbitrary g can be calculated explicitly from the convolution integral of Eq. (5) of Ref. 10 and its generalization to finite wave number [as described in connection with Eq. (15)]. This is because the critical slowing down of diffusion permits us to neglect the time dependence of the concentration fluctuations, relative to the time scale of the hydrodynamic modes. Consequently, λ is simply a linear response function based on the transport of some frozen-in distribution of fluctuations. To calculate λ from the Kubo formula, as in Ref. 10, it is not necessary to assume that the concentration fluctuations have an equilibrium distribution.¹²

From the above remarks it is clear that it is a straightforward task to carry out the necessary integration for λ based upon any arbitrary g . But for the special case of interest here $g \propto \delta(k - k_0)$, we can even spare ourselves this trouble by recalling that the OZ form for g is nothing other than a pole in the complex k^2 plane, located at $k^2 = -\kappa^2$. By formally setting $\kappa^2 = k_0^2$ (which no longer has any direct connection with the initial equilibrium value of κ) and rotating the pole by 180° clockwise about the origin, we can bring the pole to the positive real axis, at $k^2 = k_0^2$. Taking now the imaginary part of the resulting expression for g gives the de-

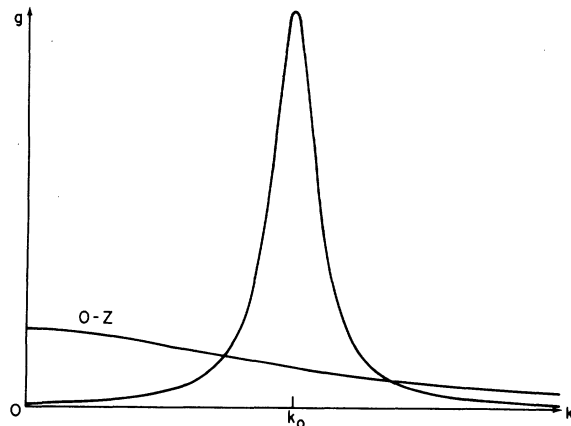


FIG. 2. Distribution of concentration fluctuations g vs wave number k for equilibrium (OZ) and advanced spinodal decomposition centered at $k = k_0$. The distributions can be superposed with arbitrary relative weight and scale.

sired δ -function distribution in the form

$$\text{Im}g(k, -ik_0) = \frac{\pi}{2} \frac{C}{k_0} \delta(k - k_0). \quad (5)$$

We remark in passing that the corresponding correlation function in configuration space is

$$\text{Im} \frac{e^{-\kappa r}}{r} \Big|_{\kappa = ik_0} = \text{Im} \frac{e^{ik_0 r}}{r} = \frac{1}{r} \sin k_0 r, \quad (6)$$

as expected for the Fourier transform of a k spectrum concentrated on a spherical shell of radius k_0 . As g occurs linearly in the integral for λ , we impose on Eq. (2) the analytic continuation indicated in Eq. (5), to find

$$\text{Im}\lambda(k, -ik_0) = \frac{C}{8\pi\eta k_0} \text{Re}L(iv). \quad (7)$$

Here $v = |z| = k/k_0$ and the Kawasaki function has become

$$\begin{aligned} \text{Re}L(iv) &= -\frac{1}{v^2} + \left(\frac{1}{v} + \frac{1}{v^3}\right) \text{Im} \tan^{-1} iv \\ &= -\frac{1}{v^2} + \frac{1}{2} \left(\frac{1}{v} + \frac{1}{v^3}\right) \ln \frac{1+v}{|1-v|}. \end{aligned} \quad (8)$$

The logarithmic singularity at $v=1$ is exhibited in Fig. 1. It is due to the divergent behavior of the long-wavelength hydrodynamic modes, which would contribute even more strongly in the integration if it were not for their transverse nature.

The treatment of the above paragraph is easily modified to correspond to a peak of small but finite width. Rotation of κ by $\pi/2 - \delta$, where $0 < \delta \ll 1$, replaces $\pi k_0^{-1} \delta(k - k_0)$ in Eq. (5) by $\delta / [(k - k_0)^2 + k_0^2 \delta^2]$, with a full width at half maximum of $2k_0 \delta$. This replaces Eq. (8) by

$$\text{Re}L(iv + \delta) = -\frac{1}{v^2} + \frac{1}{2} \left(\frac{1}{v} + \frac{1}{v^3}\right) \ln \frac{1+v}{|1-v+i\delta|} \quad (9)$$

plus terms of $O(\delta)$. The Onsager coefficient now no longer diverges at $v=1$ but instead takes on a

finite value corresponding to

$$\text{Re}L(i + \delta) = -1 + \ln \frac{2}{\delta}, \quad (10)$$

plus $O(\delta^2 \ln^2 \delta)$. This is illustrated by the dashed curve in Fig. 1 which has been drawn for $\delta = \frac{1}{20}$ (or a full width at half maximum in the peak in g of $k_0/10$). In this case, where the spinodal decomposition is rather far advanced, Eq. (10) is equal to 2.69. This relatively sharp structure in the Onsager coefficient will tend to promote growth at $k = k_0$ and enhance the peak more than would be the case without the hydrodynamic singularity. Because of the linearity of the problem, the Onsager coefficient for more complicated distributions can be obtained from superpositions of curves of the type shown in Fig. 1.

To summarize, the spinodal decomposition depends upon a wave-number-dependent thermodynamic force and a wave-number-dependent Onsager coefficient. The latter is a constant in the solids, but its k dependence cannot be ignored in the fluids. In general, this requires a straightforward integration⁷ that has to be carried out at each stage of the spinodal decomposition, based upon the concentration fluctuations which have developed up to that point. But the problem simplifies in the two special cases: (a) the beginning, where the familiar Kawasaki equilibrium expression can be used, and (b) the end, where an analytic continuation of the Kawasaki expression can be applied. In the latter case, the hydrodynamic logarithmic singularity enhances further peaking of the k distribution of the concentration fluctuations.

I wish to thank the Alexander von Humboldt Foundation for a Senior American Scientist Award during which time the main part of this work was carried out. This research was supported by the U.S. National Science Foundation under Grants Nos. DMR 76-82345 and DMR 76-24472.

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¹²This is planned to be explicitly demonstrated elsewhere.