Dispersion relation around a kink solution in binary fluids undergoing spinodal decomposition

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A numerical study is presented of the dispersion relation for the linearized operator about the kink or interfacial wall solution to a model of spinodal decomposition of an incompressible binary fluid. The essential spectrum of the linearized operator does not stay well separated from the Nambu-Goldstone- (NG-) like mode representing purely interfacial motion. For large wave vector k along the interface, the NG-like mode decays as $\omega \sim k^3$, while for small wave vector it decays as $\omega \sim k$. However, the bottom of the essential spectrum decays like $\omega \sim k^2$ and at small enough k, it intersects the point spectrum, the NG-like mode. The dispersion relation of the NG-like modes as one varies the viscosity indicates a nonuniversal crossover behavior from $\omega \sim k^3$ to $\omega \sim k$, due to the interaction between NG-like mode and the essential spectrum.

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The asymptotic growth law of the average pattern size L in the spinodal decomposition process of an incompressible binary fluid (critical quench case) in three-space appears to be given by $L \sim t$ with a possible crossover from $L \sim t^{1/3}$ at earlier times [1]. Actual experimental results [2], computational studies [3,4], and dimensional analysis from an interfacial equation of motion [5] suggest that the $L \sim t$ is a universal asymptotic relation. However, numerical simulations based on this equation exhibit unusual behavior and sometimes instability at small values of the viscosity. The dispersion relation [6] for the Cahn-Hilliard [7] (CH) equation has proved useful in studying the pre-asymptotic and asymptotic growth law in spinodal decomposition in binary alloys at critical quench [8,4]. In the CH case, the dispersion relation was empirically found to be universal, explaining the empirically found pre-asymptotic universality in the ordinary spinodal decomposition. Thus it is expected that the study of the dispersion relation of waves on the interface of a model appropriate to incompressible binary-fluid phase separation is highly relevant to understanding the pre-asymptotic behavior of fluid systems.

In this paper, the linearized operator of small fluctuations about the kink solution is studied for a model by Kawasaki [9]. The essential spectrum is found not to be separated from the point spectrum. The study of the dispersion relation for the Nambu-Goldstone (NG) branch of the point spectrum and its interaction with the essential spectrum leads us to the conclusion that the pre-asymptotic universality found in the CH case [8] does not exist.

In the CH case, the point spectrum is a branch continuous to the true NG mode for the kink solution. This will be referred to as the NG branch. The essential spectrum of the CH case was separated from the NG branch except at $k=0$, where k is the wave vector along the flat interface. In the present case, as in the CH case, the bottom of the essential spectrum is found to follow $\omega \sim k^2$ at small k while the NG branch follows $\omega \sim k$. Thus the essential spectrum is not separated from the NG branch even at finite k.

The equation of motion for the phase separation of a binary incompressible fluid is [9]

$$\frac{\partial \psi}{\partial t} = M\nabla^2\mu(\mathbf{r}) - \nabla\psi(\mathbf{r})\cdot\int d^d r' \mathsf{T}(\mathbf{r}-\mathbf{r}')\cdot\nabla'\psi(\mathbf{r}')\mu(\mathbf{r}') , \tag{1}$$

where $\mu \equiv -D\nabla^2\psi + \mu_0(\psi)$ is the chemical potential and the Oseen tensor $\mathsf{T}(\mathbf{r}')$ is defined through

$$\int d^d r\, \mathsf{T}(\mathbf{r})\exp(-i\mathbf{k}\cdot\mathbf{r}) \equiv \mathsf{T}(\mathbf{k}) = \frac{1}{\eta k^2}\left[\mathsf{I} - \frac{\mathbf{k}\otimes\mathbf{k}}{k^2}\right] , \tag{2}$$

where η is the kinematic viscosity, I is the identity matrix, and $\otimes$ is the outer product.

Unfortunately, the linearized operator is very complex in this case, so one is content to set up the eigenvalue problem in such a way as to be able to numerically extract out the behavior with accuracy.

Define $\psi_0(z)$ as the equilibrium wall solution from $-D\partial_z^2\psi(z) + \mu_0(\psi(z)) = 0$, where $\psi(0)=0$, $\psi(\infty)=\psi_+$, the upper bulk equilibrium value, and $\psi(-\infty)=\psi_-$, the lower bulk equilibrium value. To find the equation of motion for small fluctuations about the wall solution, it is assumed that $\psi(r,t) = \psi_0(z) + u(r)e^{-\lambda t}$. To first order in $u(r)$ one gets

$$\begin{aligned} -\lambda u(\mathbf{r}) = {} & M\nabla^2[\mu_0'(\psi_0(z))u(\mathbf{r}) - D\nabla^2 u(\mathbf{r})] \\ & - (\nabla\psi_0(z))\cdot\int d^d r\, \mathsf{T}(\mathbf{r}-\mathbf{r}')\cdot(\nabla'\psi_0(z)) \\ & \times[\mu_0'(\psi_0(z'))u(\mathbf{r}) - D\nabla^2 u(\mathbf{r})] , \end{aligned} \tag{3}$$

where $\mu_0'(\psi) \equiv \delta\mu_0/\delta\psi$. The first term of the right-hand side of Eq. (3) is the linearized Cahn-Hilliard operator. Only the z component of $\nabla\psi_0(z)$ survives, and one may Fourier transform in the two-space transverse to the z axis. First define

$$\mathsf{T}^k_{zz}(z)=\int \frac{dk_z}{2\pi} e^{ik_z z}\frac{1}{\eta(k^2+k_z^2)}\left[1-\frac{k_z^2}{k^2+k_z^2}\right], \quad (4)$$

where $\mathbf{k}$ is a Fourier mode in the x and y coordinates. Likewise define

$$L_k(z)=-D(\partial_z^2-k^2)+\mu_0'(\psi_0(z)) . \quad (5)$$

The Fourier transform of Eq. (3) in coordinates transverse to z now reads

$$-\lambda u_k(z)=M(\partial_z^2-k^2)L_k(z)u_k(z) -\psi_0'(z)\int dz'\mathsf{T}^k_{zz}(z-z')\psi_0'(z')L_k(z')u_k(z') . \quad (6)$$

Let $G^k(z-z')$ be the Green's function defined as $(\partial_z^2-k^2)G^k(z-z')=\delta(z-z')$, with the boundary condition $G_k\to 0$ as $|z|\to\infty$. Define $E_k(z-z')=-2kG^k(z-z')$ and apply G^k to Eq. (6) to get

$$\frac{\lambda}{2k}\int dz''E_k(z-z'')u_k(z'')=ML_k(z)u_k(z)+\frac{1}{2k}\int dz''E_k(z-z')\psi_0'(z'')\int dz'\mathsf{T}^k_{zz}(z''-z')\psi_0'(z')L_k(z')u_z(z') . \quad (7)$$

Solving for $\mathsf{T}^k_{zz}(z-z')$ and $G^k(z-z')$ yields

$$\mathsf{T}^k_{zz}(z-z')=\frac{1}{4\eta}\left[\frac{1}{k}+|z-z'|\right]e^{-k|z-z'|}, \quad G^k(z-z')=-\frac{1}{2k}e^{-k|z-z'|} . \quad (8)$$

Integration by parts transforms the second integral of the second term on the right-hand side of Eq. (7) and one arrives at

$$\frac{\lambda}{2k}\int dz' e^{-k|z-z'|}u_k(z') =ML_k(z)u_k(z)+\frac{D}{8\eta}\int dz'' e^{-k|z-z''|}\psi_0'(z'')\left[\left[2\psi_0'(z'')u_k(z'')+\int dz' e^{-k|z''-z'|}\psi_0'(z')u_k(z')\right] +k\left[\int dz'\{\mathrm{sgn}(z''-z')\psi_0''(z')+|z''-z'|\psi_0'(z')\}e^{-k|z''-z'|}u_k(z')\right]\right] . \quad (9)$$

If one substitutes the NG mode, $\psi_0'(z)=u_k(z)$, as an approximation for small k, and $e^{-k|z|}\approx 1$, one finds that $\lambda\sim k$ as expected.

To be more explicit, let us use

$$\mu=-D\nabla^2\psi+\psi-A\tanh[\tanh^{-1}(A^{-1})\psi] , \quad (10)$$

the chemical potential relevant to the cell dynamical system (CDS) method [8,10] used in the existing three-dimensional incompressible binary-fluid simulations [3,4]. The general asymptotic results should not critically depend on the potential used. The various eigenvalue branches are determined as functions of k. The parameters D and M in the CDS models [10,4], called D_{CDS} and M_{CDS}, respectively, are proportional to the D and M used in this paper. In three-dimensional space, $D=\frac{11}{40}D_{\mathrm{CDS}}$ and $D=\frac{1}{3}D_{\mathrm{CDS}}$ due to the definition of the neighbor average used. $D_{\mathrm{CDS}}=0.7$, $A=1.3$, $M_{\mathrm{CDS}}=1.0$, and $\eta=1.0$ are chosen to make contact with results in another paper [4].

The spectrum of Eq. (9) is computed by solving it as a generalized eigenvalue problem $(\lambda/2k)\mathcal{B}u=\mathcal{A}u$. $\mathcal{B}$ is the discrete version of the left-hand side operator of Eq. (9) and $\mathcal{A}$ is the right-hand side operator. The discrete eigenvalue problem is computed over a lattice spanning $-10\le z\le 10$, using 384 equally spaced points. Figure 1 shows the branches of $\omega/(2k)$ vs k. Note that the lowest branch becomes nearly a constant at small k which implies that $\omega\sim k$. If it may be assumed that there is only one representative length scale other than the thickness of the interface (i.e., the correlation length), and if the essential spectrum does not interfere with the NG branch, then this would imply that the $L\sim t$ asymptotic law is exact. This is the NG branch of the point spectrum which corresponds to the decay of interfacial fluc-

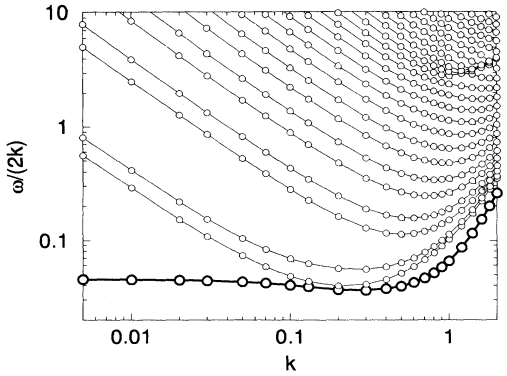

FIG. 1. Plot of $\omega/(2k)$ vs k for $\eta=1$. Computed on the interval $-10\le z\le 10$. White circles denote computed eigenvalues. The lowest branch, plotted with a dark black line, is the NG-like mode which describes interfacial motion. The upper branches are extended states which are the finite-size version of the essential spectra. ω and k are in units of the inverse cos(time step) and lattice spacing, respectively.

tuations analogous to those found in the binary-alloy case. However, there are several pairs of modes that lie above the NG mode. As shown below, they are the finite-size representations of the essential spectrum, and intersect the point spectrum.

Figure 2 gives the result of the same eigenvalue problem on a larger system size, $-30 \le z \le 30$, over 512 equally spaced points. The density of the upper modes becomes higher, which indicates that the modes above the NG mode are in the essential spectrum of the infinite system. These problematic modes now impact on the NG branch. Note that the NG branch from the previous smaller system (Fig. 1) follows a branch through the essential spectrum. The eigenfunction corresponding to this branch, an NG-like mode, are identical to the NG branch found in the previous smaller system. These eigenfunctions tend to decay exponentially at the tails, while the other "eigenfunctions" show wavelike behavior at large z, as is shown later. Unfortunately, the existence of an essential spectrum which is not well separated from the point spectrum means it is impossible to construct a proof analogous to the Cahn-Hilliard case [8] on the $k \to 0$ behavior of the NG branch.

To make a more definitive examination of the dispersion relation as related to the growth law, the computed eigenvalues are replotted with k vs ω^{-1} in Fig. 3. This is convenient since dimensionally $\omega^{-1} \sim t$ and is thus more like a growth law plot of $\langle k \rangle$ vs t. Figure 3 is a log-log plot of k vs ω^{-1} on an even larger system defined on $-60 \le z \le 60$. The plot of the NG branch has the expected form of $k \sim \omega^{1/3}$ for small ω^{-1} or short time, and $k \sim \omega$ for large ω^{-1} or long time. Note that the bottom of the essential spectrum, which in this plot is the top set of essential spectrum lines, behaves like $\omega \sim k^2$. The dispersion relation $\omega \sim k^2$ is reminiscent of ordinary bulk diffusion, although in the present case this is the bottom of the essential spectrum.

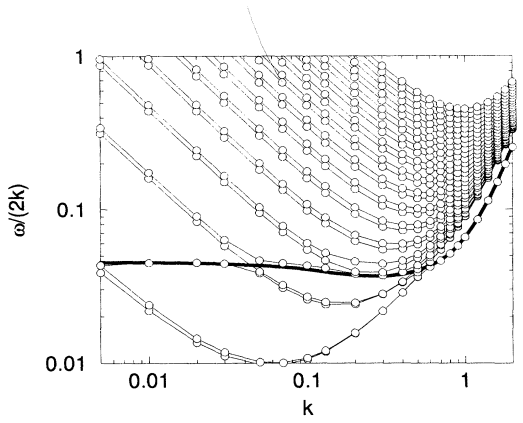

FIG. 2. Plot of $\omega/(2k)$ vs k for $\eta = 1$, computed on the interval $-30 \le z \le 30$. Computed eigenvalues are denoted by white circles. The dark black line is the NG-like mode dispersion relation, computed on the interval $-10 \le z \le 10$. In the $-10 \le z \le 10$ case, it did not intersect the extended states. In the present case, the lowest branch for $k > 0.6$ is the NG-like mode. The lowest branch for $k < 0.6$ are extended states. The set of points which lie along the dark black line are NG-like modes, although they lie within the essential spectrum.

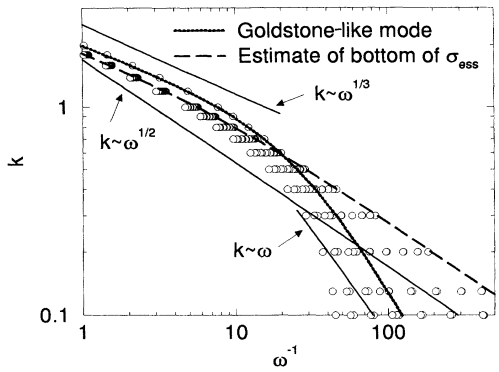

FIG. 3. Plot of k vs ω^{-1} for $\eta = 1$. The NG-like branch computed on the interval $-10 < z < 10$ is represented by the dotted line. The white circles represent the various eigenvalues computed on the interval $-60 \le z \le 60$. Points calculated for the larger system which lie close to the NG-like branch computed on the small system are themselves NG-like modes. The dashed line is the bottom of the essential spectrum as estimated from the linearized Cahn-Hilliard term of Eq. (3) by Eq. (11). Note the various power-law behaviors of the different branches in different regimes.

The bottom of the essential spectrum is expected to be roughly that of CH case for large η since the k^2 term in the binary-fluid dispersion relation is multiplied by η^{-1}. The bottom of the CH essential spectrum can be computed explicitly using a theorem by Rota [11,8] as

$$\omega_{\text{bottom ess}} = MDk^4 + M\mu'(\psi_0(\pm\infty))k^2 , \tag{11}$$

where $\mu'(\psi) = \delta\mu/\delta\psi$, and $\psi_0(z)$ is the equilibrium wall solution. In our case, $\psi'(\psi_0(z \to \infty)) \sim 0.459$, $M = \frac{11}{40}$, and $D = (\frac{11}{40})0.7$. The essential spectrum could be ignored in the CH case since they were isolated away from the slowest decaying branch, the NG branch for which $\omega \sim k^3$ for small k [8].

The effect of larger η can be seen by examining the eigenvalues for $\eta = 10$ in Fig. 4. In the infinite volume lim-

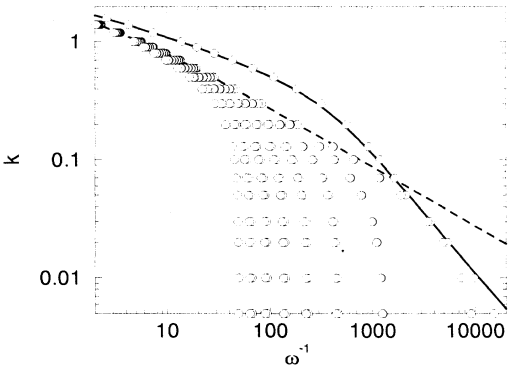

FIG. 4. Plot of k vs ω^{-1} for $\eta = 10$. The circles represent eigenvalues computed on the interval $-60 \le z \le 60$. The dark black line represents the lowest branch computed on the smaller interval. The dotted line represents the bottom of the essential spectrum estimated from the linearized Cahn-Hilliard term.

it, the bottom of the essential spectrum should be almost like the Cahn-Hilliard case and thus, as η gets larger, the NG branch separates further from the essential spectrum while the NG branch is in the $\frac{1}{3}$ regime. Eventually, the NG branch becomes $\omega \sim k$, and must intersect with the bottom of the essential spectrum. If η is large, then the NG branch behaves essentially like $\omega \sim k$ when it hits the essential spectrum. If η is not very large, the NG branch will hit the essential spectrum before it reaches the asymptotic behavior of $\omega \sim k$. In the case of $\eta = 1$ the latter occurs.

It is interesting to inspect the form of the eigenfunctions generated by the above which correspond to the NG branch and the lowest paired eigenvalues which represent the bottom of the essential spectrum. The eigenfunctions for $\eta = 10$ are shown in Fig. 5. The NG-like mode has the form of the normal kink solution NG mode. The NG mode represents simple translations of the interface. The NG-like mode is the z-axis part of a decaying interfacial fluctuation of wave-vector k transverse to z. The general form of these eigenfunctions are qualitatively independent of η. The discrete representatives of the essential spectrum in Fig. 5 have two forms. The first look somewhat like the NG mode in the middle, but has a symmetric wavelike structure at large z. This implies interfacial motion linearly couples with relaxations of bulk fluctuation. In this case, the wall moves, while one phase loses bulk and the other gains. The other form is a antisymmetric wavelike structure which implies a type of bulk mode which does not move the interface, but is a relaxation of fluctuation in the bulk amplitude. In this case, the complementary bulk phases exchange material and either rid or rather their own phase.

It must be stressed that these are decaying fluctuations so that if the fluctuation does not exist, they will have no effect on the kinetics. The decay of fluctuations which differs from the $\omega \sim k$ type could modify the growth law in the full nonlinear problem. On the other hand, if the bulk fluctuations are already tamed as the system enters the essential spectrum region, it may be that there is no coupling, and the interfacial fluctuations decay by the NG-like mode even if it exists in the essential spectrum. During domain connection and disconnection, which happens frequently in near critical quench situations, the bulk is often perturbed out of equilibrium. In this case, the essential spectrum may play a role in the kinematics.

In Fig. 6, the NG branch dispersion relations of many different η are scaled by plotting $\eta^{1/2}k$ vs $\eta^{-3/2}\omega^{-1}$. While this causes the curves to qualitatively overlap in the small and intermediate k regions, one can see that the crossover region admits many rather different knee bends. In this sense, there is no universality in the way the crossover to $L \sim t$ occurs. The same type of dispersion relation universality as in the Cahn-Hilliard case does not appear here. The curves do coincide roughly, and taken together could accidentally suggest a universal curve.

In test simulations [4], where the CDS model parameters were fixed as mentioned above, but η was adjusted, two main difficulties appeared. The first occurred at very low viscosity, e.g., $\eta \sim 0.1$. In this case, the bulk phase of the domains reached only about 0.8 times the equilibrium bulk value, even as the domain morphology coarsened as expected. The other problem occurred at about $\eta \sim 0.5$. In this case, the domains reached the equilibrium value, but the simulation was unstable afterwards. Small time steps and accurate updating of the velocity field were necessary to do the simulation. These difficulties appear to be related to the essential spectrum and point spectrum emerging. This is further discussed in Ref. [4].

In summary, the dispersion relation of the NG branch of the point spectrum corresponding to the relaxation of interfacial fluctuations was shown to obey the form $\omega \sim k$ at small k by the numerical study of the linearized operator. However, the point spectrum merges with the essential spectrum which arises primarily from the CH term in the dynamics. This suggests that the pre-asymptotic

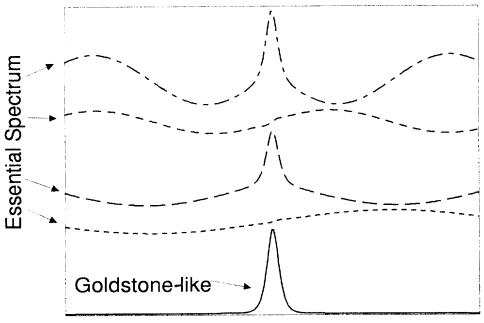

FIG. 5. Representative eigenfunctions computed for $\eta = 10$ at $k = 0.2$ on interval $-30 \le z \le 30$. The various functions are placed in order of their corresponding eigenvalue. The lowest mode is represented in solid black. It is an NG-like mode, which generates translation of the interface. The four lowest extended states are represented by broken lines. The extended states have two types, one symmetric, with an NG-like central part. The antisymmetric form does not translate the interface.

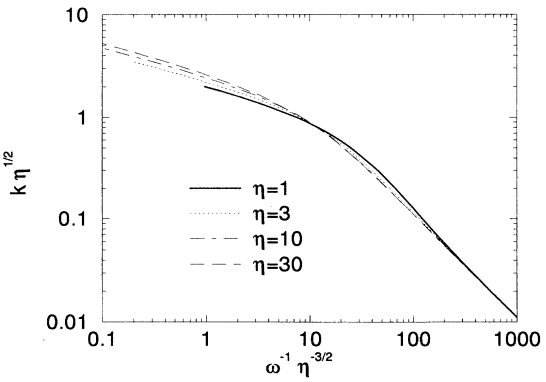

FIG. 6. The NG-like mode dispersion relations for various η are potted with all other model parameters fixed. The scaling $k \to \eta^{1/2}k$ and $\omega^{-1} \to \eta^{-3/2}\omega$ brings the curves nearly together; however, the actual knee of the curve is not the same.

universality found for the CH case does not exist in the binary-fluid case and the existence of the essential spectrum does appear to have a material effect binary-fluid spinodal decomposition particularly in simulations.

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