



Fluctuations in the structure of interfaces

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Abstract

We study the stability matrix (the matrix of second derivatives of the free energy functional with respect to the density at each point in the system) for various phenomenological models of interfaces between coexisting phases. The eigenvectors and eigenvalues of that matrix are the eigenmodes, and their inverse susceptibilities, of fluctuations of the interface. We find that, due to the presence of the interface, several discrete eigenvalues typically appear in addition to the continuous bands of eigenvalues of the bulk phases. Some features appear to be generic, while others depend on the details of the model. © 1997 Elsevier Science B.V.

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1. Introduction

The equilibrium profile of an interface between two coexisting phases can be found by minimizing a suitable excess free energy functional. If one is interested in small fluctuations of the density profile around this minimum, the appropriate object to study is the stability matrix, the matrix of second derivatives of the free energy functional with respect to the density at each point in the system. The eigenvectors and eigenvalues of this matrix are the eigenmodes of the fluctuations of the system, and the inverse susceptibilities of the system to those eigenmodes. For a system in a stable equilibrium configuration, all susceptibilities must, of course, be positive. In addition, the stability matrix is closely related to the direct correlation function; hence, the scattering function can also be expressed in terms of its eigenvalues and eigenvectors [1,2].

In earlier work [3], the eigenvalues of the stability matrix were calculated to check the stability of an interface in a model of a system of coexisting lamellar phases. There, it was found that the introduction of the interface into the system caused only small changes in the set of eigenvalues: the continua that belonged to the bulk phases remained essentially unchanged, while a few discrete eigenvalues detached themselves from them. An examination of the associated eigenvectors has since shown that two of them are localized near the interface, and two near the ends of the (finite) system that was used for the calculation. So the interface between those two phases gives rise to two discrete eigenvalues. This problem is closely analogous to that of lattice vibrations in a harmonic lattice with defects [4].

Here, we extend the study of the eigenvalues and eigenvectors of the stability matrix to more general phenomenological models of interfaces between coexisting phases. In the next section, we give a general discussion of the problem in mean field approximation, and then specialize to two

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cases for which explicit results were obtained. The first of these is the familiar squared gradient theory, with various suitable choices for the bulk free energy $F(\rho)$, for which analytic results can be found. Then we give numerical results for a more general model. In both cases, the picture is confirmed that a number of discrete eigenvalues, associated with the presence of the interface, is added to the continua of eigenvalues that arise from the bulk phases. The number of such discrete eigenvalues depends on the details of the model. In addition, one or more continua of eigenvalues that are also associated with the interface can exist.

2. Fluctuations of the interface

The density profile in an interface between two coexisting phases is depicted schematically in Fig. 1, as a function of z , the coordinate perpendicular to the interface. The mean density $\rho(z)$ varies smoothly from the vapor density ρ_v at $z = -\infty$ to the liquid density ρ_l at $z = \infty$. We model the

particles of the fluid as hard spheres, with diameter b , interacting via a (spherically symmetric) attractive potential $\phi(r)$. In mean field theory, the excess free energy (per unit area) of an interface in such a system, with density profile $\rho(r)$ and surface area A , is given by [5,6]

$$\sigma = \frac{1}{A} \int d^3r \left\{ F[\rho(r)] + \frac{1}{2} \rho(r) \int_{r,r'>b} \times d^3r' \phi(r') [\rho(r+r') - \rho(r)] \right\} \quad (1)$$

This expression contains two contributions. The first, $F[\rho(r)]$, is the free energy excess (per unit volume) of a homogeneous fluid of density $\rho(r)$. It represents the cost of having values of the density, in the interfacial region, that are different from the equilibrium liquid and vapor densities, ρ_l and ρ_v . In the mean field approximation it is given by

$$F(\rho) = F_{\text{hs}}(\rho) - a\rho^2 \quad (2)$$

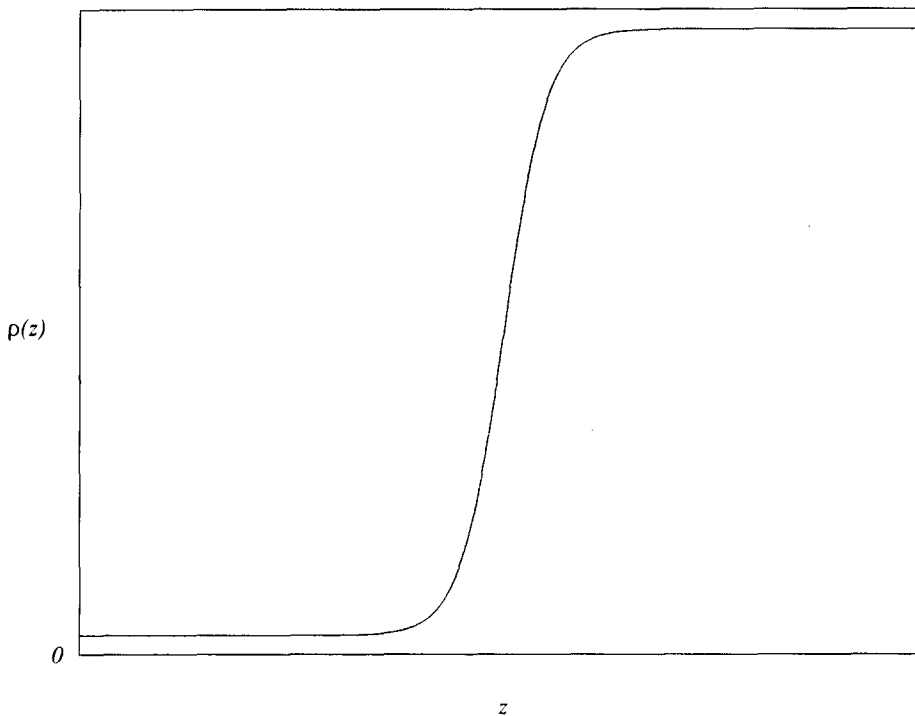


Fig. 1. Schematic density profile of a liquid–vapor interface.

where $F_{\text{hs}}(\rho)$ is the corresponding quantity for a reference system of hard spheres, and

$$a = -\frac{1}{2} \int_{r>b} d^3r \phi(r) \quad (3)$$

is the van der Waals constant a , representing the effect of the attractive interaction $\phi(r)$ between the molecules of the fluid. $F_{\text{hs}}(\rho)$ can be calculated from one of various approximate equations of state for a hard-sphere system, such as the van der Waals (with $a=0$) or Carnahan–Starling [7] equation of state. $F(\rho)$ is qualitatively as shown in Fig. 2, with two equal minima at the two coexisting densities ρ_1 and ρ_2 . The second term in Eq. (1) is the extra free energy due to the inhomogeneity of the density in the interfacial region. (The integral is over values of $r'=|r'|$ larger than the particle diameter b .) That second term is the difference (in mean field approximation) between the interaction energy of a homogeneous system and that of a system with density profile $\rho(r)$.

The density profile that minimizes the free

energy (1) is found by solving the Euler–Lagrange equation obtained by setting the first functional derivative of σ equal to zero:

$$\frac{\delta\sigma}{\delta\rho(\mathbf{r})} = 0 \quad (4)$$

To verify that a stationary point $\bar{\rho}(\mathbf{r})$ found from Eq. (4) is actually a minimum, the second functional derivative evaluated at $\bar{\rho}(\mathbf{r})$,

$$A(\mathbf{r},\mathbf{r}') = \left. \frac{\delta^2\sigma}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right|_{\bar{\rho}} \quad (5)$$

has to be positive. The eigenfunctions and eigenvalues of the operator A are the eigenmodes of the fluctuations of the interface, and the inverse susceptibilities of these modes, respectively. In order for a profile to be stable, all susceptibilities must be positive [8,9]. The eigenvalues and eigenvectors play a role, not only in determining the stability of the interfacial profile $\rho(\mathbf{r})$, but also in finding the correlation function and scattering function of

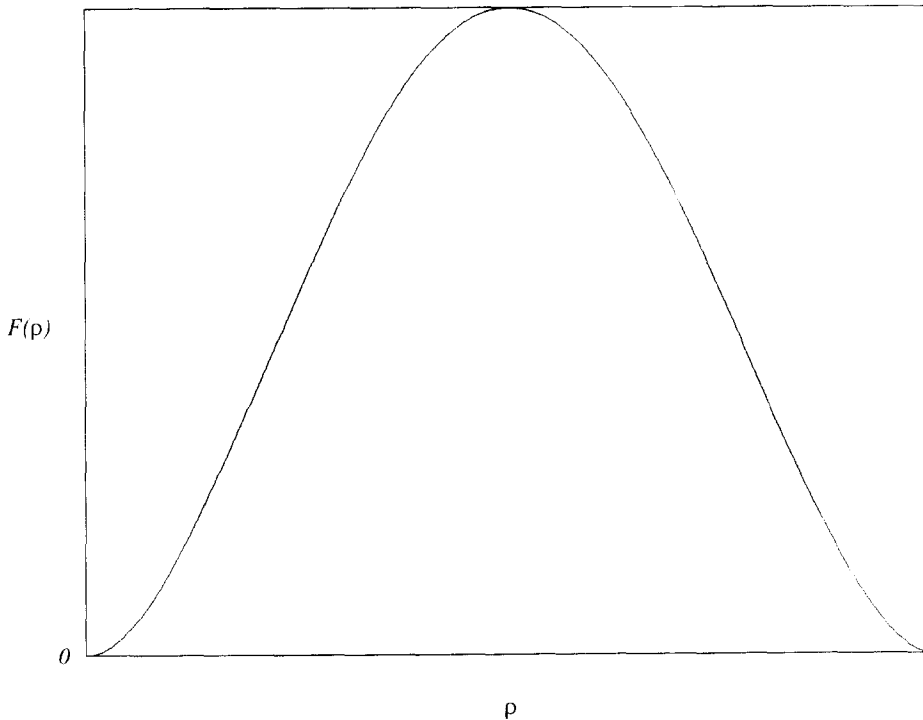


Fig. 2. The excess free energy density $F(\rho)$ between the vapor and liquid densities.

the system with an interface. The direct correlation function $c^{(2)}(\mathbf{r}, \mathbf{r}')$ is simply related to the second derivative A [1,2]:

$$c^{(2)}(\mathbf{r}, \mathbf{r}') = \frac{\delta(\mathbf{r} - \mathbf{r}')}{\bar{\rho}(\mathbf{r})} - \frac{A}{k_B T} A(\mathbf{r}, \mathbf{r}') \quad (6)$$

We will designate the eigenvalues and (normalized) eigenfunctions of the second functional derivative of σ by λ_n and $\phi_n(\mathbf{r})$, where n labels the different eigenfunctions. (In most cases n will be a continuous index.) They satisfy the equation

$$\int A(\mathbf{r}, \mathbf{r}') \phi_n(\mathbf{r}') d^3 r' = \lambda_n \phi_n(\mathbf{r}) \quad (7)$$

As was first observed by Wertheim [1], one solution of the eigenvalue equation (7) is $\bar{\rho}'(\mathbf{r})$, the derivative of the equilibrium profile. It has an eigenvalue $\lambda=0$, indicating that fluctuations of that form cost no energy. Those fluctuations correspond to a translation of the interfacial profile as a whole (as can be seen by expanding $\bar{\rho}(z + \delta z)$), which indeed costs no energy. The existence of this eigenmode with eigenvalue 0 is a general property that does not depend on the details of the model.

In the next sections we will calculate the eigenvalues and eigenfunctions for two different versions of the excess free energy σ . First, we will make the small-gradient approximation in the inhomogeneous term, resulting in a squared-gradient van der Waals type description. This case was extensively discussed by Evans [8], and an analytical calculation of the eigenvalues and eigenfunctions for the specific choice of a quartic polynomial for $F(\rho)$ was done by Zittartz [10]. We will use and discuss some results for this case as an example. Second, we examine, numerically, the more general case, with the full integral non-locality as in Eq. (1), for a specific choice for the interaction $\phi(r)$ and the bulk excess free energy $F(\rho)$. Although the details of these two versions are different, there are various features that appear to be more or less generic.

2.1. The squared-gradient approximation

In this section we make the approximation that gradients in $\rho(\mathbf{r})$ are small; or, in other words, that the thickness of the interface (which is of the order

of the correlation length ξ) is large, which is the case near the critical point. If we expand the difference of densities in the integral term in Eq. (1) to second order in \mathbf{r}' , we find that the first-order term does not contribute to the integral, by symmetry. The second-order term gives a contribution of

$$\int d^3 r' \phi(\mathbf{r}') [\rho(\mathbf{r} + \mathbf{r}') - \rho(\mathbf{r})] \approx -m \nabla^2 \rho(\mathbf{r}) \quad (8)$$

with

$$m = -\frac{1}{6} \int d^3 r \phi(\mathbf{r}) r^2 \quad (9)$$

The excess free energy σ is then, after an integration by parts,

$$\sigma = \int d^3 r \left\{ F[\rho(\mathbf{r})] + \frac{1}{2} m [\nabla \rho(\mathbf{r})]^2 \right\} \quad (10)$$

The Euler–Lagrange equation that follows from this is

$$F'[\rho(\mathbf{r})] - m \nabla^2 \rho(\mathbf{r}) = 0 \quad (11)$$

The equilibrium interface is planar, and we will choose the z -direction to be perpendicular to it. Then, the solution $\bar{\rho}(z)$ of this equation depends only on z . The second functional derivative of σ , evaluated at the stationary profile $\bar{\rho}(z)$, is [8]

$$\frac{\delta^2 \sigma}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = F''[\bar{\rho}(z)] \delta(\mathbf{r} - \mathbf{r}') - m \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \quad (12)$$

The eigenvalue equation (7) then becomes a differential equation

$$F''[\bar{\rho}(z)] \phi_n(\mathbf{r}) - m \nabla^2 \phi_n(\mathbf{r}) = \lambda_n \phi_n(\mathbf{r}) \quad (13)$$

Eq. (13) is equivalent in form to a Schrödinger equation for a particle in an external potential given by $V(z) = F''[\bar{\rho}(z)]$ [8]. Thus, the eigenmodes of the fluctuations of the interface are the eigenfunctions of a quantum mechanical potential well problem, while the eigenvalues λ_n are the energy levels associated with those eigenfunctions. A typical example of the potential is shown in Fig. 3. Since the interface is planar, the potential $V(z)$ depends only on z . Thus, the eigenfunctions are those of a free particle, i.e. plane waves, in the x -

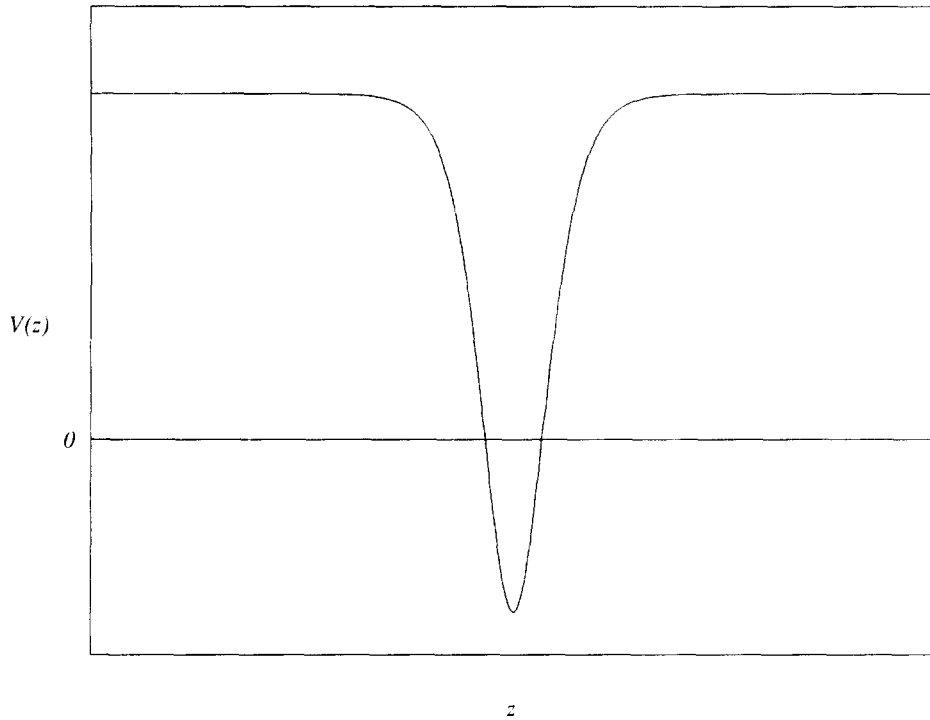


Fig. 3. The effective potential $V(z)$.

and y -directions:

$$\phi_{\mathbf{p},\nu}(\mathbf{r}) = \frac{1}{L} \exp[i(p_x x + p_y y)] \psi_\nu(z) \quad (\mathbf{p} = (p_x, p_y)) \tag{14}$$

for a system of size $L \times L$. Each of the eigenvalues λ_n then consists of the sum of an eigenvalue $\bar{\lambda}_n$, corresponding to the z -dependent part $\psi_\nu(z)$ of the eigenfunction, and a trivial contribution from the plane wave part:

$$\lambda_{\mathbf{p},\nu} = \bar{\lambda}_\nu + m(p_x^2 + p_y^2) \tag{15}$$

Since only the z -dependence of $\phi_{\mathbf{p},\nu}(\mathbf{r})$ is non-trivial, we will focus on it and its associated eigenvalues $\bar{\lambda}_\nu$, but in reality each eigenvalue $\bar{\lambda}_\nu$ is only the lower edge of a continuum of states with various values of the momentum \mathbf{p} in the x - y plane. For a potential such as shown in Fig. 3, there will in general be a number of bound states with discrete eigenvalues $\bar{\lambda}_\nu$, and a continuum of eigenvalues above these. Differentiating the Euler-Lagrange equation (11) with respect to z

shows that $\psi_1(z) = \bar{\rho}'(z)$ is indeed an eigenfunction with eigenvalue $\bar{\lambda}_1 = 0$, as was asserted before. For a profile with the generic shape shown in Fig. 1, the eigenfunction $\psi_1(z)$ is qualitatively as in Fig. 4(a); it is the nodeless ground state eigenfunction. Consequently, all other eigenvalues $\bar{\lambda}_\nu$ will be positive, since they correspond to higher, excited levels.

By making various specific choices for the bulk free energy $F(\rho)$ one can find solutions of the eigenvalue equation (13) analytically. The most obvious choice is that of the quartic polynomial

$$F(\rho) = C(\rho - \rho_\nu)^2(\rho - \rho_1)^2 \tag{16}$$

This leads to the problem solved by Zittartz in the context of finding a harmonic approximation to the partition function of the Ising model [10]. It gives rise to the familiar hyperbolic tangent profile

$$\bar{\rho}(z) = \frac{(\rho_1 + \rho_\nu)}{2} + \delta\rho_0 \tanh(z/\xi) \tag{17}$$

with $\delta\rho_0 = (\rho_1 - \rho_\nu)/2$ and $\xi = \sqrt{m/2C\delta\rho_0^2}$.

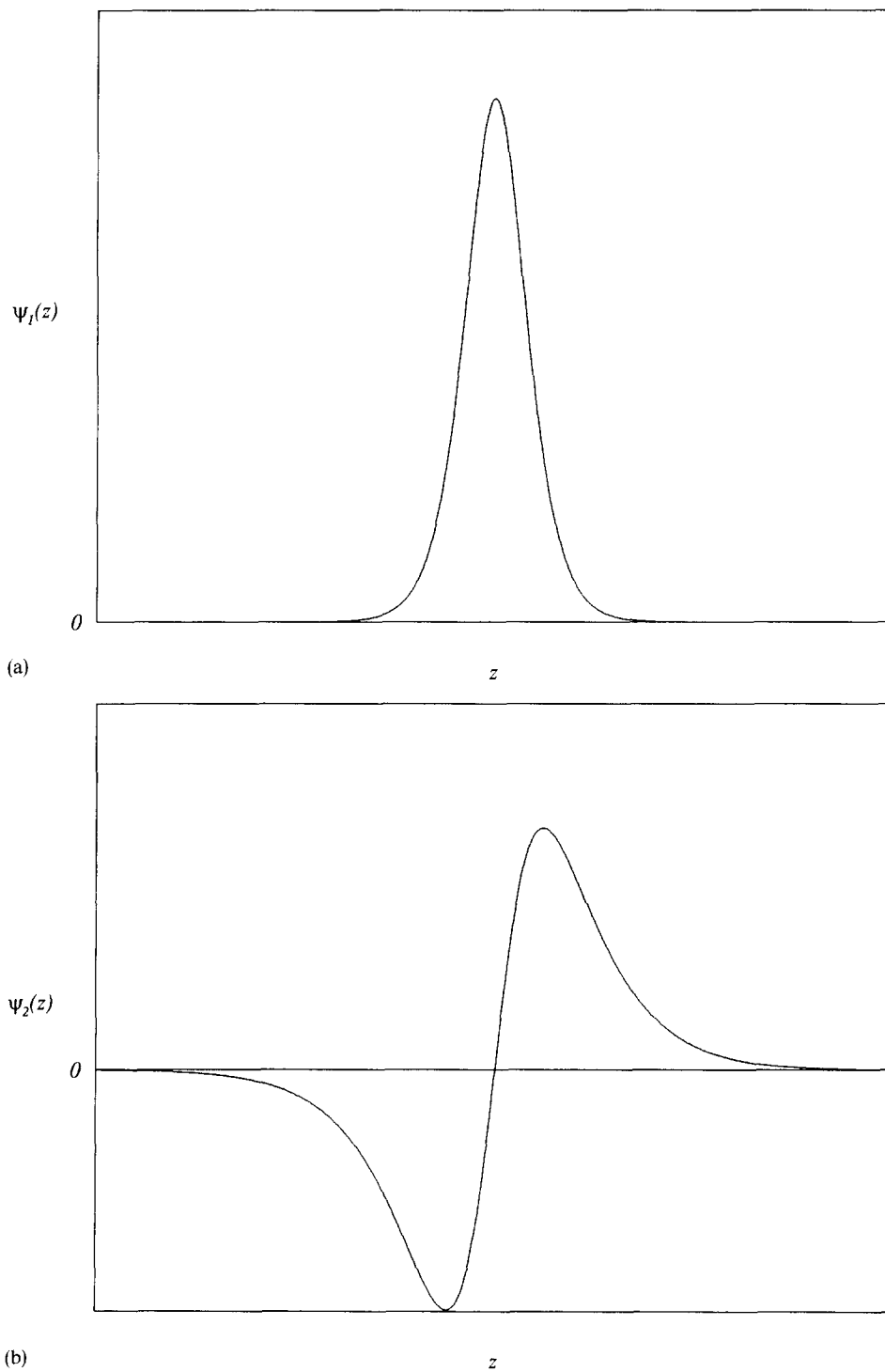


Fig. 4. The first two eigenfunctions: (a) $\psi_1(z)$; (b) $\psi_2(z)$.

Then, the eigenvalue equation determining the z -dependent part of the eigenfunctions, $\psi_v(z)$, can be transformed into an associated Legendre equation by making the substitution $t = \tanh(z/\xi)$. Then it is seen that the functions $\psi_v(z)$ are eigenfunctions of the associated Legendre equation with $n=2$, $\psi_v(z) = P_2^v[\tanh(z/\xi)]$, with $v^2 = 4 - \bar{\lambda}_v/2C\delta\rho_0^2$. There are two discrete eigenvalues, corresponding to $v=2$ and $v=1$, $\bar{\lambda}_1=0$ and $\bar{\lambda}_2=6C\delta\rho_0^2$, followed by a continuum $\bar{\lambda}_v=2C\delta\rho_0^2(4-v^2)$, with $v^2 \leq 0$. (By the WKB approximation one estimates that there should be $\sqrt{6-1}/2=1.95$ bound states, which is consistent.) The corresponding wave functions, $\psi_1(z)$ and $\psi_2(z)$, the ground state and the first excited state of the potential well, are shown in Fig. 4. The wave functions in the continuum are (non-localized) modified plane waves. $\psi_1(z)$ is indeed the derivative of the equilibrium profile, corresponding to a translation in the z -direction. $\psi_2(z)$ corresponds to a fluctuation that makes the density profile alternately steeper and less steep than the equilibrium profile. These changes are favored by, respectively, the local and non-local terms in the free energy (Eq. (10)). This fluctuation causes the contribution of one term to increase, and the other to decrease, while the total free energy increases in both cases.

To see what influence the interface has on these eigenvalues, we compare them with the case where there is no interface but only bulk liquid or vapor. The solutions of the eigenvalue equation in that case are simple plane waves, $e^{i\mathbf{p} \cdot \mathbf{r}}/L^{3/2}$, with eigenvalues $\lambda_p = mp^2 + 8C\delta\rho_0^2$. The general picture, then, that follows from the above example with a quartic polynomial for $F(\rho)$ is that this continuum of eigenvalues remains, albeit with modified eigenfunctions, while one or more eigenvalues, associated with localized eigenfunctions, appear below the continuum. The lowest of these is the ground state, corresponding to an eigenvalue $\lambda=0$. The exact number of such discrete eigenvalues depends on the details of the function $F(\rho)$. Several other choices for $F(\rho)$ lead to models that can be solved analytically. If one takes

$$F(\rho) = C \cos^2 \left(\frac{\pi}{2} \frac{2\rho - \rho_1 - \rho_v}{\rho_1 - \rho_v} \right) \quad (18)$$

only one discrete eigenvalue, $\lambda=0$, is found, with a continuum above it. For the choice $F(\rho) = C(\rho_1 - \rho)^3(\rho - \rho_v)^3$ the eigenvalue $\lambda=0$ is itself the bottom limit of the continuum, but it still has a localized eigenfunction. Finally, $F(\rho)$ can be constructed from three sections of parabolas, in such a way that the function and its first derivative are continuous. Then, by the proper choice of a parameter, any number of discrete eigenvalues can be obtained.

2.2. Numerical results for the integral non-locality

If we do not make the squared-gradient approximation, but instead keep the full form of the excess free energy σ as in Eq. (1), the Euler–Lagrange equation is

$$F''[\rho(\mathbf{r})] + \int_{r,r'>b} d^3r' \phi(r') [\rho(\mathbf{r}+\mathbf{r}') - \rho(\mathbf{r})] = 0 \quad (19)$$

Again, we will denote the solution of this equation by $\bar{\rho}(z)$. The eigenvalue equation with the second functional derivative of σ , Eq. (7), is now

$$F''[\bar{\rho}(z)]\phi_n(\mathbf{r}) + \int_{r,r'>b} d^3r' \phi(r') [\phi_n(\mathbf{r}+\mathbf{r}') - \phi_n(\mathbf{r})] = \lambda_n \phi_n(\mathbf{r}) \quad (20)$$

The x - and y -dependent parts of the eigenfunctions are again plane waves, and as before we will focus on the z -dependent part $\psi_v(z)$, and its associated eigenvalues $\bar{\lambda}_v$. In the following, for simplicity, we only discuss the case $k_x = k_y = 0$.

The only solution of Eq. (20) that can easily be found is once again $\psi_1(z) = \bar{\rho}'(z)$ with eigenvalue $\bar{\lambda}_1 = 0$. It again results from the translational symmetry of the problem. The other eigenvalues and eigenfunctions of the problem can only be found by solving Eq. (20) numerically. Also, the equilibrium profile $\bar{\rho}(z)$ has to be found numerically from Eq. (19) [6]. We have done so by discretizing the problem, and solving Eq. (19) iteratively as a matrix equation. Eq. (20) then also becomes a matrix equation, the eigenvalues and eigenvectors of which can easily be found.

As in Section 2.1 we will compare the eigenvalues and eigenfunctions of the systems with and

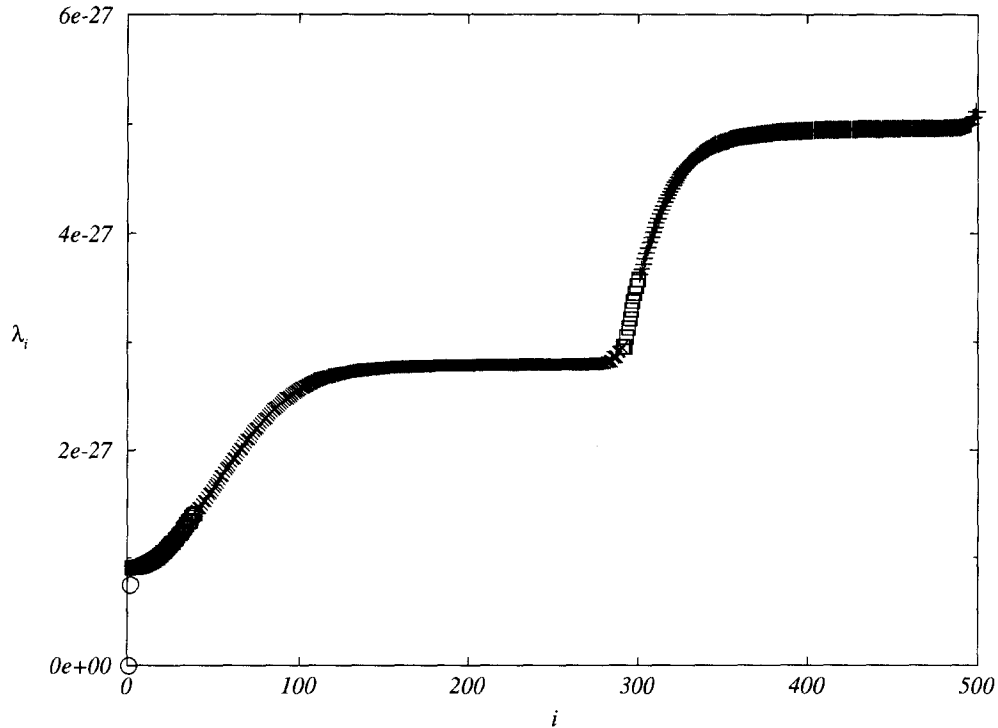


Fig. 5. The eigenvalues for the case of the integral non-locality. The lowest two eigenvalues (○) are the two discrete eigenvalues discussed in the text. Above them are a continuum of interface eigenvalues (□), then the continuum due to the bulk liquid (×), another continuum of interface eigenvalues (□) and finally the continuum due to the bulk vapor (+). The eigenvalues are in order of increasing magnitude.

without an interface. The eigenvectors of the homogeneous liquid or vapor are again plane waves, $e^{ip \cdot r}/L^{3/2}$, and the eigenvalues are given by $\lambda(p) = F''(\rho_{l,v}) + 2a + \tilde{\phi}(p)$, where $\tilde{\phi}(p)$ is the Fourier transform of the attractive interaction potential $\phi(r)$. For a specific choice of $\phi(r)$, the Fourier transform $\tilde{\phi}(p)$ will cover a certain range of values as p runs from 0 to ∞ . (In contrast to the case of the previous section there is now in general an upper limit to this range.) This translates into a band of values $\lambda(p)$ that are allowed eigenvalues in the bulk system. Note that the locations of the bands for the bulk liquid and vapor are in general not the same; they are shifted relative to each other by an amount $F''(\rho_l) - F''(\rho_v)$, the difference in curvature of the excess free energy $F(\rho)$ at the two coexisting densities.

The effect of introducing the interface is once

again to add extra eigenvalues, corresponding to eigenmodes that are localized around the interface, to the continua of the bulk phases. A particular example of this is shown in Fig. 5, for a discretized system of 500 points. That figure is the result of a calculation where the hard sphere part of the excess free energy, $F_{hs}(\rho)$, is of the form leading to the Carnahan–Starling equation of state. The attractive interaction between the particles is chosen to be $\phi(r) = -\alpha/r^6$. In this case, there are two types of eigenvalues that are added to the bulk bands. First, there are the two lowest eigenvalues, $\bar{\lambda}_1$ and $\bar{\lambda}_2$. They are both discrete, $\bar{\lambda}_1 = 0$ as was mentioned before, and $\bar{\lambda}_2$ has some non-zero value below the bottom of the continuum. The eigenfunctions associated with these two eigenvalues have qualitatively the same shape as in the previous section (Fig. 4).

Above these two discrete eigenvalues the contin-

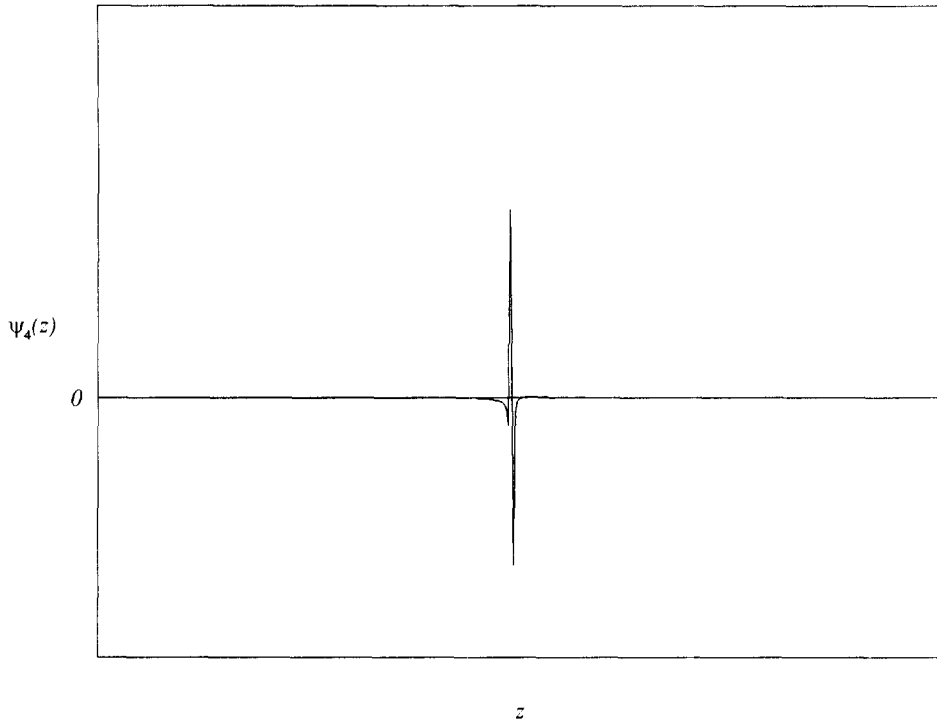


Fig. 6. The fourth eigenfunction, which is part of the continuum of interface eigenfunctions.

uum begins. However, in contrast to the previous case, here the eigenfunctions at the bottom of the continuum are still localized around the interface, and the eigenvalues do not overlap with the bands of the bulk phases. In fact, the continuum of eigenvalues consists of the two bands of the bulk phases (which for our choice of parameters do not overlap with each other), with below and between them two continuous bands of eigenvalues that are due to the presence of the interface, and whose eigenfunctions are localized there. An example of such a localized eigenfunction is shown in Fig. 6. The eigenfunctions in the bulk bands are delocalized, extending into the phase from which the band arises. An eigenfunction extending into the liquid phase is shown in Fig. 7.

3. Discussion

From the models studied above, it appears that there are some generic features in the spectrum of

eigenvalues of the stability matrix for a system with an interface. In most cases, (at least) two discrete eigenvalues exist below the continuum due to the bulk phases. The first of these corresponds to a translational motion of the whole interfacial profile, and it is known to exist for any model. The second corresponds to a fluctuation in the density profile itself; the fluctuation is a shifting of energy between the two terms in the expression for the excess free energy, one favoring a sharp interface, and the other favoring a diffuse one. This eigenvalue is not always present, and indeed many other eigenvalues can exist in addition to these two. Still, these two eigenvalues appear in several of the models studied, both in the squared-gradient models that can be solved analytically (Section 2.1), and in the more general models of Section 2.2, including several models that are most often used in studies of the structure of interfaces. This suggests that they do represent a general feature of interfacial systems.

Since the eigenvalues and eigenvectors of the

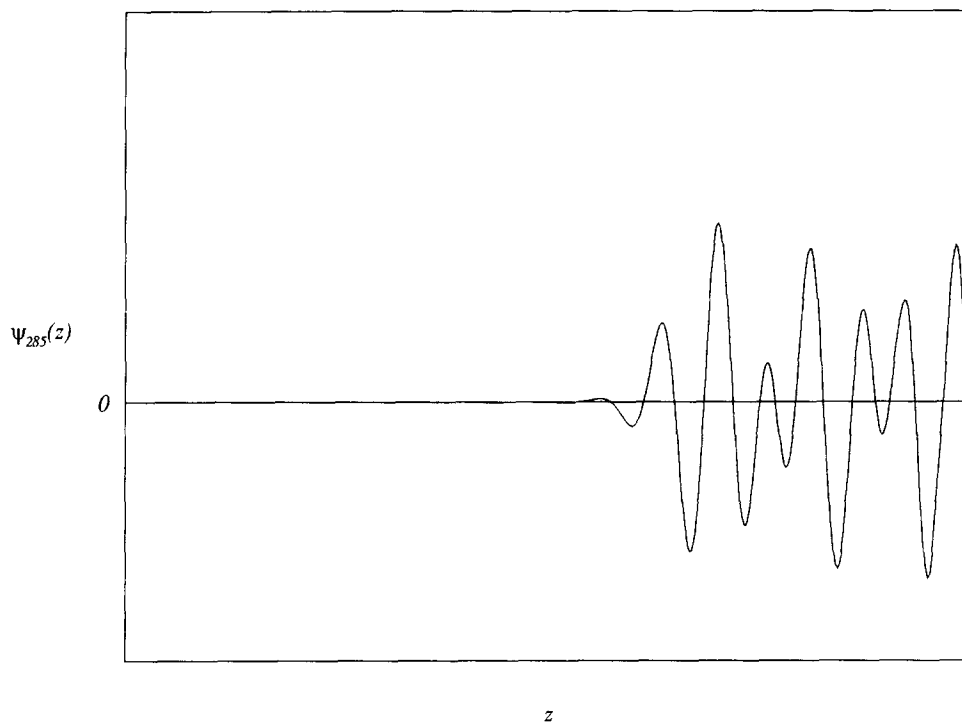


Fig. 7. The 285th eigenfunction, which is part of the continuum of bulk liquid eigenfunctions.

stability matrix play a role in determining the correlation function and the scattering function of the system, it is interesting to see what the consequences of the discrete eigenvalues are for these quantities in systems with interfaces. Work along these lines is in progress.

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