

Structure of the liquid-vapor interface: A nonperturbative approach to the theory of interfacial fluctuations

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This paper is concerned with the fluctuations of the liquid-gas surface. We study the approach to the strong fluctuation regime as the strength of the external field pinning an interface is decreased. By means of a variational approach we treat self-consistently the order parameter and its correlations in three dimensions. Our numerical results show that the width of the profile increases as the external field decreases according to a logarithmic law. We relate this behavior to the capillary-wave-like excitations of the interface and discuss the limitations of the present approach.

I. INTRODUCTION

The existence of an intrinsic interface between two coexisting subcritical fluid phases is still the source of some controversy and constitutes an intriguing problem in the statistical mechanics of inhomogeneous media.¹⁻⁴ Two different views of the problem have emerged. According to the classical van der Waals theory of the liquid-vapor interface there exists an intrinsic interfacial profile, whose structure remains well defined in the thermodynamic limit and at two-phase coexistence, i.e., in the absence of an external field. In some cases the theories, originating from van der Waals's ideas, are very successful in describing the microscopic short-range structure of the fluid. The mean-field approach predicts that two coexisting phases are separated by a transition region where the density profile varies on the scale of the bulk correlation length ξ_b . In fact, one finds that the length scale which controls the presence of inhomogeneities in the bulk fluid is the same as that which determines the interfacial thickness. As ξ_b goes to infinity upon approaching the bulk critical point the interface broadens and eventually disappears. The occurrence of such a broadening is merely due to critical fluctuations and to the coalescence of the two bulk phases at the critical point. Unfortunately, the mean-field approach neglects important long-wavelength fluctuations.

The idea of an intrinsic density profile was questioned by Buff, Lovett, and Stillinger,⁵ who showed that the above picture was missing a central feature of the interfacial problem. These authors realized that the interface is in continuous motion due to the thermal excitation of long-wavelength capillary-wave modes. Physically these low-energy, soft modes, predicted by the Goldstone theorem,⁶ are a consequence of the translational symmetry spontaneously broken by the presence of an interface.

According to the capillary-wave model⁵ (CWM) the width of the interface between two coexisting fluid phases diverges in the thermodynamic limit at all subcritical

temperatures, if the number of spatial dimensions d is equal to or less than 3. The long-wavelength fluctuations of the boundary surface are responsible for the absence of phase separation.

This important result is to be contrasted with the findings of the mean-field theory (MFT) which predicts a broadening of the interface only upon approaching the critical point.

The simplicity of the CWM and of the related "drum-head" model⁷ derives assuming a $(d-1)$ -dimensional Hamiltonian: one treats the liquid-vapor system from a diametrically opposite point of view and deals only with the degrees of freedom associated with the interface and not with either bulk phase.

Within the CWM the interface separating the two phases can move in a fashion similar to that of a vibrating membrane. The average position of the interface (and also the equal-time height-height correlation function) is found to diverge as $\ln L$, when the perimeter L of the membrane goes to infinity. Conversely, in the case of an unbounded interface subject to an external pinning field of strength g the above divergence is proportional to $-\ln g$ when $g \rightarrow 0$.

However, as pointed out by Huse, van Saarloos, and Weeks,⁸ this picture ignores bulk fluctuations such as bubble formation of the opposite phase and overhangs of the interface and breaks down on length scales shorter than ξ_b .

Clearly, either picture emphasizes only a particular aspect of the fluid behavior; instead, one would like to treat bulk and surface degrees of freedom on equal footing. Such an approach should combine the capability to describe bulk properties of the first of the two schemes mentioned above with the aptness of the second to take into account long-wavelength interfacial fluctuations.

Many years ago Zittartz⁹ studied the corrections due to the fluctuations about the mean-field profile. Assuming a particularly simple three-dimensional Hamiltonian he considered the stability of the solution of the mean-

field equation, which describes the interface. He showed that the amplitude of the fluctuations diverges at bulk coexistence, i.e., when the bulk external fields vanish. He also found that the fluctuations in the same limit contribute to the free energy a nonanalytic term proportional to $-g \ln g$, in agreement with CWM predictions. However, this treatment, based on a type of random-phase approximation, the so-called one-loop approximation, did not consider the feedback of these fluctuations on the order-parameter profile, which remained well defined even in the zero-field limit. Later, Wertheim¹⁰ proved without making use of specific models that the fluctuations parallel to the interface are long ranged and in the case of a fluid subject to a gravitational field have a characteristic correlation length $L_c = \sqrt{\sigma/mg}$ where σ is the liquid-vapor surface tension of the interface, m is the molecular mass, and g is the gravitational acceleration. Unfortunately, Wertheim's analysis does not provide the explicit dependence of the density profile on the external field. Weeks¹¹ was the first to provide an explicit model, whose solution shows that the position of the interface undergoes diverging fluctuations in the limit of $g \rightarrow 0$.

The goal of the present paper is to investigate the behavior of the interface separating two phases of equal free energy, when an external field, coupled with the order parameter to induce phase separation, vanishes. We shall apply a method recently proposed, which treats on equal footing the order parameter and its fluctuations.

By employing a variational principle in the framework of the functional integral formulation of statistical mechanics¹² we are able to treat self-consistently these two quantities. The self-consistency condition is contained in two coupled equations, which were solved numerically.

In Ref. 13, hereafter referred to as I, we presented the general formalism and a detailed account of its predictions concerning the bulk phase diagram of the so-called ϕ^4 Landau-Ginzburg model, a system which shows a first-order bulk transition.

We conclude this introduction by describing the plan of the present paper. In Sec. II we give a short derivation of the constitutive equations for the order parameter and its correlation. These two averages will be featured throughout the paper. In Sec. III we describe the method of solution and in Sec. IV we define the surface free energy. In Sec. V we discuss the physical meaning of our results and in Sec. VI present the conclusions.

II. THE BEST EFFECTIVE GAUSSIAN APPROXIMATION

In I we introduced a self-consistent treatment of the order parameter and its fluctuations about the average value in systems which are described by a Ginzburg-Landau Hamiltonian. In the present paper we consider the case of a fluid which is not spatially uniform due to the presence of an external field. In this section we only derive a method which holds for arbitrary type of external potential, whereas in Sec. III we shall specialize to an external source which breaks the translational invariance in a single spatial direction.

We begin by considering the so-called ϕ^4 model for a real scalar field $\phi(\mathbf{x})$ coupled to an external potential $h(\mathbf{x})$. The starting point is the reduced Hamiltonian:

$$K[\phi(\mathbf{x})] = \frac{H[\phi(\mathbf{x})]}{k_B T} = \int d^d x \left[\frac{1}{2}(\nabla\phi)^2 + \frac{\mu^2}{2}\phi^2 + \frac{\lambda}{4!}\phi^4 - h\phi \right], \quad (2.1)$$

where the coefficient μ^2 changes sign at the bare critical temperature T_c , k_B is the Boltzmann constant, and λ is a temperature-independent coupling constant. The partition function Z is given by the functional integral

$$Z = \int \mathcal{D}\phi(\mathbf{x}) \exp\{-K[\phi(\mathbf{x})]\}, \quad (2.2)$$

the dimensionless Gibbs free energy $W[h(\mathbf{x})]$ is related to Z by the relation $Z = \exp(-W)$. Since we want to avoid the use of perturbation theory we base our treatment of Eq. (2.2) on the variational estimate of the free energy of the system introduced in I. Here, we recall the salient features of the theory.

As is well known, the free energy W of a system described by the Hamiltonian K satisfies the Peierls-Feynman-Bogoliubov inequality:¹⁴

$$W \leq W^{(1)} = W_0 + \langle K - K_0 \rangle_0, \quad (2.3)$$

where W_0 is the Gibbs free energy of a suitably chosen reference system, whose Hamiltonian is K_0 , and the average $\langle \rangle_0$ is taken with respect to the reference system.

We take K_0 to be the quadratic functional:

$$K_0[\phi] = \frac{1}{2} \int d^d x \phi(\mathbf{x}) [-\nabla^2 + u(\mathbf{x})] \phi(\mathbf{x}) - \int d^d x \phi(\mathbf{x}) v(\mathbf{x}), \quad (2.4)$$

where $[-\nabla^2 + u(\mathbf{x})]$ is a positive definite kernel and $v(\mathbf{x})$ is a well-behaved function. These two functions are determined by requiring $W^{(1)}$ to be minimum with respect to variations in $u(\mathbf{x})$ and $v(\mathbf{x})$. In the Gaussian ensemble (GE) the two functions $u(\mathbf{x})$ and $v(\mathbf{x})$ are related to the average order parameter $\bar{\phi}_0(\mathbf{x}) = \langle \phi(\mathbf{x}) \rangle_0 = -\delta W_0 / \delta v(\mathbf{x})$ and to the two-point correlation function

$$G_0(\mathbf{x}, \mathbf{x}') = \langle \phi(\mathbf{x}) \phi(\mathbf{x}') \rangle_0 - \langle \phi(\mathbf{x}) \rangle_0 \langle \phi(\mathbf{x}') \rangle_0 = -\frac{\delta^2 W_0}{\delta v(\mathbf{x}) \delta v(\mathbf{x}')}$$

by the equations

$$[-\nabla^2 + u(\mathbf{x})] \bar{\phi}_0(\mathbf{x}) = v(\mathbf{x}), \quad (2.5)$$

$$[-\nabla^2 + u(\mathbf{x})] G_0(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'). \quad (2.6)$$

In order to prove these two relations one has to evaluate W_0 explicitly. Doing so we find

$$W_0 = \frac{1}{2} \ln[\det \| -\nabla^2 + u(\mathbf{x}) \|] - \frac{1}{2} \int d^d x v(\mathbf{x}) [-\nabla^2 + u(\mathbf{x})]^{-1} v(\mathbf{x}). \quad (2.7)$$

Functionally differentiating Eq. (2.7) with respect to $v(\mathbf{x})$

one arrives at Eqs. (2.5) and (2.6).

All correlation functions of order higher than the second have the property in the GE of factorizing into products of $\bar{\phi}_0(\mathbf{x})$ and $G_0(\mathbf{x}, \mathbf{x}')$. Thus

$$\begin{aligned} \langle \phi(\mathbf{x})^4 \rangle_0 &= 3 \langle \phi(\mathbf{x})^2 \rangle_0^2 - 2 \langle \phi(\mathbf{x}) \rangle_0^4 \\ &= \bar{\phi}_0(\mathbf{x})^4 + 3G_0(\mathbf{x}, \mathbf{x})^2 + 6\bar{\phi}_0(\mathbf{x})^2 G_0(\mathbf{x}, \mathbf{x}). \end{aligned} \quad (2.8)$$

The total Gibbs free energy is

$$\begin{aligned} W^{(1)} &= W_0 + \int d^d \mathbf{x} \left[\frac{1}{2} [\mu^2 - u(\mathbf{x})] \langle \phi(\mathbf{x})^2 \rangle_0 \right. \\ &\quad \left. + \frac{\lambda}{4!} \langle \phi(\mathbf{x})^4 \rangle_0 \right. \\ &\quad \left. + [v(\mathbf{x}) - h(\mathbf{x})] \langle \phi(\mathbf{x}) \rangle_0 \right]. \end{aligned} \quad (2.9)$$

The stationarity condition of $W^{(1)}$ with respect to variations of $v(\mathbf{x})$ implies the Euler-Lagrange equation

$$\begin{aligned} \frac{\delta W^{(1)}}{\delta v(\mathbf{x})} &= \int d^d \mathbf{x}' \left\{ \frac{1}{2} [\mu^2 - u(\mathbf{x}')] \frac{\delta \langle \phi(\mathbf{x}')^2 \rangle_0}{\delta v(\mathbf{x})} \right. \\ &\quad \left. + \frac{\lambda}{4!} \frac{\delta \langle \phi(\mathbf{x}')^4 \rangle_0}{\delta v(\mathbf{x})} \right. \\ &\quad \left. + [v(\mathbf{x}') - h(\mathbf{x}')] \frac{\delta \langle \phi(\mathbf{x}') \rangle_0}{\delta v(\mathbf{x})} \right\} = 0 \end{aligned} \quad (2.10)$$

and the variation with respect to $u(\mathbf{x})$

$$\begin{aligned} \frac{\delta W^{(1)}}{\delta u(\mathbf{x})} &= \int d^d \mathbf{x}' \left\{ \frac{1}{2} [\mu^2 - u(\mathbf{x}')] \frac{\delta \langle \phi(\mathbf{x}')^2 \rangle_0}{\delta u(\mathbf{x})} \right. \\ &\quad \left. + \frac{\lambda}{4!} \frac{\delta \langle \phi(\mathbf{x}')^4 \rangle_0}{\delta u(\mathbf{x})} \right. \\ &\quad \left. + [v(\mathbf{x}') - h(\mathbf{x}')] \frac{\delta \langle \phi(\mathbf{x}') \rangle_0}{\delta u(\mathbf{x})} \right\} = 0. \end{aligned} \quad (2.11)$$

Using Eq. (2.8) one sees that (2.10) and (2.11) admit the solution

$$u(\mathbf{x}) = \mu^2 + \frac{\lambda}{2} [\bar{\phi}_0(\mathbf{x})^2 + G_0(\mathbf{x}, \mathbf{x})], \quad (2.12)$$

$$v(\mathbf{x}) = \frac{\lambda}{3} [\bar{\phi}_0(\mathbf{x})^3 + 3\bar{\phi}_0(\mathbf{x})G_0(\mathbf{x}, \mathbf{x})] + h(\mathbf{x}). \quad (2.13)$$

By substituting these we obtain the following set of coupled differential equations:

$$[-\nabla^2 + \mu^2 + \frac{1}{6}\lambda\bar{\phi}_0(\mathbf{x})^2 + \frac{1}{2}\lambda G_0(\mathbf{x}, \mathbf{x})]\bar{\phi}_0(\mathbf{x}) = h(\mathbf{x}), \quad (2.14)$$

$$[-\nabla^2 + \mu^2 + \frac{1}{2}\lambda\bar{\phi}_0(\mathbf{x})^2 + \frac{1}{2}\lambda G_0(\mathbf{x}, \mathbf{x})]G_0(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'). \quad (2.15)$$

To complete these relations we observe that the average order parameter obtained by differentiating the total free energy $W^{(1)}$ with respect to $h(\mathbf{x})$ is identical to $\bar{\phi}_0(\mathbf{x})$, the order parameter obtained in the reference ensemble, i.e., $-\delta W_0 / \delta h(\mathbf{x}) = \bar{\phi}_0(\mathbf{x}) = \bar{\phi}_0(\mathbf{x})$.

To summarize we started by introducing a set of fairly general reference Gaussian ensembles, characterized by functions $u(\mathbf{x})$ and $v(\mathbf{x})$ in Eq. (2.4). The order parameter $\bar{\phi}_0(\mathbf{x})$ and the Green function $G_0(\mathbf{x}, \mathbf{x}')$ were related respectively to $u(\mathbf{x})$ and $v(\mathbf{x})$, as shown in Eqs. (2.12) and (2.13).

Next, the actual form of the probability distribution was determined by means of an optimization procedure, equivalent to imposing the requirement that the total free energy calculated in the chosen reference ensemble is the lowest among those belonging to the set. The result of this procedure leads to the two self-consistent equations (2.14) and (2.15). We name the method best effective Gaussian approximation (BEGA).

III. THE INTERFACIAL PROBLEM

We shall consider the physical situation in which an external field $h(\mathbf{x})$ varying in a single spatial direction, say, along the z axis, induces phase separation and determines the formation of an interface. Since we shall be interested in the limit in which $h(z)$ vanishes, its exact form is not crucial. Having in mind the gravitational potential acting on a horizontal liquid-vapor interface, we have chosen $h(z)$ varying from the value $-h_b$ at $z = -\infty$ to the value h_b at $z = \infty$. This was done in order to favor the presence of the phase with negative order parameter (the "gas") to the left of the interface located at $z = 0$ and of positive phase (the "liquid") at the right. For large values of h_b we expect the interface to be flat. The external field acts as a chemical potential deep in the two bulk phases. In the transition region it is assumed to vary smoothly and we choose

$$h(z) = h_b \tanh \left[\frac{z}{L} \right], \quad (3.1)$$

where L is a length proportional to ξ_b .

In order to determine $G_0(\mathbf{x}, \mathbf{x}')$ we exploit the translational invariance of the system along the plane (x, y) and introduce the lateral Fourier transform of the Green function:

$$G_0(z, z', \mathbf{Q}) = \frac{1}{(2\pi)^2} \int d^2 Q \exp(i\mathbf{Q} \cdot \mathbf{R}) G_0(\mathbf{x}, \mathbf{x}'), \quad (3.2)$$

where $\mathbf{R} = (x - x', y - y')$ and \mathbf{Q} is a two-dimensional wave vector. We rewrite Eq. (2.15),

$$\begin{aligned} \left[-\frac{d^2}{dz^2} + \mathbf{Q}^2 + \mu^2 + \frac{1}{2}\lambda\bar{\phi}_0(\mathbf{x})^2 + \frac{1}{2}\lambda G_0(z, z) \right] G_0(z, z') \\ = \delta(z - z'), \end{aligned} \quad (3.3)$$

where $G_0(z, z) = G_0(z, z; \mathbf{R} = \mathbf{0})$. Equation (3.3) is equivalent to finding the Green function for a particle described by a one-dimensional Schrödinger equation. The differential operator acting on $G_0(z, z')$ in the left-hand side of Eq. (3.3) is its Hamiltonian, whose eigenmodes $\psi_{n, \mathbf{Q}}(\mathbf{x})$ describe the fluctuations of the system about the average value of the order parameter. Each individual mode contributes to G_0 , in a measure which depends on

its energy cost (i.e., the eigenvalue ε_n) according to the well-known spectral representation of the Green function:

$$G_0(\mathbf{x}, \mathbf{x}') = \frac{1}{(2\pi)^2} \sum_n \int d^2Q \frac{\psi_{n,Q}(\mathbf{x})\psi_{n,Q}(\mathbf{x}')}{(\varepsilon_n + Q^2)}. \quad (3.4)$$

By choosing $h(z)$ to be proportional to the order-parameter density profile Zittartz⁹ was able to obtain explicitly the analytical expression of $G_0(\mathbf{x}, \mathbf{x}')$, within the one-loop approximation. In our scheme this level of approximation is obtained by setting $\frac{1}{2}\lambda G_0(\mathbf{x}, \mathbf{x}) = 0$ in the left-hand side (lhs) of Eqs. (2.14) and (2.15). Zittartz showed that, below the bulk critical temperature, the kink solution has two eigenmodes of negative energy whose wave functions are localized in the interfacial region. The symmetric mode of lower energy corresponds to a local shift of the interface, whereas the first excited state describes a squeezing mode of the interface.

The solution of the coupled equations (2.14) and (2.15) in the case of a homogeneous system is straightforward, since it involves only Fourier transforms (see Ref. 13). In the inhomogeneous case in order to solve the coupled equations we employed a numerical iterative technique. We started from the initial guess $G_0(\mathbf{x}, \mathbf{x}) = G_0^{\text{bulk}}$ and solved the differential equation (2.14) for $\bar{\phi}(\mathbf{x})$ by means of a fourth-order Runge-Kutta method.¹⁵ We choose a trial solution, which obeys the initial condition $\bar{\phi}(z) = \phi_b$ at $z = \infty$ and then integrate the solution back to $z = 0$.

We then calculated the Green function consistent with such a trial profile; the resulting $G_0(\mathbf{x}, \mathbf{x}')$ was inserted again into the equation for the profile (2.14) and this procedure was carried on until the process converged. To determine $G_0(\mathbf{x}, \mathbf{x}')$ we did not attempt to use the spectral representation (3.4), but rather applied a method we briefly illustrate below. One introduces a quantity E :

$$-E = \frac{\lambda}{2}(\phi_b^2 + G_0^{\text{bulk}}) + \mu^2 + Q^2 = \xi_b^{-2} + Q^2 \quad (3.5)$$

and the "one-body" potential:

$$U(z) = \frac{\lambda}{2}[\bar{\phi}^2(z) + G_0(z, z) - \phi_b^2 - G_0^{\text{bulk}}]. \quad (3.6)$$

Equation (3.3) is rewritten as

$$\left[-\frac{d^2}{dz^2} + U(z) - E \right] G_0(z, z'; E) = \delta(z - z'). \quad (3.7)$$

In order to construct the Green function $G_0(\mathbf{x}, \mathbf{x}')$ it is necessary to find the two independent solutions of the homogeneous equation associated with (3.7) for arbitrary values of the energy E . Let $\psi^+(z, E)$ and $\psi^-(z, E)$ be, respectively, the irregular solution at $z = +\infty$, where it diverges like $\exp(\sqrt{-E}z)$, and the irregular solution at $z = -\infty$, where it behaves like $\exp(-\sqrt{-E}z)$. The required Green function is given by

$$G_0(z, z'; E) = -\frac{1}{w(E)} [\psi^+(z, E)\psi^-(z', E)\Theta(z - z') + \psi^-(z, E)\psi^+(z', E)\Theta(z' - z)], \quad (3.8)$$

where $w(E)$, the Wronskian, is a function of the energy only:¹⁶

$$w(E) = \left[\psi^-(z, E) \frac{d}{dz} \psi^+(z, E) - \psi^+(z, E) \frac{d}{dz} \psi^-(z, E) \right]. \quad (3.9)$$

The Green function $G_0(\mathbf{x}, \mathbf{x})$ is obtained from $G_0(z, z; E)$ by means of the formula

$$G_0(\mathbf{x}, \mathbf{x}) = \frac{1}{4\pi} \int_{-\xi_b^{-2} - Q_c^2}^{-\xi_b^{-2}} dE G_0(z, z; E), \quad (3.10)$$

where Q_c is an ultraviolet cutoff introduced in order to regularize the integrals. In the Appendix we report the numerical technique which was employed in order to construct $G_0(z, z; E)$.

IV. SURFACE TENSION

The surface tension of an interface is usually defined in the absence of external fields. The effect of an external potential, in fact, is not only to distort the interfacial profile, but also to shift the bulk system away from the two-phase coexistence line.

Following Van Leeuwen and Sengers¹⁷ we defined the surface tension as the free energy excess per unit area of the actual system over the free energy of a reference system characterized by a discontinuous jump in the density profile. This jump equals the difference between the order parameter in the two opposite bulk phases. An advantage of the above definition is that one can analyze separately bulk and surface contributions to the free energy. The surface excess free energy per unit area is defined as

$$\sigma = \int_{-\infty}^{\infty} dz \left[\frac{1}{2} \left(\frac{d\bar{\phi}}{dz} \right)^2 + \frac{\mu^2}{2} \bar{\phi}^2 + \frac{\lambda}{4!} \bar{\phi}^4 - h\bar{\phi} - \frac{\lambda}{8} G_0^2(z, z) \right] + \frac{1}{2} \ln[G_0^{-1}(z, z')] - \int_{-\infty}^{\infty} dz \omega_b(z), \quad (4.1)$$

where $\omega_b(z) = \Theta(z)\omega^+ + \Theta(-z)\omega^-$, $\phi_b^\pm = \lim_{z \rightarrow \pm\infty} \phi(z)$ and

$$\omega^\pm = \left[\frac{\mu^2}{2} (\phi_b^\pm)^2 + \frac{\lambda}{4!} (\phi_b^\pm)^4 - h_b^\pm \phi_b^\pm - \frac{\lambda}{8} (G_b)^\pm + \frac{1}{2} \ln[(G_b)^\pm] \right], \quad (4.2)$$

$$G_b = \left[\frac{1}{2\pi} \right]^3 \int_{-\infty}^{\infty} dk \int d^2Q \frac{1}{(k^2 + Q^2 + \xi_b^{-2})}. \quad (4.3)$$

Throughout this work a cylindrical Brillouin zone was employed to calculate the Green function and the logarithm of the functional determinant:

$$\frac{1}{2}\ln[G_0^{-1}(z,z')] = \frac{1}{2} \left[\frac{1}{2\pi} \right]^2 \left[\int_0^\infty d\eta n(\eta) \int d^2Q \ln(Q^2 + \xi_b^{-2} + \eta) + \sum_n \int d^2Q \ln(Q^2 + \Delta^2 + \varepsilon_n) \right], \quad (4.4)$$

where the sum is restricted to the eigenvalues of negative energy and the quantity n is the density of states given by the well-known formula

$$n(E) = -\frac{1}{\pi} \text{Im} \int dz G_0(z,z;E). \quad (4.5)$$

In the case of a uniform system $n(\eta)$ reduces to $n_b = 1/2\pi\sqrt{\eta}$. We checked numerically that the integral of the difference between this limiting value and the value when $U(z)$ is nonzero, i.e., in the presence of an interface, satisfies the sum rule:

$$N_b = \int_0^\infty d\eta [n(\eta) - n_b(\eta)], \quad (4.6)$$

where N_b is the number of bound states, as required by the quantum-mechanical Levinson's theorem.¹⁸

Finally, we notice that the expression (4.1) displays a similarity with the free energy often employed within the density-functional approach and provides an alternative interpretation of our method. Let us consider (4.1) as a functional, $\Gamma \equiv \sigma$ of $\bar{\phi}$ and G_0 . Thus $\Gamma(\bar{\phi}, G_0)$ can be regarded as a generalized Ginzburg-Landau functional, which depends not only on the average value of the field, but also on its correlation $\langle \phi(\mathbf{x})\phi(\mathbf{x}') \rangle$. Physical solutions require¹⁹

$$\frac{\delta\Gamma(\bar{\phi}, G_0)}{\delta\bar{\phi}(\mathbf{x})} = 0 \quad (4.7)$$

and

$$\frac{\delta\Gamma(\bar{\phi}, G_0)}{\delta G_0(\mathbf{x}, \mathbf{x}')} = 0, \quad (4.8)$$

which are equivalent, respectively, to (2.14) and (2.15).

V. RESULTS OF CALCULATIONS

In this section we illustrate the numerical results obtained by solving on a computer the system of equations (2.14) and (2.15). To begin with, we judged it appropriate to neglect the influence of the bulk excitations on the density profile. In fact, only in the critical region do these fluctuations become a dominant mechanism in determining the shape of the interfacial profile. On the other hand, they cause a trivial renormalization of the latter, which must be accounted for and treated separately.

In fact, the self-consistent method we choose has the effect of shifting the bulk phase boundaries, with respect to the corresponding boundaries predicted by the mean-field theory. The absolute value of the BEGA order parameter at a given temperature will be smaller than its MFT counterpart and the bulk correlation length longer

than the corresponding MFT quantity.

The premise above is necessary in order to define a genuine measure of the interfacial broadening due to capillary-wave-like excitations. The criterion we followed in order to single out the specific effect of inhomogeneous fluctuations consists in comparing the BEGA and MFT profiles after a suitable rescaling of these two quantities. We measured the distances in units of the length $\xi_0 = (\frac{1}{3}\lambda\phi_b^2)^{-1/2}$ and define $u(y = z/\xi_0) = \bar{\phi}(z)/\phi_b$ and $\gamma(y) = (\xi_0^2/\phi_b)h(z)$. Rewriting Eq. (2.14) in the new variables we obtain

$$\{-\nabla^2 + \frac{1}{2}(u^2 - 1) + \kappa[g(y,y) - g_b] + \gamma_\infty\}u(y) = \gamma(y), \quad (5.1)$$

where $g(y,y) = \xi_0^{d-2}G_0(z,z)$, g_b is the y independent value of $g(y,y)$ in the homogeneous bulk state, and the dimensionless coupling constant κ is given by

$$\kappa = \frac{1}{2}\lambda\xi_0^{4-d}, \quad (5.2)$$

where $\gamma_\infty = \gamma(y = \infty)$. The boundary conditions are $u(y) = \pm 1$ when $y \rightarrow \pm\infty$. We took as reference profile the solution $u_0(y)$ of Eq. (5.1) obtained by setting κ equal to zero and probed the capillary waves by varying the strength of the external field $h(z)$. Clearly, a large value of h_b has the effect of hindering these excitations, since the potential breaks the translational invariance of the free interface and thus pins the Goldstone modes. As h_b goes to zero one expects to observe larger and larger interfacial fluctuations. This behavior is illustrated in Figs. 1 and 2 where we calculated for two different values of h_b

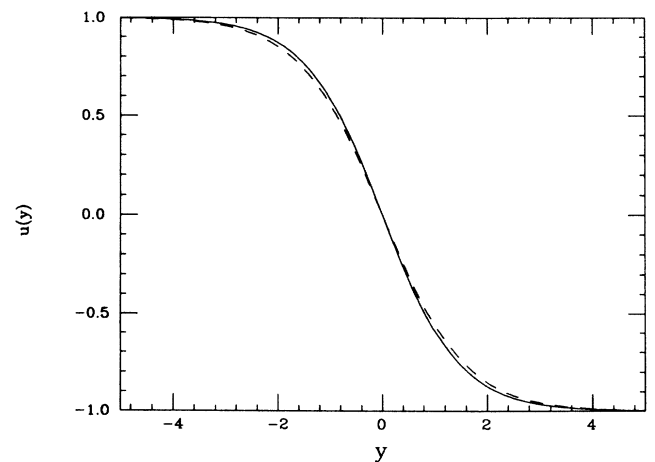


FIG. 1. Order-parameter interfacial profile for $h_b = 0.1$ and $\kappa = 0.13$. The solid line represents the mean-field result; dashed line, the BEGA result.

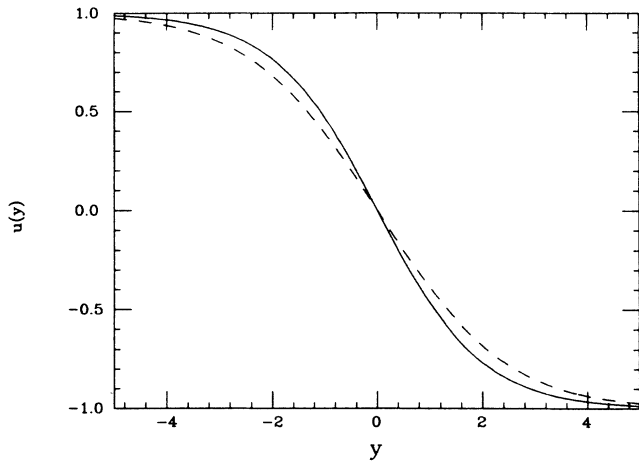


FIG. 2. Order-parameter interfacial profile for $h_b=0.0011$ and $\kappa=0.13$. The solid line corresponds to the MFT result, the dashed line to BEGA.

the profiles $u(y)$ and $u_0(y)$. For the larger field the difference is very small, indicating an almost complete suppression of capillary-wave-like modes. When the field tends to zero the energy required to excite these fluctuations decreases and we observe a larger and larger deviation from the reference profile $u_0(y)$ as shown in Fig. 2 obtained for a value of the field $h_b=10^{-4}$. In Figs. 3 and 4 we show the diagonal element of the surface correlation function $G_s(z,z)=G(z,z)-G_b$ which is characterized by two features: its width is increased in view of the fact that the excitations are less localized, whereas its height is smaller with respect to the one loop level result for G_s . The first of these two phenomena can be understood by recalling that u is smoother than the corresponding u_0 and that the ground-state wave function, which dominates the spectral sum (3.4), is proportional to $u'(y)$. The second phenomenon is a renormalization effect due to the Hartree field, which causes a shift of the eigenvalues with respect to the noninteracting case $\kappa=0$.

We explored the behavior of $u(y)$ for values of the field h_b varying over an interval of eight decades ($10^{-1}, 10^{-8}$). The accuracy of the numerical procedure was checked by solving the case $\kappa=0$ (i.e., working at the one-loop level) and testing its results against the analytical form of G_0 extracted from the work of Zittartz. This comparison gave us confidence that the algorithm was reliable down to $h_b=10^{-8}$. However, even before this limit was reached, for $h_b \approx 10^{-5}$ we found that the shape of the profile was not sensitive to further reductions of h_b . The discussion of the origin of this phenomenon will be postponed.

A more compact way of describing the results of the theory is to define a quantity to measure the interfacial broadening due to the capillary waves:

$$L = \int_{-\infty}^{\infty} [u(y) - u_0(y)] y dy . \quad (5.3)$$

We plotted the difference of first moments of the profile (5.3) against the square root of the logarithm of the exter-

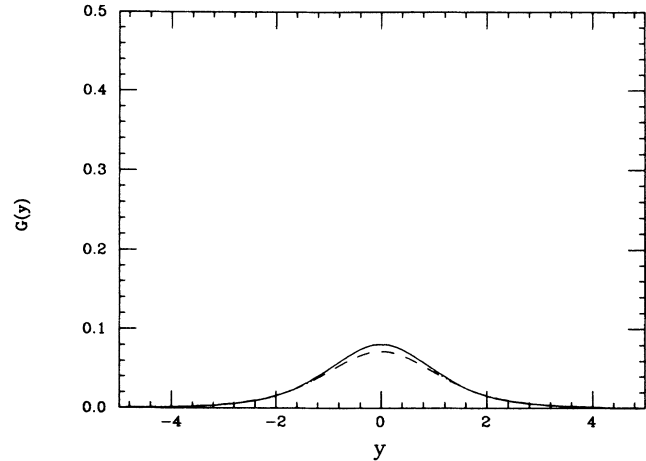


FIG. 3. $G_c(y,y)$ for $h_b=0.001$ and $\kappa=0.13$. Solid line, MFT result; dashed line, BEGA result.

nal field amplitude h_b as shown in Fig. 5. For large and intermediate values of the field we observe a linear behavior, while for smaller values of the field, as we already noticed in the study of the surface profile, the quantity L reaches a plateau value.

The question is the following: does this phenomenon represent a real feature of the model or is it an artifact due to the approximate treatment of correlations, upon which the present theory is based? To answer this question we wish to consider a number of sum rules for the order parameter and its correlations. These relations are a particular application of the Ward-Takahashi identities.¹²

Let us consider the Hamiltonian (2.1) and apply an infinitesimal translation ϵ to the field $\phi(\mathbf{x}) \rightarrow \phi(\mathbf{x} + \epsilon)$ and to the source $h(\mathbf{x}) \rightarrow h(\mathbf{x} + \epsilon)$. Since $W^{(1)}$ is invariant under this transformation we have

$$\delta W^{(1)} = -\epsilon \int d^d x \bar{\phi}(\mathbf{x}) \nabla h(\mathbf{x}) = 0 . \quad (5.4)$$

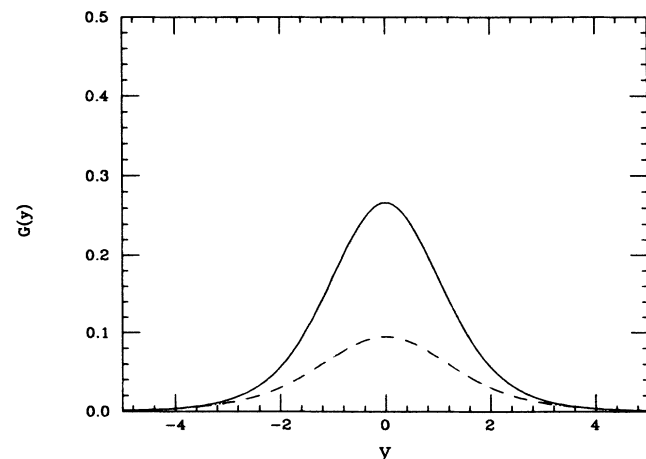


FIG. 4. $G_c(y,y)$ for $h_b=0.001$ and $\kappa=0.13$. Solid line, MFT; dashed line, BEGA.

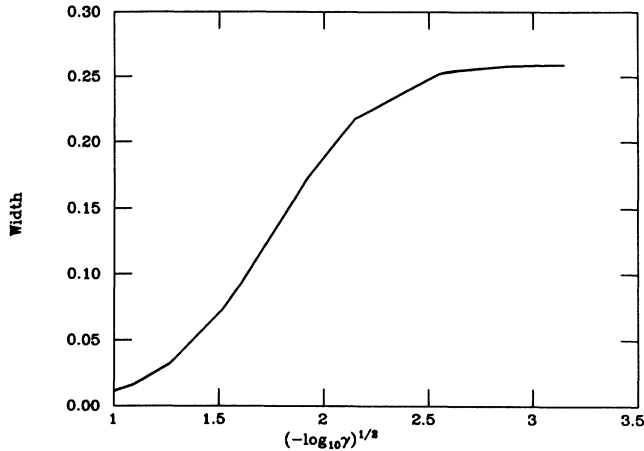


FIG. 5. Reduced width of the interfacial profile vs square root of the logarithm of the reduced amplitude γ_∞ of the external field for the value of the dimensionless coupling constant $\kappa=0.05$.

The second equality (5.4), which represents a zeroth-order sum rule for the average profile, is a consequence of the fact that a uniform translation of the system does not produce stresses into the system and leaves its free energy unchanged.

Functionally differentiating the integral which appears in (5.4) with respect to $h(\mathbf{x})$ one obtains

$$\nabla \bar{\phi}(\mathbf{x}) = \int d^d x' \frac{\delta \bar{\phi}(\mathbf{x}')}{\delta h(\mathbf{x})} \nabla h(\mathbf{x}'). \quad (5.5)$$

Using the definition of connected two-point Green function:

$$G_c(\mathbf{x}, \mathbf{x}') = \frac{\delta \bar{\phi}(\mathbf{x})}{\delta h(\mathbf{x}')}, \quad (5.6)$$

we obtain the first-order sum rule:

$$\nabla \bar{\phi}(\mathbf{x}) = \int d^d x' G_c(\mathbf{x}, \mathbf{x}') \nabla h(\mathbf{x}'). \quad (5.7)$$

The sum rule (5.7) was first written down by Wertheim and by Lovett, Mou, and Buff²⁰ based on the original work of Triezenberg and Zwanzig.²¹ An infinite set of sum rules of higher order can be obtained by further functional differentiation.

The translational invariance imposes several constraints between the correlations of different orders. We can recast Eq. (5.7) for the average profile in the form

$$\frac{d \bar{\phi}(z)}{dz} = \int_{-\infty}^{\infty} dz' G_c(z, z', \mathbf{Q}=0) \frac{dh(z')}{dz'}, \quad (5.8)$$

where $G_c(z, z', \mathbf{Q}=0)$ is the $\mathbf{Q}=0$ component of the transverse Fourier transform of the connected Green function $G_c(\mathbf{x}, \mathbf{x}')$ which can be obtained by solving the following equation derived in I:

$$\begin{aligned} & [-\nabla^2 + \mu^2 + \frac{1}{2} \lambda \bar{\phi}(\mathbf{x})^2 + \frac{1}{2} \lambda G_0(\mathbf{x}, \mathbf{x})] G_c(\mathbf{x}, \mathbf{x}') \\ & + \frac{1}{2} \lambda \bar{\phi}(\mathbf{x}) \int d^d x'' K(\mathbf{x}, \mathbf{x}'') G_c(\mathbf{x}'', \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'), \end{aligned} \quad (5.9)$$

with the kernel $K(\mathbf{x}, \mathbf{x}')$ defined by

$$\begin{aligned} K(\mathbf{x}, \mathbf{x}') &= \frac{\delta G_0(\mathbf{x}, \mathbf{x}')}{\delta \bar{\phi}(\mathbf{x}')} \\ &= \int d^d x'' \frac{\delta G_0(\mathbf{x}, \mathbf{x}')}{\delta h(\mathbf{x}'')} \frac{\delta h(\mathbf{x}'')}{\delta \bar{\phi}(\mathbf{x}')} \\ &= \int d^d x'' \frac{\delta G_0(\mathbf{x}, \mathbf{x}')}{\delta h(\mathbf{x}'')} G_c^{-1}(\mathbf{x}'', \mathbf{x}'). \end{aligned} \quad (5.10)$$

Equation (5.8) shows that G_c^{-1} in the limit of $h \rightarrow 0$ contains a zero eigenvalue associated with the translational invariance of the system, i.e., a rigid shift of the interface. Thus we expect $G_c(z, z', \mathbf{Q})$ to diverge in the limit of long-wavelength transverse fluctuations ($\mathbf{Q} \rightarrow 0$). At this stage, it would be tempting to identify G_0 with G_c . However, the presence of the last term in the right-hand side (rhs) of Eq. (5.9) shows that the two Green functions are different. G_0 , in fact, was defined as the order-parameter deviation in the reference system characterized by K_0 , whereas G_c , which satisfies a fluctuation dissipation theorem, was obtained by direct functional differentiation of $W^{(1)}$. The situation is to be contrasted with the equality between the averages $\langle \phi(\mathbf{x}) \rangle_0$ and $\langle \phi(\mathbf{x}) \rangle$ discussed in Sec. II.

This phenomenon is a manifestation of the incomplete thermodynamic consistency of the theory. In order to test the limit of validity of our approach we inserted G_0 into Eq. (5.8). In Fig. 6 we display the curve obtained by calculating the integral

$$I = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' G_0(z, z', \mathbf{Q}=0) \frac{dh(z')}{dz'} \quad (5.11)$$

against the line which represents the value $\bar{\phi}(\infty) - \bar{\phi}(-\infty)$, the integral of the lhs of Eq. (5.8). The difference between the two curves is a measure of the inaccuracy of the BEGA. On the other hand, we shall trust the results obtained in the region where the discrepancy is not too large.

Before concluding this section, it is worthwhile to di-

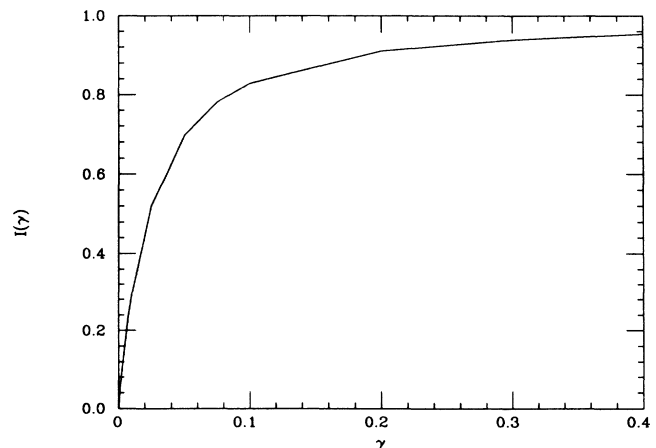


FIG. 6. The integral I , defined by Eq. (5.11) plotted against the reduced amplitude γ_∞ of the bulk field.

gress briefly to examine the consequences of identifying G_c with G_0 and of making the ansatz that only the ground-state mode contributes to the latter. In the single-mode approximation one writes

$$G_c(z, z') = \frac{1}{N^2} \int d^{d-1} Q \frac{\bar{\phi}(z)' \bar{\phi}(z')'}{(\epsilon_0 + Q^2)}, \quad (5.12)$$

with $N^2 = \int dz [\bar{\phi}(z)']^2$. The above expression is consistent with Wertheim's work and by construction satisfies the exact sum rule (5.8) if one assumes ϵ_0 to be a linear function of the external field. Inserting this form of G_c into Eq. (5.1) and taking the external field proportional to the profile (2.15) we obtain a second-order nonlinear differential equation involving only $\bar{\phi}$ and its first two derivatives. Using the scaled variables u and y , introduced above, the first integral of Eq. (5.1) can easily be calculated by quadrature and reads

$$\frac{du}{dy} = \frac{n^2}{A} \left[2 \exp \left[\frac{A}{2n^2} (1-u^2) \right] - \frac{A}{n^2} (1-u^2) - 2 \right]^{-1/2}, \quad (5.13)$$

where

$$A = \frac{\kappa}{4\pi} \ln \left[\frac{Q_c^2 + \epsilon_0}{\epsilon_0} \right].$$

The profile slope at the dividing surface $y=0$ is

$$\frac{du}{dy} = \frac{n^2}{A} \left\{ \left[2 \exp \left[-\frac{A}{2n^2} \right] + \frac{A}{n^2} - 2 \right] \right\}^{1/2}. \quad (5.14)$$

The above formula shows explicitly the vanishing of the derivative of the profile when the field goes to zero, i.e., when $A \rightarrow \infty$, as $\sqrt{1/A}$. Unfortunately, the normalization condition $n^2 = \int_{-\infty}^{\infty} dy u(y)^2$ shows that $A = -\ln \gamma$. Thus the profile vanishes linearly with $-1/\ln \gamma$, instead of showing the expected $\sqrt{(-1/\ln \gamma)}$ behavior. Thus we expect that the behavior of the true profile is somehow in the middle between the BEGA solution and the result of the approximate treatment of the last paragraph. In particular, we believe that mode-mode coupling must be present and renders the approach to the zero-field limit slower.

This result suggests the possibility of improving the present approach by treating separately the capillary-wave modes. This goal can be achieved by employing a reference ensemble, which does not contain the ground-state translational mode, to perform the Gaussian average and thus include the effects of capillary waves.

Another possible direction which could be taken in order to avoid the above problem would be to treat, with the present formalism, all the fluctuations but the capillary-wave modes along the lines proposed by Rudnick and Jasnow.²² These authors showed how to eliminate the contribution from the Goldstone modes to the partition function by introducing suitable constraints.

VI. FINAL REMARKS

To summarize we have formulated a self-consistent theory for nonuniform systems. Our approach, which can easily be generalized to Hamiltonians more complicated than the present ϕ^4 model, provides a good indication of how long-ranged correlations feedback to the profile.

To put things into perspective one should contrast the present results with the situation one encounters in MFT. There one observes a finite-thickness interfacial profile and long-ranged transverse correlations.

We studied the relation between the slow decay of correlations parallel to the interface and the thickness of the profile.

Our results support the modern viewpoint according to which, for $d \leq 3$, the capillary waves simultaneously induce long-ranged correlations and tend to wash out the profile. The broadening of the latter fitted a logarithmic law for intermediate and large values of the external field.

Unfortunately, as the pinning potential vanishes the accuracy of our method worsens since the variational estimate of the ground-state energy is not adequate and we find a situation in which both the interfacial thickness and the correlation $G_0(\mathbf{x}, \mathbf{x})$ remain finite as $h(\mathbf{x}) \rightarrow 0$. Seen from a different angle it was shown that this phenomenon can be attributed to the lack of thermodynamic consistency of the theory.

Finally, we recall that attempts to go beyond this picture starting from a three-dimensional description of the fluid have not produced so far the expected result for the density profile in the zero-field limit.

We also believe the present method can prove fruitful in studying surface phase transitions and fluctuations of liquid drops, etc.

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APPENDIX

In mathematical physics the number of potentials for which the Green function is known in closed analytical form is relatively limited. On the other hand in the case of a piecewise constant potential, such as a collection of square-well potentials of arbitrary width and depth, it is straightforward to construct $G_0(z, z')$, since it only requires the matching of the solutions at the boundaries, where the potential is discontinuous.

One starts by dividing the z axis in a number N of intervals whose extrema are z_0, z_1, \dots, z_N . In each interval one approximates the potential $U(z)$ by its value at midpoint. This procedure gives a discretized version of Eq. (3.3).

The wave functions of energy E of the associated Schrödinger problem $\psi^\pm(x, E)$, which describe, respectively, waves traveling to the right and to the left, have the following representation:

$$\psi^\pm(z, E) = a_j^\pm \exp(-i\gamma_j z) + b_j^\pm \exp(i\gamma_j z), \quad (\text{A1})$$

where $\gamma_j^\pm = [E - U((z_{j-1} + z_j)/2)]$ and $z_{j-1} < z < z_j$. It is easy to derive a recursive relation for the amplitudes a_j^\pm and b_j^\pm using the continuity of the wave functions and of their derivatives at the extrema of each interval. The matching conditions involving the coefficients of the transmitted and deflected waves read

$$a_j^\pm = \frac{\exp(i\gamma_j z_j)}{2} \left[\left(1 + \frac{\gamma_{j-1}}{\gamma_j} \right) \exp(-i\gamma_{j-1} z_j) a_{j-1}^\pm + \left(1 - \frac{\gamma_{j-1}}{\gamma_j} \right) \exp(i\gamma_{j-1} z_j) b_{j-1}^\pm \right] \quad (\text{A2})$$

and

$$b_j^\pm = \frac{\exp(-i\gamma_j z_j)}{2} \left[\left(1 - \frac{\gamma_{j-1}}{\gamma_j} \right) \exp(-i\gamma_{j-1} z_j) a_{j-1}^\pm + \left(1 + \frac{\gamma_{j-1}}{\gamma_j} \right) \exp(i\gamma_{j-1} z_j) b_{j-1}^\pm \right]. \quad (\text{A3})$$

The choice of coefficients $a_N^+ = 0, b_N^+ = 1$ and $a_0^- = 1, b_0^- = 0$ satisfies the boundary condition at $\pm\infty$. Starting with a_0^- and b_0^- one generates all the remaining $2N$ amplitudes, by means of the recursive relations (A2) and (A3). By means of the corresponding backward process starting from a_N^+ and b_N^+ one obtains the a_j^+, b_j^+ coefficients. By inspection one sees that the Wronskian is

$$w(E) = -2i\gamma_0 a_N^-.$$

Finally the diagonal part of the Green function, taking into account the symmetry $z \rightarrow -z$ of the problem, can be written

$$G_0(z, z; E) = \frac{[a_j^- \exp(-i\gamma_j z) + b_j^- \exp(i\gamma_j z)][a_{N-j}^- \exp(-i\gamma_j z) + b_{N-j}^- \exp(i\gamma_j z)]}{w(E)}, \quad z_j < z < z_{j+1}. \quad (\text{A4})$$

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