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Spinodal decomposition of a one-component fluid: A hydrodynamic fluctuation theory and comparison with computer simulation

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We present a theory of spinodal decomposition which is based on the linearized hydrodynamic equations including the stochastic fluctuations in stress tensor and heat flux and which accounts for nonlocal driving force through pressure gradient. The equation of state is obtained using liquid-state perturbation theory, and the transport coefficients are obtained from the Enskog theory of dense fluids. The theory thus has no adjustable parameters. The time-dependent structure factor calculated from the theory is in good quantitative agreement with molecular-dynamics experiments for early times. An effective amplification factor extracted from the experimental results also agrees well with the theoretical dispersion of the growing mode. Extension of our theory to binary-fluid mixtures shows that, within the linear regime, hydrodynamic flow effects are negligible and the Cahn-Cook description is adequate.

I. INTRODUCTION

Twenty years ago, Cahn[1] pioneered the diffusion theory of spinodal decomposition for describing the phase-separation dynamics of thermodynamically unstable solid solution. Eight years later, H. E. Cook[2] introduced a significant generalization of the Cahn theory by including fluctuations in the diffusion flux. Important theoretical developments within the framework of the Cahn-Cook diffusion fluctuation theory followed, noteworthy contributions to the nonlinear dynamics regime coming from Langer and co-workers[3] and Kawasaki and Ohta.[4] Since the middle 1970's, experimental investigation of spinodal decomposition in binary-fluid mixtures has occupied an important part of phase-transition research,[5] and the Cahn-Cook-Langer theory has been adopted as the principal theoretical description for the interpretation of the laboratory measurements. In contrast to past developments, we present the first dynamical theory of spinodal decomposition based on the hydrodynamic equations which include the stochastic fluctuations in the stress tensor and the heat flux. The nonlocal driving force arising from density inhomogeneities is specified by the van der Waals or generalized van der Waals prescription[6] and is accounted for through the pressure gradient in the dynamical equations. Comparison is made with a molecular-dynamics computer experiment for a one-component fluid.[6,7] The time-dependent structure factor caculated from the theory is in good quantitative agreement with experiment for early times. An effective amplification factor extracted from the experimental results also agrees well with the theoretical dispersion of the growing mode. Extension of our theory to binary-fluid mixtures shows that within the linear regime, hydrodynamic flow effects are neglegible and Cahn-Cook description is adequate.

II. THEORY

A. Linear hydrodynamics

The time-dependent structure factor $S(\vec{k},t)$ is related to the Fourier component of density fluctuations $\rho(\vec{k},t)$ by

$$S(\vec{k},t)=\frac{1}{V\rho_0}\langle \rho(\vec{k},t)\rho^*(\vec{k},t)\rangle \ , \tag{2.1}$$

where

$$\rho(\vec{k},t)=\int d^3r\, e^{-i\vec{k}\cdot\vec{r}}[\rho(\vec{r},t)-\rho_0] \ ,$$

ρ_0 being the homogeneous mass density. We use linear hydrodynamic theory with fluctuations[8] to evaluate the time evolution of density fluctuations and, hence, $S(\vec{k},t)$. Normally the equations of hydrodynamics are written for mass density ρ, fluid velocity $\vec{v}$, and entropy density s.[8] For our calculation, we only need the longitudinal part of fluid velocity $\psi\equiv\vec{\nabla}\cdot\vec{v}$, since the transverse part of the velocity decouples from the other variables in the linear regime. We also choose to express the entropy density in terms of density and temperature fluctuations through the thermodynamic relationship

$$ds=\frac{1}{T_0}c_v dT=\frac{1}{\rho_0^2}\left[\frac{\partial p}{\partial T}\right]_\rho d\rho\ ,$$

where c_v is the heat capacity at constant volume and p is the pressure. The set of hydrodynamic variables

$$\vec{\mathrm{V}}(r,t)\equiv\mathrm{col}(\rho,\psi,T)$$

satisfies the following equations:

$$\frac{\partial p}{\partial t}+\rho_0\psi=0\ , \tag{2.2}$$

$$\rho_0\frac{\partial\psi}{\partial t}+\nabla^2 p-\vec{\nabla}\vec{\nabla}:\overleftrightarrow{\sigma}'=0\ , \tag{2.3}$$

$$\rho_0 c_v\frac{\partial T}{\partial t}+T_0\left[\frac{\partial p}{\partial T}\right]_\rho\psi+\vec{\nabla}\cdot\vec{\mathrm{q}}=0\ , \tag{2.4}$$

where the viscous stress tensor $\overleftrightarrow{\sigma}'$, and heat flux $\vec{\mathrm{q}}$ are given by

$$\sigma_{ik}'=\eta\left[\frac{\partial v_i}{\partial x_k}+\frac{\partial v_k}{\partial x_i}-\frac{2}{3}\delta_{ik}\frac{\partial v_j}{\partial x_j}\right]+\zeta\frac{\partial v_j}{\partial x_j}\delta_{ik}+s_{ik}\ , \tag{2.5}$$

$$\vec{\mathrm{q}}=-\kappa\vec{\nabla}T+\vec{\mathrm{g}}\ . \tag{2.6}$$

In Eqs. (2.5) and (2.6), κ, η, and ζ are thermal conductivity, shear, and bulk viscosities, respectively. The hydrodynamic fluctuations in $\overleftrightarrow{\sigma}'$ and $\vec{\mathrm{q}}$ are represented by $\overleftrightarrow{s}$ and $\vec{\mathrm{g}}$. Following Landau and Lifshitz,[8] we assume that $\overleftrightarrow{s}$ and $\vec{\mathrm{g}}$ obey Gaussian-Markov process

$$\langle\overleftrightarrow{s}\rangle=\langle\vec{\mathrm{g}}\rangle=\langle\overleftrightarrow{s}\vec{\mathrm{g}}\rangle=0\ , \tag{2.7a}$$

$$\begin{aligned}\langle s_{ik}(\vec{\mathrm{r}}_1,t_1)s_{lm}(\vec{\mathrm{r}}_2,t_2)\rangle\\ &=2T_0[\eta(\delta_{il}\delta_{km}+\delta_{im}\delta_{kl})+(\zeta-\tfrac{2}{3}\eta)\delta_{ik}\delta_{lm}]\\ &\quad\times\delta(\vec{\mathrm{r}}_1-\vec{\mathrm{r}}_2)\delta(t_1-t_2)\ ,\end{aligned} \tag{2.7b}$$

$$\begin{aligned}\langle g_i(\vec{\mathrm{r}}_1,t_1)g_j(\vec{\mathrm{r}}_2,t_2)\rangle\\ &=2\kappa T_0^2\delta_{ij}\delta(\vec{\mathrm{r}}_1-\vec{\mathrm{r}}_2)\delta(t_1-t_2)\ .\end{aligned} \tag{2.7c}$$

Since our objective is to investigate the limitations of a linear theory for one-component fluid (at the level of Cahn-Cook linear theory of binary solid solutions), we assume that the nonlocal driving force during spinodal decomposition enters only in the pressure gradient term. We denote the thermodynamic quantities for a constrained single-phase in the two-phase fluid region by a superscript †. In terms of a van der Waals-like picture,[6] we have

$$\begin{aligned}\vec{\nabla}p&=\vec{\nabla}p^\dagger+\rho_0\int d^3r'\mathscr{L}(\vec{\mathrm{r}}-\vec{\mathrm{r}}')\vec{\nabla}'\rho(r')\\ &=\left[\frac{\partial p^\dagger}{\partial p}\right]_T\vec{\nabla}\rho+\left[\frac{\partial p^\dagger}{\partial T}\right]_\rho\vec{\nabla}T\\ &\quad+\rho_0\int d^3r'\mathscr{L}(\vec{\mathrm{r}}-\vec{\mathrm{r}}')\vec{\nabla}'\rho(r')\ ,\end{aligned} \tag{2.8}$$

where we have introduced a nonlocal operator $\mathscr{L}(\vec{\mathrm{x}})$ to describe the inhomogeneity which we specify later on. Since the hydrodynamic Eqs. (2.2) to (2.4) are linear first-order differential equations for the initial value problem associated with spinodal decomposition, we can obtain the solution using the Fourier-Laplace transform technique. If we denote by $f(\vec{\mathrm{k}},z)$

$$f(\vec{\mathrm{k}},z)=\int_0^\infty dt\,e^{-zt}\int d^3r\,e^{-i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}}f(\vec{\mathrm{r}},t)\ . \tag{2.9}$$

and using Eqs. (2.2)–(2.6) and (2.8), we obtain

$$\overleftrightarrow{M}\cdot\vec{\mathrm{V}}(\vec{\mathrm{k}},z)=\vec{\mathrm{V}}(\vec{\mathrm{k}},t=0)+\vec{\mathscr{F}}(\vec{\mathrm{k}},z)\ , \tag{2.10}$$

where

$$\begin{aligned}\vec{\mathscr{F}}(\vec{\mathrm{k}},z)=\mathrm{col}[\,&0,-k_ik_js_{ij}(\vec{\mathrm{k}},z)/\rho_0\ ,\\ &-ik_jg_j(\vec{\mathrm{k}},z)/\rho_0c_v]\ .\end{aligned} \tag{2.11}$$

Summation over repeated indices is implied

$$\overleftrightarrow{M}=\begin{bmatrix} z & \rho_0 & 0\\ -b(k)k^2 & z+D_Vk^2 & -ak^2\\ 0 & aT_0/c_v & z+D_Tk^2\end{bmatrix} \tag{2.12}$$

and

$$b(k)=\frac{1}{\rho_0}\left[\frac{\partial p^\dagger}{\partial\rho}\right]_T+\mathscr{L}(k),$$

$$D_V=(\tfrac{4}{3}\eta+\zeta)/\rho_0,\quad a=\frac{1}{\rho_0}\left[\frac{\partial p^\dagger}{\partial T}\right]_\rho,$$

and $D_T=\kappa/\rho_0c_v$. Equation (2.10) can formally be solved and inverted to obtain $\vec{\mathrm{V}}(\vec{\mathrm{k}},t)$. For $\rho(\vec{\mathrm{k}},t)$ we get

$$\begin{aligned}\rho(\vec{\mathrm{k}},t)=L^{-1}\Bigg[&\frac{\mathscr{M}_{11}}{\det M}\rho(\vec{\mathrm{k}},t=0)-\frac{\mathscr{M}_{21}}{\det M}\psi(\vec{\mathrm{k}},t=0)\\ &+\frac{\mathscr{M}_{31}}{\det M}T(\vec{\mathrm{k}},t=0)+\frac{\mathscr{M}_{21}}{\det M}s_{ij}(\vec{\mathrm{k}},z)\frac{k_ik_j}{\rho_0}\\ &-\frac{\mathscr{M}_{31}}{\det M}g_j(\vec{\mathrm{k}},z)\frac{ik_j}{\rho_0c_v}\Bigg]\ ,\end{aligned} \tag{2.13}$$

where

$$\mathscr{M}_{11}=z^2+(D_T+D_V)k^2z+(D_TD_Vk^2+a^2T_0/c_v)k^2$$
$$\equiv z^2+\mu z+\nu \;, \tag{2.14}$$
$$\mathscr{M}_{21}=\rho_0(z+D_Tk^2)\equiv\rho_0(z+\nu_3) \;, \tag{2.15}$$
$$\mathscr{M}_{31}=-\rho_0ak^2 \;, \tag{2.16}$$

and

$$\begin{aligned}\det M &= z^3+(D_T+D_V)k^2z^2 \\ &\quad+\left[\left\{\frac{a^2T_0}{c_v}+\rho_0b(k)\right\}k^2+D_TD_Vk^4\right]z \\ &\quad+\rho_0D_Tb(k)k^4 \\ &\equiv z^3+a_2z^2+a_1z+a_0 \\ &=(z-\alpha_1)(z-\alpha_2)(z-\alpha_3) \;.\end{aligned} \tag{2.17}$$

We have introduced the notations μ, ν, ν_3, a_2, a_1, a_0, and the (complex) roots α_1, α_2, α_3 which we use and discuss later. We have also used the symbol L^{-1} to indicate the inverse Laplace transform. It is appropriate to assume that, in a typical quench of a spinodal decomposition experiment, the fluctuations $\psi(\vec{k},t=0)$ and $T(\vec{k},t=0)$ are negligible compared to the initial density fluctuation $\rho(\vec{k},t=0)$. With this assumption we substitute Eq. (2.13) in Eq. (2.1) and use Eq. (2.7) to obtain the time-dependent structure factor. The result can be analytically given in terms of (complex) roots of the cubic Eq. (2.17), as

$$S(\vec{k},t)=\sum_{i=1}^{3}\sum_{j=1}^{3}\left[P_iP_j^*S(\vec{k},0)e^{(\alpha_i+\alpha_j^*)t}-2T_0k^4\left\{D_VQ_iQ_j^*+\frac{T_0a^2}{c_v}D_Tk^2R_iR_j^*\right\}(1-e^{(\alpha_i+\alpha_j^*)t})/(\alpha_i+\alpha_j^*)\right] \;, \tag{2.18}$$

where R_i $(i=1,2,3)$ are the cyclic permutations of $R_1\equiv[(\alpha_1-\alpha_2)(\alpha_1-\alpha_3)]^{-1}$, $P_i=(\alpha_i^2+\mu\alpha_i+\nu)R_i$, and $Q_i=(\alpha_i+\nu_3)R_i$. Equation (2.18) is the basic result of the linear hydrodynamic theory.

We note from Eq. (2.18) that the first term arises from the initial value and the remainder is a consequence of the hydrodynamic fluctuations $\vec{g}$ and $\vec{s}$. Since $\sum_i\sum_jP_iP_j^*$ can be shown to be unity, one recovers the proper initial value, and we see that hydrodynamic fluctuations begin contributing only for $t>0$.

If initially the system is in a stable one-phase configuration (i.e., $\mathrm{Re}\,\alpha_i<0$), the result in Eq. (2.18) evolves, as $t\rightarrow\infty$, towards the original equilibrium structure factor

$$S(\vec{k},\infty)=-\sum_i\sum_j\left\{D_VQ_iQ_j^*+\frac{T_0a^2}{c_v}D_Tk^2R_iR_j^*\right\}2T_0k^4/(\alpha_i+\alpha_j^*)=T_0/\rho_0b(k) \;. \tag{2.19}$$

It is straightforward to prove the second equality in Eq. (2.19) at $k=0$. More generally, it may be appropriate to follow the procedure analogous to that in Sec. 133 of Ref. 8.

In contrast to the time evolution in a one-phase system, we expect the quantity $b(k)$ to be more interesting for the spinodal decomposition experiments. For homogeneous systems,

$$b(k)\equiv\left[\frac{1}{\rho_0}\left\{\frac{\partial p^{\dagger}}{\partial\rho}\right\}_T+\mathscr{L}(k)\right]$$

reduces to c_T^2/ρ_0, where c_T is the isothermal sound speed. However, within the unstable region of the two-phase coexistence, $(\partial p^{\dagger}/\partial\rho)_T$ is negative and the ratio of heat capacities γ is less than one; i.e., $\rho_0b(0)=c_T^2$ and

$$\left[\frac{a^2T_0}{c_v}\frac{1}{\rho_0b(0)}\right]=(\gamma-1)$$

are both negative but the product (a^2T_0/c_v) remains positive. In order to apply the result of linear hydrodynamics to the specific situation of spinodal decomposition, we have to specify the prescription for the equation of state and various transport coefficients.

B. Equations of state and transport coefficients

Liquid-state perturbation theories have been sucessfully applied to the study of the thermodynamics of a constrained single-phase system within the two-phase coexistence region.[6,9] The reference system in these theories is one with hard-sphere interaction. In our dynamical calculation, it is therefore appropriate to use similar ingredients.

From the Enskog theory of dense fluids,[10] we have the following expressions for the three transport coefficients:

$$\eta=\eta_0(1+0.8y+0.761y^2)/Y \;, \tag{2.20a}$$
$$\zeta=\eta_0(1.002y^2)/Y \;, \tag{2.20b}$$
$$\kappa=\kappa_0(1+1.2y+0.755y^2)/Y \;, \tag{2.20c}$$

where η_0, κ_0 are the low-density values of the shear viscosity and thermal conductivity, respectively, $Y = y/(\frac{2}{3}\pi\rho_0\sigma^3)$, and Y is the factor by which the binary collision frequency is increased in the Enskog theory. This factor is usually determined from the knowledge of the equation of state, $p^\dagger(\rho,T)$:

$$y = \frac{1}{\rho_0 kT}\left[T\left[\frac{\partial p^\dagger}{\partial T}\right]_\rho\right] - 1 \ . \qquad (2.21)$$

We use WCA perturbation theory[11] to obtain the equation of state $p^\dagger(\rho,T)$ and hence $(\partial p^\dagger/\partial T)_\rho$ and $(\partial p^\dagger/\partial\rho)_T$. In addition, we need to specify only the nonlocal driving term $\mathscr{L}(k)$ introduced in Eq. (2.8). Traditionally, one would use the square-gradient theory which was introduced by van der Waals[12] to discuss the liquid-vapor interface and by Cahn[1] in the study of spinodal decomposition of solid solutions. This would imply

$$\mathscr{L}_{\text{vdW}}(k) = Ak^2 \ . \qquad (2.22a)$$

In any extension of van der Waals theory, one has to explicitly or implicitly specify the direct-correlation function $c(k)$. An approximate prescription of $c(k)$ used by Abraham[6] gives the generalized van der Waals theory for $\mathscr{L}(k)$,

$$\mathscr{L}_{\text{gvdW}}(k) = 4\pi\int_0^\infty (\cos kx - 1)\Omega_0(x)dx \ , \qquad (2.22b)$$

with

$$\Omega_0(x) = \int_x^\infty u(x)g_2^\dagger(x,\rho_0)x\,dx \ ,$$

where the pair-correlation function $g_2^\dagger$ is calculated for the Lennard-Jones fluid using the WCA perturbation theory.[11] We have used in our computations both the prescriptions (2.20a) and (2.20b) to see how sensitive the qualitative features of $S(\vec{k},t)$ are to the choice of $\mathscr{L}(k)$. $\mathscr{L}_{\text{vdW}}(k)$ and $\mathscr{L}_{\text{gvdW}}(k)$ are compared in Fig. 1.

C. Hydrodyamic modes within unstable region

The dispersion of hydrodynamic modes can be extracted from Eq. (2.17) by setting $\det M = 0$. We obtain the three modes $\alpha_i(k)$ by solving the cubic equation. For a three-dimensional Lennard-Jones system, the phase diagram has been previously investigated using WCA perturbation theory, and the coexistence curve, as well as region of instability, has been determined.

We choose $\rho_0 = 0.35, T_0 = 0.8$ to study the dispersion of modes $\alpha_i(k)$ since this point lies almost in the middle of the unstable region and numerical simulation of spinodal decomposition has been made starting at this point. For this (ρ_0, T_0), the various quantities entering the numerical analysis[13] of the theory are: $D_T = 1.137$, $D_V = 0.850$, $c_v = 1.8$, $a = 2.184$, $b(0) = -8.93$, and the van der Waals constant $A = 7.127$, which is extracted from the small-k limit of Eq. (2.22b). In Fig. 2(a) we display $\alpha_i(k)$ for van der Waals ansatz and in Fig. 2(b) the same for the generalized van der Waals prescription. As expected both of these agree for small k and the general qualitative features are also identical for all k values. For $k < 0.035$, we have three unequal real roots and for larger-k values, we get one real and a pair of complex roots. The real root [always denoted by $\alpha_1(k)$ in the subsequent discussion and by a solid line in Figs. 2(a) and 2(b)] is positive up to some critical wave number k_c and is negative thereafter. Thus for $k < k_c$, we have a growing mode which is related to the hydrodynamic instability in the phase-separation process. In order to understand its physical origin, we have studied the small-k expansion of all the three modes $\alpha_i(k)$. The results are

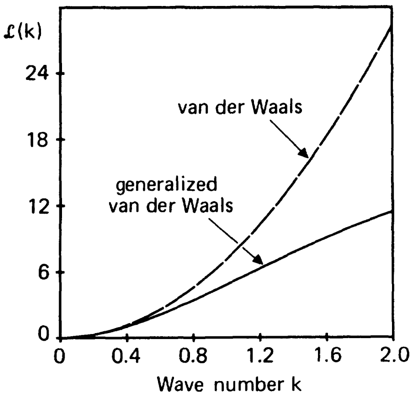

FIG. 1. Comparison of $\mathscr{L}_{\text{vdW}}(k)$ and $\mathscr{L}_{\text{gvdW}}(k)$ for a three-dimensional Lennard-Jones system ($\rho_0 = 0.35$, $T_0 = 0.8$). See Eq. (2.22) in text.

$$\begin{aligned} \alpha_1(k) &= \alpha_{11}k - \alpha_{12}k^2 + O(k^3) \ , \\ \alpha_2(k) &= -\alpha_{11}k - \alpha_{12}k^2 + O(k^3) \ , \qquad (2.23a) \\ \alpha_3(k) &= -\alpha_{32}k^2 + O(k^4) \ , \end{aligned}$$

where

$$\begin{aligned} \alpha_{11} &= [-\rho_0 b(0) - a^2 T_0/c_v]^{1/2} \\ &= \left[-\left[\frac{\partial p^\dagger}{\partial\rho}\right]_T \gamma\right]^{1/2} \ , \\ \alpha_{12} &= \frac{1}{2}\left[D_V + D_T\left[1 + \frac{1}{\gamma}\right]\right] \ , \qquad (2.23b) \\ \alpha_{32} &= D_T/\gamma \ . \end{aligned}$$

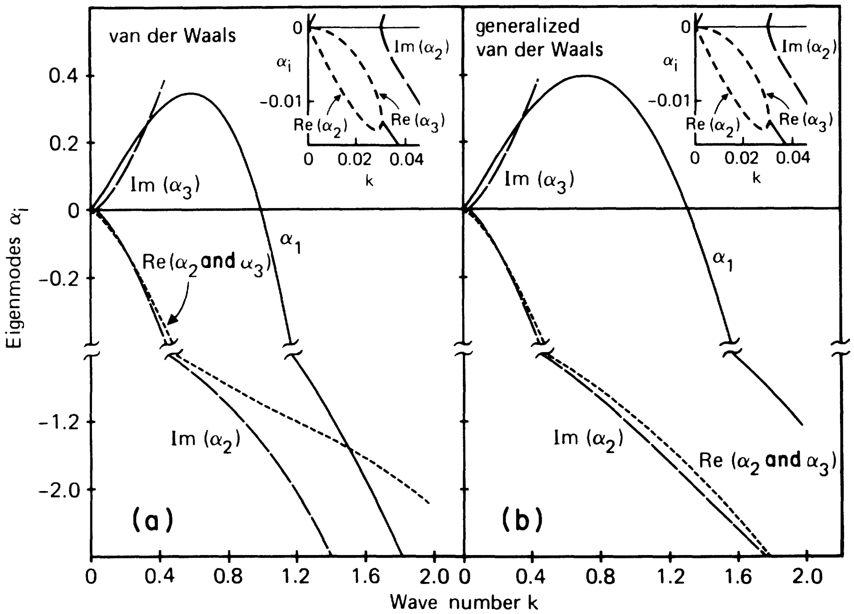

FIG. 2. Dispersion of the hydrodynamic modes within the unstable region of Lennard-Jones liquid-vapor coexistence ($\rho_0 = 0.35$, $T_0 = 0.8$) using (a) van der Waals theory and (b) generalized van der Waals theory. The inserts show the small-k behavior of the modes (see text).

Here we have identified $a^2T_0/[\rho_0 b(0)c_v]$ with $(\gamma-1)$ which is normally positive but is negative in the unstable region. These results are reminescent of the dissipative heat diffusion mode $[\alpha_3(k)]$ and a pair of (normally propagating) sound modes, α_1 and α_2. In the stable one-phase region, $(\partial p/\partial\rho)_T$ is a positive number, and α_{11} becomes pure imaginary, ic_0, where c_0 is the adiabatic sound speed. In the unstable part of the phase diagram, however, $(\partial p/\partial\rho)_T$ is negative, and we get α_{11} as a real positive number. Thus we see that at the spinodal line and within the spinodal, the complex pair of sound modes turn into real roots, and one of these, $\alpha_1(k)$, acquires the characteristics of a growing mode. For $\alpha_i(k)$ given in Figs. 2(a) and 2(b), we have found that the small-k expansion, Eq. (2.23), gives correct results up to a k of about 0.03.

One further characteristic of the growing mode can be directly inferred from the dispersion equation $\det M = 0$, Eq. (2.17). At a well-defined wave vector $k = k_c$, the quantity $b(k_c)$, and hence also the constant coefficient $a_0(k_c)$, becomes zero. Thus one of the roots becomes zero. This is the growing mode root α_1, since α_2 and α_3 are found to have their real part to be negative for all k. The critical wave vector k_c depends only on thermodynamic properties since it is determined from

$$b(k_c) \equiv \left[\frac{1}{\rho_0} \left[\frac{\partial p^\dagger}{\partial\rho} \right]_T + \mathscr{L}(k_c) \right] = 0 \,. \qquad (2.24)$$

For van der Waals ansatz,

$$k_c = \left[-\frac{1}{\rho_0 A} \left[\frac{\partial p^\dagger}{\partial\rho} \right]_T \right]^{1/2} .$$

These results are well known.[6]

III. STRUCTURE FACTOR: COMPARISON OF THEORY AND EXPERIMENT

Using the hydrodynamic modes α_i of van der Waals (vdW) and generalized van der Waals (gvdW) theory [Figs. 2(a) and 2(b), respectively], we numerically evaluate Eq. (2.18) to obtain the time-dependent structure factor. The results are plotted in Figs. 3(a) and 3(b) for different times after the quench. For $S(k,0)$ we use the experimental data[6] just after the quench to be able to compare the theoretically predicted time evolution with experiment. Figures 3(a) and 3(b) show a very similar overall behavior of $S_{\rm gvdW}$ and $S_{\rm vdW}$. The structure factor in generalized van der Waals theory is broader than $S_{\rm vdW}$ because the critical wave number k_c(gvdW) is larger than k_c(vdW). The faster growth of $S_{\rm (gvdW)}$ reflects the greater positive values of α_1(gvdW) in comparison to α_1(vdW).

In Fig. 4 the experimental structure factor is plotted for several times after the quench. For small times (lowest curves), theory and experiment agree quite well. For later times, linearized hydrodynam-

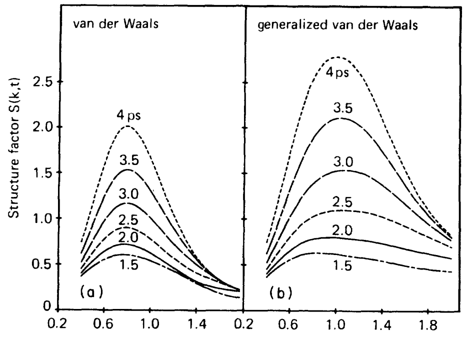

FIG. 3. Theoretical structure factor $S(\vec{k},t)$ vs k for various times after quench. (a) van der Waals ansatz for $\mathscr{L}(k)$, (b) generalized van der Waals $\mathscr{L}(k)$.

TABLE I. Peak position of structure factor comparison between theoretical and experimental values.

t(ps)	$k_{\max}$ theory vdW	$k_{\max}$ theory gvdW	$k_{\max}$(expt)
2	0.78	0.92	0.78
3	0.78	1.06	0.74
4	0.77	0.98	0.72
5	0.76	0.92	0.68
6	0.74	0.88	0.67

ic theory clearly overestimates the absolute values of $S(k,t)$. Nonlinear contributions will slow down this growth rate. In addition, we have listed in Table I, as a function of time, the wave number $k_{\max}$, at which the structure factor has a maximum. The experiment shows a decrease of $k_{\max}$ with increasing times due to the coarsening process. Qualitatively, this feature is described even by our linear theory.

In order to make a sensitive comparison of our theory with the molecular dynamics experiment, we deduce an "effective growing mode α_{eff}" from the experimental time-dependent structure factor $S_{\text{expt}}(k,t)$ in the following way: (1) in Eq. (2.17), $S(k,t)$ is taken to be equal to the measured $S_{\text{expt}}(k,t)$; (2) α_1 is assumed to be unknown, and is denoted by α_{eff}; (3) α_2,α_3 are assumed to be given by theory Eq. (2.18); and (4) a solution for $\alpha_{\text{eff}}(k)$ is obtained and compared with the theoretical α_1. This procedure was done using α_2,α_3 from the van der Waals dispersion [Fig. 2(a)] and from the generalized van der Waals dispersion [Fig. 2(b)]. In Fig. 5 we present the comparisons for both prescriptions and for several times after the temperature quench. These times are the earliest measurements in the simulation experiment where linear behavior is most probable. It is very gratifying that the effective amplification factor α_{eff} is of the same qualitative magnitude as the α_1 for each prescription, even though the theory has no adjustable parameters. Quantitatively, the generalized van der Waals description yields α_1 and α_{eff} that are in very good agreement over the entire range of wave numbers at the earliest times. However, α_{eff} from the approximate van der Waals picture deviates unphysically for large wave numbers, and the magnitudes of α_1 and α_{eff} are not in as good agreement. Furthermore, this is in contrast to the results of a similar analysis based on the diffusion-fluctuation dynamical theory of Cahn-Cook, where comparison between the effective amplification factor and the theoretical mode did not show good quantiative agreement (see Fig. 25 of Ref. 6). For later times,

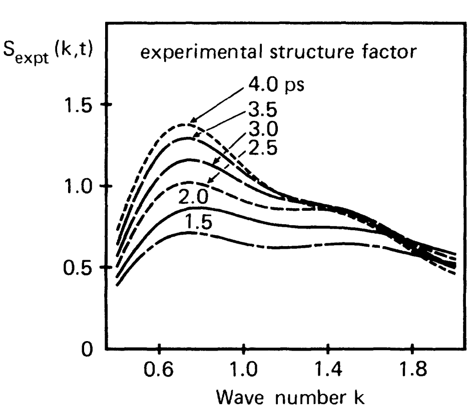

FIG. 4. Experimental structure factor $S_{\text{expt}}(\vec{k},t)$ vs k. Results of molecular dynamics experiments for several times after the quench (see Ref. 6).

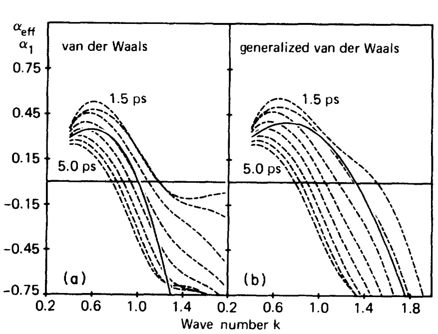

FIG. 5. Comparison of the theoretical growing mode α_1 (solid line) predicted by (a) van der Waals and (b) generalized van der Waals theory with the effective amplification factor α_{eff} (dashed lines) obtained using experimental structure factor measurements for a Lennard-Jones fluid quenches to the unstable region of the phase diagram ($\rho_0=0.35$, $T_0=0.8$).

nonlinear coarsening destroys the agreement with linear theory.

IV. SPINODAL DECOMPOSITION IN BINARY MIXTURES

The hydrodynamic instability in binary mixtures during the spinodal decomposition occurs because the thermodynamic derivative of chemical potential μ with respect to concentration c, $(\partial\mu/\partial c)_{p,T}$, becomes negative within the spinodal region in the c-T plane. The generalization of the linear theory (see Sec. II) to binary mixtures can be made in a straightforward manner. To a good approximation the intensity in x-ray diffraction experiments involves only the concentration fluctuations and the time-dependent structure factor is written as

$$S(\vec{k},t)=\langle\, |c_k(t)|^2 \rangle \; . \tag{4.1}$$

The appropriate hydrodynamic variables are c, p, ψ, and T. The set of coupled hydrodynamic equations including the hydrodynamic fluctuations are[14] (in $\vec{k},t$ space)

$$\rho_0\frac{\partial c_k}{\partial t}=-\alpha k^2\left\{(g_0''+2K_0k^2)c_k(t)-\frac{1}{\rho_0^2}\left[\frac{\partial\rho}{\partial c}\right]_{p,T}p_k(t)+\left[\left[\frac{\partial\mu}{\partial T}\right]_{c,p}+\frac{\beta}{\alpha}\right]T_k(t)\right\}-i\vec{k}\cdot\vec{f}^c(\vec{k},t)\; , \tag{4.2}$$

$$\left[\frac{\partial\rho}{\partial c}\right]_{p,T}\frac{\partial c_k}{\partial t}+\left[\frac{\partial\rho}{\partial p}\right]_{c,T}\frac{\partial p_k}{\partial t}+\left[\frac{\partial\rho}{\partial T}\right]_{c,p}\frac{\partial T_k}{\partial t}=-\rho_0\psi_k(t)\; , \tag{4.3}$$

$$\rho_0\frac{\partial\psi_k}{\partial t}=k^2p_k(t)-(\zeta+\tfrac{4}{3}\eta)k^2\psi_k(t)-\vec{k}\vec{k}:\vec{s}_k(t)\; , \tag{4.4}$$

$$-\rho_0\left[\left[\frac{\partial\mu}{\partial T}\right]_{c,p}+\frac{\beta}{\alpha}\right]\frac{\partial c_k}{\partial t}+\frac{T_0}{\rho_0}\left[\frac{\partial\rho}{\partial T}\right]_{c,p}\frac{\partial p_k}{\partial t}+\rho_0c_p\frac{\partial T_k}{\partial t}=-\kappa k^2T_k(t)+i\vec{k}\cdot\vec{g}_k(t)-\frac{T_0\beta}{\alpha}i\vec{k}\cdot\vec{f}^c(\vec{k},t)\; , \tag{4.5}$$

where the hydrodynamic fluctuations $\vec{f}^c$ and $\vec{g}$ are related to the Onsager coefficients α and β as

$$\langle f_i^c(t_1)f_j^c(t_2)\rangle=2T_0\alpha\delta_{ij}\delta(t_1-t_2)\; , \tag{4.6}$$

$$\begin{aligned}\langle f_i^c(t_1)g_j(t_2)\rangle&=\langle g_i(t_1)f_j^c(t_2)\rangle\\&=2T_0^2\beta\delta_{ij}\delta(t_1-t_2)\; .\end{aligned} \tag{4.7}$$

Owing to the coupling of concentration and temperature fluctuations, Eq. (2.7c) is modified to

$$\langle g_i(t_1)g_j(t_2)\rangle=2T_0^2(\kappa+T_0\beta^2/\alpha)\delta_{ij}\delta(t_1-t_2)\; . \tag{4.8}$$

The fluctuations in the viscous stress tensor are unaffected and $\vec{s}_k(t)$ still satisfies an equation identical to Eq. (2.7b) with the viscosities appropriate to binary mixtures. Also $\vec{s}_k$ is uncorrelated with both $\vec{g}$ and $\vec{f}^c$. In Eq. (4.2), the concentration term is at the level of linear theory of van der Waals; the second derivative of Gibbs free-energy density appears since $c_k(t)$ is the mass concentration fluctuation. In a nonlinear theory, this term would be modified as (in $\vec{r},t$ space)

$$\alpha\vec{\nabla}\cdot[g''(c)-2K(c)\nabla^2]\vec{\nabla}c\; , \tag{4.9}$$

where $g(c)$ and $K(c)$ have to be specified. Cahn[15] has discussed a theory with the choice $K(c)=K_0$ and $g''(c)=g_0''+g'''(\delta c)+1/2g''''(\delta c)^2$. In the linear theory, coupling of $c_k(t)$ to the hydrodynamic variables p_k and T_k occurs through the second and third terms on the right-hand side of Eq. (4.2). It is known that the coefficients of pressure diffusion and thermal diffusion which represent these couplings are very small at liquid densities.[16] Thus to an excellent approximation concentration fluctuations decouple in a linear theory. Introduction of hydrodynamic fluctuation $\vec{f}^c$ in Eq. (4.2) then puts the theory on the level of the Cahn-Cook[1,2] theory. For fluid mixtures, nonlinearities can occur either through $g(c)$,$K(c)$ as in the expression (4.9) or they can also occur through the bilinear convection term $\rho_0\vec{v}\cdot\vec{\nabla}c(\vec{r},t)$ which would be present in nonlinear hydrodynamics. Such a nonlinearity would couple $c_k(t)$ to $\psi_k(t)$ and has been considered by Kawasaki and Ohta.[4] At the level of linear hydrodynamics, however, we see that the linear Cahn-Cook description[1,2] is an adequate approximation, in contrast to one-component system.

V. CONCLUSION

We have demonstrated that linear hydrodynamics, including stochastic fluctuations and nonlocal driving force, gives a good description of spinodal decomposition at early times for a one-component fluid. We have also constructed a similar theory for two-component fluid mixtures. We find that within the linear regime of spinodal decomposition of a binary fluid, the coupling of concentration fluctuations to the hydrodynamic flow effects is negligible, and the Cahn-Cook theory is obtained.

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