CONVERGENT APPROXIMATION FOR THE 2-BODY CORRELATION FUNCTION IN AN INTERFACE

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A convergent approximation is proposed for a mean field density-density correlation function in a system with a two-phase interface. It is based on a fourth-order expansion of the Hamiltonian in terms of fluctuations around the equilibrium profile. The approach is illustrated by one and three dimensional calculations for systems characterized by the Ginzburg-Landau functional.

I. INTRODUCTION

Density correlations in the vicinity of equilibrium planar interfaces have been extensively studied by numerous authors [1-4]. Several methods, including the density functional theory [5,6], the capillary wave model [3,4], and the eigenstate expansion of the fluctuations [2,5,6] were used to calculate the correlation function. Most existing approaches have to confront a problem of divergence, caused by the vanishing energy cost of rigid shifts of the interface in an infinite system without external potential. We will focus in this work on the Hamiltonian second derivative \( \frac{\delta^2 H[\rho]}{\delta \rho(z_1) \delta \rho(z_2)} \) eigenstate expansion method (sometimes also called “field theoretical method”, [2]). In the framework of this method the divergence manifests itself in the term \( \phi_0(z_1) \phi_0(z_2)/\lambda_0 \) where \( \phi_0(z) \) and \( \lambda_0 \) are the “zero” eigenstate and eigenvalue; \( \phi_0(z) \equiv d \rho_0(z)/dz \) where \( \rho_0(z) \) is the equilibrium density profile. The eigenvalue \( \lambda_0 \) is zero for vanishing external localizing field. The traditional physical explanation for the divergence is the following: the density fluctuations corresponding to the interface shifts, to the first order of shift amplitude, have component only along the zero eigenstate, \( \Delta \rho(z) = \rho_0(z + \Delta z) - \rho_0(z) = d \rho_0(z)/dz \Delta z + O(\Delta z)^2 \), and free wandering of the interface as a whole results in the ambiguity in defining the density-density correlation function. In the framework of the capillary wave model ([3]) this ambiguity is overcome by renormalizing the equilibrium density profile by taking into account the free wandering mode. As a result, average width of the renormalized interface diverges for vanishing external field, and the zero-order term contribution to the density-density correlation function tends to zero. However, after such renormalization, one loses information about instantaneous and local fluctuations of the interface.

In an attempt to resolve this ambiguity, we would like to focus our attention on the question of divergence of the zero eigenstate term. The main motivation of our approach lies in the following.

It is true that in an infinite system without a confining external field the energy cost of rigid shifts of the planar two-phase interface is zero, \( H[\rho(z_0 + \Delta z)] = H[\rho(z_0)] \). Yet this does not mean that the amplitude \( \rho_0 \) of the density fluctuation proportional to the zero eigenstate, \( \delta \rho(z) = a \rho_0(z) \) can grow infinitely without a free-energy penalty. Physically it follows from the fact, that although the position of the interface is undetermined, the actual values of the density near the interface cannot go significantly beyond the density of either of the bulk phases. For all the realistic Hamiltonian functionals describing stable systems, this non-divergence is controlled by a positive coefficient in front of the highest power of the density. For the Ginzburg-Landau functional

\[
\mathcal{H}[\rho] = \int \left( \frac{d}{dz} \rho(z) \right)^2 + \left( 1 - \rho^2(z) \right)^2 dz
\]  

(1)

the latter is \( +\rho^4(z) \). The divergence that appears when only the harmonic (second-order) terms of the expansion of the Hamiltonian are used is the direct consequence of neglect of all higher-order terms. Hence, to eliminate the divergence of the zero-eigenstate term in the correlation function, it is natural to try using higher-order terms of the expansion of the Hamiltonian around the equilibrium density profile (see [2] where the equilibrium profile was calculated using higher-order terms). It turns out that fourth-order terms are sufficient to keep the zero-eigenstate contribution finite. We propose an approximate method to consider these fourth order terms; this method is formally introduced in Section II. Concrete examples for the Ginzburg-Landau Hamiltonian for one- and three-dimensional systems are presented in Sections III and IV.

However, after eliminating the divergence of the zero-order eigenstate term, it is natural to ask, which eigenstate or combination of eigenstates of the second derivative matrix describe the macroscopic shifts of the interface \( \Delta \rho(z) = \rho_0(z + \Delta z) - \rho_0(z) \)? The expansion coefficient of this density fluctuation along the zero eigenstate remains finite even for infinite shifts,
for $\Delta z \to +\infty$. This statement could serve as another argument for a finite average value of the amplitude of fluctuation along $\rho_0'(z)$. The same is true for all other bound (localized) eigenstates. Yet the projection of the shift $\rho_0(z + \Delta z) - \rho_0(z)$ onto low-lying continuum states diverges as $\Delta z \to \infty$. For the Ginzburg-Landau Hamiltonian the mean-field equilibrium density profile is $\rho_0(z) = \tanh(z)$, and the first non-localized eigenstate of the second derivative matrix is proportional to $(3\tanh(z) - 1)/2$. The integral

$$\int_{-\infty}^{+\infty} (\tanh(z + \Delta z) - \tanh(z))(3/2\tanh(z) - 1/2)dz \to 2\Delta z$$

diverges linearly for $\Delta z \to \infty$. It means that since macroscopic shifts have no energy cost, the appropriate linear combination of low-lying continuum states with some of the coefficients growing proportionally to the magnitude of the shift also has no energy cost. The finiteness of the average values of all the continuum spectrum amplitudes is another artifact of second-order truncation; in particular, it is a result of the neglect of the mixing of different harmonics in the third and higher-order terms. Consequently, our approximation is convergent only because, after going to the higher-order expansion in the zero term, we stopped short of going beyond the harmonic approximation for terms containing the lowest-lying continuum states.

However, the main contribution to the correlations near the interface comes from the bound states, while continuum states are more relevant for the correlations in the bulk phases. A possible merit of our approximation is the improvement in the accuracy of density correlation calculations in the vicinity of the interstate. To compare our results to experimental data, theoretical calculations should be supplemented by a priori knowledge of the macroscopic localization of the interface.

For a three-dimensional system the situation is similar. For square-gradient energy functionals, the perturbation $\Delta \rho(x, y, z) = \rho_0(z + f(x, y)) - \rho_0(z)$ of an initially flat interface has the energy cost

$$\Delta F = \int_{-\infty}^{+\infty} |\rho'_0(z)|^2dz \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} |\nabla f(x, y)|^2dxdy$$

For long-wavelength fluctuations, $f(x, y) \sim \exp[i(k_x x + k_y y)]$, $|\vec{k}| \ll 1$, the energy cost of such fluctuations vanishes as $|k|^2$. However, considering the expansion of the density fluctuations over the system of eigenstates (now in 3D) of the Hamiltonian second derivative matrix, $\psi_i(\vec{r}) \equiv 1/L \phi_i(z) \exp(i k_x x) \exp(i k_y y)$, the divergent contribution comes not from the terms with localized $\phi_i$, but from the bottom of the continuum of $z$-coordinate eigenstates. To illustrate that, in section IV we calculate the convergent contribution to the correlation function from the $\phi_0(z) \exp(i k_x x) \exp(i k_y y)$ eigenstate.

II. FORMALISM

A density-density correlation function $g(z_1, z_2)$ is defined as a thermal average of a product of density fluctuations $\Delta \rho(z) = \rho(z) - \rho_0(z)$ around the equilibrium density profile $\rho_0(z)$:

$$g(z_1, z_2) \equiv \langle \Delta \rho(z_1) \Delta \rho(z_2) \rangle.$$

For simplicity, in this section we consider a one-dimensional case, $\rho = \rho(z)$. Following we express it as a functional integral over all possible density profiles,

$$g(z_1, z_2) = (1/Z) \int D\rho \Delta \rho(z_1) \Delta \rho(z_2) \exp\{-\mathcal{H}[\rho]\}$$

where $\mathcal{H}[\rho] \equiv H[\rho]/k_bT$ is a reduced Hamiltonian functional, and the partition function $Z$ serves as the normalization constant,

$$Z = \int D\rho \exp\{-\mathcal{H}[\rho]\}$$

In the mean-field approximation that we will use through this work, the equilibrium density profile $\rho_0(z)$ is determined as the one that minimizes the Hamiltonian,
\[
\frac{\delta \mathcal{H}[\rho]}{\delta \rho(z)} \bigg|_{\rho = \rho_0} = 0. \tag{8}
\]

To evaluate (8), we proceed by calculating the eigenstates of the integral operator with the kernel \( \frac{\delta^2 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2)} \bigg|_{\rho = \rho_0} \):

\[
\int \frac{\delta^2 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2)} \bigg|_{\rho = \rho_0} \phi_i(z_2) dz_2 = \lambda_i \phi_i(z_1). \tag{9}
\]

There is always a special eigenstate corresponding to \( \phi_0(z) = d\rho_0(z)/dz \) which has zero eigenvalue \( \lambda_0 = 0 \) since

\[
\int \frac{\delta^2 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2)} \bigg|_{\rho = \rho_0} \frac{d\rho_0(z_2)}{dz_2} dz_2 = \frac{d}{dz} \frac{\delta \mathcal{H}[\rho]}{\delta \rho(z)} \bigg|_{\rho = \rho_0} = 0. \tag{10}
\]

The Hamiltonian is usually real and contains only even powers of differential operators; it makes the integral operator in Eq. (10) Hermitian. The system of eigenstates \( \phi_i \) is complete and orthogonal; we also assume that it is normalized with unit weight function and all eigenfunctions \( \phi_i \) are made real. An arbitrary density fluctuation \( \Delta \rho(z) = \rho(z) - \rho_0(z) \) can be expanded over the complete set of functions \( \{ \phi_i(z) \} \):

\[
\Delta \rho(z) = \sum_{i=0}^{\infty} a_i \phi_i(z), \quad a_i = \int \Delta \rho(z) \phi_i(z) dz \tag{11}
\]

Using the expansion (11), the functional integral (3) can be expressed as

\[
g(z_1, z_2) = \frac{1}{Z} \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \int \ldots \int a_i a_j \phi_i(z_1) \phi_j(z_2) \exp\{-\mathcal{H}[\rho_0 + \sum_{k=0}^{\infty} a_k \phi_k]\} \prod_{m=0}^{\infty} da_m \tag{12}
\]

where the normalization constant

\[
Z = \int \ldots \int \exp\{-\mathcal{H}[\rho_0 + \sum_{k=0}^{\infty} a_k \phi_k]\} \prod_{m=0}^{\infty} da_m. \tag{13}
\]

We assume here that the integrals in both numerator and denominator are convergent. As we mentioned in the Introduction, it is not true for the single specific direction in the space of coefficients \( \{ a_i \} \), corresponding to the rigid macroscopic shifts of the interface. However, as a result of the approximations made below, this divergence will not affect the further calculations.

Traditionally, \( \mathcal{H}[\rho_0 + \sum_{k=0}^{\infty} a_k \phi_k] \) is expanded to the second order around the equilibrium density profile, the orthogonality conditions for the \( \phi_i \) are used, and the corresponding Gaussian integrals factorized (13). As a result, the familiar expression for the density-density correlation function is recovered:

\[
g(z_1, z_2) = \sum_{i=0}^{\infty} \langle a_i^2 \rangle \phi_i(z_1) \phi_i(z_2), \tag{14}
\]

where \( \langle a_i^2 \rangle = 1/\lambda_i \). As we already mentioned, the zero term diverges since \( \lambda_0 = 0 \).

However, as we discussed in the Introduction, from physical considerations \( \langle a_i^2 \rangle \) must have finite value. It is indeed the case if in Eqs. (12), (13) one goes to higher than second order in the expansion of \( \mathcal{H}[\rho] \).

In our case, the expansion of \( \mathcal{H}[\rho] \) up to the fourth order in the density fluctuation around the equilibrium profile is sufficient:

\[
\mathcal{H}[\rho_0 + \sum_{k=0}^{\infty} a_k \phi_k] \approx \\
\sum_{k=0}^{\infty} a_k \int \frac{\delta \mathcal{H}[\rho]}{\delta \rho(z)} \bigg|_{\rho = \rho_0} \phi_k(z) dz + \\
\frac{1}{2} \sum_{k,j=0}^{\infty} a_k a_j \int \int \frac{\delta^2 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2)} \bigg|_{\rho = \rho_0} \phi_k(z_1) \phi_j(z_2) \prod_{j=1}^{2} dz_j + \tag{15}
\]

...
The equilibrium density profile for symmetric boundary conditions \( \rho \) and the third and fourth-order functional derivatives of \( \rho \) are essential for our treatment. If we substitute this expansion into the expressions for the correlations function (12), (13), for non-pathological forms of the Hamiltonian functional it will produce a finite value for \( \langle a_0^2 \rangle \). However, in their complete form Eqs. (12), (13), (15) are hardly tractable. Assuming that we are far enough from a critical point, we use the following approximation to evaluate \( \langle a_0^2 \rangle \). We assume that the second-order expansion works well enough for all \( \langle a_0^2 \rangle = 1/\lambda_i \) with \( i \neq 0 \) and drop from Eq. (13) all terms that do not contain \( a_0 \). In the remaining terms we replace all combinations of \( a_i, a_ia_j, a_ia_ja_k, \{i, j, k\} \neq 0 \) by their average values obtained with the second-order expansion:

\[
\langle a_i \rangle = 0, \\
\langle a_ia_j \rangle = \delta_{ij} \frac{1}{\lambda_i}, \\
\langle a_ia_ja_k \rangle = 0. \tag{16}
\]

This approximations allow us to express \( \langle a_0^2 \rangle \) in the form of the following integral:

\[
\langle a_0^2 \rangle = \frac{\int x^2 \exp\{-\alpha x^4 - \beta x^2 - \gamma x - \delta x^3\} dx}{\int \exp\{-\alpha x^4 - \beta x^2 - \gamma x - \delta x^3\} dx}, \tag{17}
\]

with coefficients \( \alpha, \beta, \gamma \) given by

\[
\alpha = \frac{1}{4!} \int \int \int \frac{\delta^4 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2) \delta \rho(z_3) \delta \rho(z_4)}|_{\rho=\rho_0} \phi_0(z_1) \phi_0(z_2) \phi_0(z_3) \phi_0(z_4) \prod_{j=1}^{4} dz_j, \\
\beta = \frac{1}{4} \sum_{i=1}^{\infty} \frac{1}{\lambda_i} \int \int \int \frac{\delta^4 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2) \delta \rho(z_3) \delta \rho(z_4)}|_{\rho=\rho_0} \phi_i(z_1) \phi_i(z_2) \phi_0(z_3) \phi_0(z_4) \prod_{j=1}^{4} dz_j, \tag{18}
\]

\[
\gamma = \frac{1}{4!} \prod_{i=1}^{\infty} \frac{1}{\lambda_i} \int \int \int \frac{\delta^4 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2) \delta \rho(z_3) \delta \rho(z_4)}|_{\rho=\rho_0} \phi_i(z_1) \phi_i(z_2) \phi_0(z_3) \phi_0(z_4) \prod_{j=1}^{4} dz_j, \\
\delta = \frac{1}{4!} \prod_{i=1}^{\infty} \frac{1}{\lambda_i} \int \int \int \frac{\delta^4 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2) \delta \rho(z_3) \delta \rho(z_4)}|_{\rho=\rho_0} \phi_0(z_1) \phi_0(z_2) \phi_0(z_3) \phi_0(z_4) \prod_{j=1}^{4} dz_j.
\]

### III. Ginzburg-Landau Hamiltonian

To illustrate our approach let us consider a simple 1D system with the Ginzburg-Landau Hamiltonian \( \mathcal{H}[\rho] \). The equilibrium density profile for symmetric boundary conditions \( \rho(-l) = -1, \rho(+l) = 1, l \to \infty \) is \( \rho_0(z) = \tanh(z) \). The eigenvalue equation \( \mathcal{H}[\rho] \) takes the differential form

\[
-2 \frac{d^2}{dz^2} \phi_i(z) - 4 \phi_i(z) + 12 \tanh^2(z) \phi_i(z) = \lambda_i \phi_i(z), \tag{19}
\]

and the third and fourth-order functional derivatives of \( \mathcal{H}[\rho] \) are:

\[
\frac{\delta^3 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2) \delta \rho(z_3)}|_{\rho=\rho_0} = 24 \tanh(z_1) \delta(z_1 - z_2) \delta(z_2 - z_3). \tag{20}
\]
\[
\frac{\delta^4 \mathcal{H}[\rho]}{\delta \rho(z_1) \delta \rho(z_2) \delta \rho(z_3) \delta \rho(z_4)} \bigg|_{\rho = \rho_0} = 24 \delta(z_1 - z_2) \delta(z_2 - z_3) \delta(z_3 - z_4). \tag{21}
\]

In fact, the expansion (13) is now exact for \( \mathcal{H}[\rho] \) since all higher-order variational derivatives are identically equal to zero. To proceed further we need to calculate \( \alpha, \beta, \gamma, \) and \( \delta \) as defined in Eq. (18). From parity consideration, the coefficients \( \gamma \) and \( \delta \) are zero.

The calculation of \( \alpha \) is straightforward:

\[
\alpha = \frac{9}{16} \int_{-\infty}^{+\infty} \frac{dz}{\cosh^6(z)} = \frac{18}{35}. \tag{22}
\]

The coefficient \( \frac{9}{16} \) appears from the normalization condition:

\[
\int_{-\infty}^{+\infty} \phi_i^2(z) dz = 1. \tag{23}
\]

To evaluate \( \beta \) we need to know the eigenstates \( \phi_i(z) \) of Eq. (19):

\[
\beta = \frac{9}{2} \sum_{i=1}^{\infty} \int_{-\infty}^{+\infty} \frac{\phi_i^2(z)}{\lambda_i} \frac{dz}{\cosh^4(z)}. \tag{24}
\]

The sum in Eq. (24) contains a contribution from one bound state, \( \phi_1(z) = \sqrt{3/2}\sinh(z)\cosh^{-2}(z), \lambda_1 = 6 \) and continuum states \( (i \geq 2) \) To evaluate the sum over the continuum, we use expressions obtained in [6] (Eq. (3.15 - 3.20)):

\[
\frac{9}{2} \sum_{i=2}^{\infty} \int_{-\infty}^{+\infty} \frac{\phi_i^2(z)}{\lambda_i} \frac{dz}{\cosh^4(z)} = \frac{9}{4} \int_{-\infty}^{+\infty} \frac{dk}{2\pi (k^2 + 4)^2} \frac{1}{2(k^2 + 1)} \int_{-\infty}^{+\infty} \frac{\phi_k(z)}{\cosh^4(z)} dz \tag{25}
\]

where the continuum eigenstates \( \phi_k(z) \) are

\[
\phi_k(z) = \exp(ikz)[1 + k^2 + 3ik\tanh(z) - 3 \tanh^2(z)]. \tag{26}
\]

The normalization of \( \phi_k(z) \) is taken into account in the \( k \)-dependent factor of the outer integral in (25). Both integrations in (25) are straightforward and finally we obtain for \( \beta \)

\[
\beta \approx \frac{6}{35} + 0.022 \approx 0.193 \tag{27}
\]

The contribution from the continuum to the value of \( \beta \) is \( \approx 13\% \). We substitute these values of \( \alpha \) and \( \beta \) into Eq. (17), and, in the first order in \( \beta/\sqrt{\alpha} \), obtain for \( \langle a_0^2 \rangle \):

\[
\langle a_0^2 \rangle \approx \int \frac{x^2 \exp\{-\alpha x^4\}(1 - \beta z^2)dz}{\int \exp\{-\alpha x^4\}(1 - \beta z^2)dz} = \frac{1}{\sqrt{\alpha}} \frac{\Gamma^2(\frac{1}{4}) - \frac{\beta}{\sqrt{\alpha}} \Gamma^2(\frac{3}{4})}{\pi \sqrt{2} \frac{\beta}{\sqrt{\alpha}} \Gamma^2(\frac{3}{4})} \approx 0.415 \tag{28}
\]

It is interesting to note that if one ignores all cross-terms (contribution from \( \beta \)) in Eq. (17), \( \langle a_0^2 \rangle \approx 0.471 \). For the Ginzburg-Landau Hamiltonian, \( \frac{\beta}{\sqrt{\alpha}} \approx 0.27 \) plays the role of a small parameter in the approximations (16) - (18), as well as in (28). Hence there is a certain degree of numerical justification of heuristic assumptions made in (16) - (18). To obtain the final result for the density-density correlation function (14) we use the following method. When the external potential \( V(z) = cz \), linear in the coordinate \( z \) measured form the interface location \( z = 0 \), is added to the Hamiltonian, the zero eigenvalue becomes proportional to the coefficient in front of this term: \( \lambda_0 \propto c \). In (8) an expression for the correlation function \( G_c(z_1, z_2) \) (Eq. (4.17) in [1]) is obtained in the presence of an external potential \( V(z) \), with \( V(z) \to c \tanh(z) \) when \( c \to 0 \). It is shown that the zero eigenvalue \( \lambda_0/c \to 1 \) for \( c \to 0 \). Since for \( i \geq 1 \) all \( \lambda_i \) go to constant limits when the external potential is turned off, the “truncated” correlation function \( \bar{g} \) (without the zero eigenstate term) can be expressed as:

\[
\bar{g}(z_1, z_2) = \sum_{i=1}^{\infty} \frac{\phi_i(z_1)\phi_i(z_2)}{\lambda_i} \lim_{c \to 0} \frac{d}{dc} c G_c(z_1, z_2). \tag{29}
\]
To recover the “non-truncated” correlation function \( g(z_1, z_2) \) we add to \( \bar{g}(z_1, z_2) \) from (29) the correct contribution from the zero-order term,

\[
g(z_1, z_2) = \bar{g}(z_1, z_2) + \frac{3}{4 \cosh^2(z_1) \cosh^2(z_2)} \langle a_0^2 \rangle.
\]

(30)

with \( \langle a_0^2 \rangle \) given by (28). Sketches of the density-density correlation function (30) are presented in Figs. 1, 2. It is straightforward to demonstrate that far from the interface \((z_1, z_2 \gg 1)\), the density-density correlation function (30) goes to the correct bulk phase limit,

\[
g_{\text{bulk}}(z_1, z_2) = \frac{\exp(-2|z_1 - z_2|)}{8}.
\]

(31)

Fig. 1. A contour plot of the density-density correlation function \( g(z_1, z_2) \).
IV. 3D CALCULATION

The next logical step is to generalize this approach to a more realistic 3D system. For simplicity, we consider the same Ginzburg-Landau Hamiltonian as in (1)

$$H[\rho] = \int (|\nabla \rho|^2 + \{1 - \rho^2(\vec{r})\}^2) d\vec{r}$$  \hspace{1cm} (32)

The equilibrium density profile for the symmetric boundary conditions $\rho(z = -l) = -1$, $\rho(z = +l) = 1$, $l \to \infty$ is the same as in the 1D case, $\rho_0(z) = \tanh(z)$. The three-dimensional analog of the eigenvalue equation (19) reads

$$-2\Delta \psi_i(\vec{r}) - 4\psi_i(\vec{r}) + 12 \tanh^2(z) \psi_i(\vec{r}) = \lambda_i \psi_i(\vec{r})$$  \hspace{1cm} (33)

Since the “potential” term in (33) depends only on $z$, the variables can be separated, $\psi_i(\vec{r}) = \phi_i(z) \xi_i(x, y)$. We assume that in the $xy$ plane the system is confined to a square box of size $L$ with periodic boundary conditions. Then the
The components of the eigenstates of (33) are the normalized plane waves \( \xi_k(x, y) = (1/L) \exp(ik_x x) \exp(ik_y y) \) with \( k_{(x,y)} = 2\pi n_{(x,y)}/L, n_{(x,y)} = 0, \pm 1, \pm 2 \ldots \). Expanding density variations over the complete set of functions \( \psi_{i\bar{k}}(\vec{r}) \) and taking the thermal average, we obtain for the density-density correlation function (compare to (13)):

\[
g(\vec{r}_1, \vec{r}_2) = \frac{1}{Z} \sum_{i, \bar{k}_1, \bar{k}_2} \sum_{j, \bar{k}_3} \cdots \int a_{i, \bar{k}_1} a_{j, \bar{k}_2} \psi^*_{i\bar{k}_1}(\vec{r}_1) \psi^*_{j\bar{k}_2}(\vec{r}_2) \exp\{-\mathcal{H}[\rho_0 + \sum_{m, \bar{k}_3} a_{m\bar{k}_3} \psi^*_{m\bar{k}_3}]\} \prod_{n, \bar{k}_4} da_{n\bar{k}_4}.
\]

Similarly to (13), \( Z \) is a normalization constant:

\[
Z = \int \cdots \int \exp\{-\mathcal{H}[\rho_0 + \sum_{m, \bar{k}_1} a_{m\bar{k}_1} \psi^*_{m\bar{k}_1}]\} \prod_{n, \bar{k}_2} da_{n\bar{k}_2}.
\]

Here and below we use the shorthand notation: for sums, products, and subscript indexes symbol \( \bar{k} \) means the set of \( xy \) eigenstate indexes \( \{n_x, n_y\} \). After expanding (34) to the second order in the density variation, an expression analogous to (14) is recovered:

\[
g(\vec{r}_1, \vec{r}_2) = \sum_{i, \bar{k}} (\alpha a_{i\bar{k}}^2) \rho^*_{i\bar{k}}(\vec{r}_1) \rho^*_{i\bar{k}}(\vec{r}_2),
\]

with \( \langle a_{i\bar{k}}^2 \rangle = 1/(\lambda_i + 2k^2) \). As in (14), a similar problem arises for the \( \lambda_0 = 0 \) eigenstate: for \( L \to \infty \) the sum on \( \bar{k} \) diverges at the lower limit.

To avoid the divergence occurring in the \( \lambda_0 = 0 \) term, we suggest the same recipe as in the one-dimensional case: to continue the expansion of the Hamiltonian to the fourth order. For simplicity, we neglect mixing of the eigenstates with different \( \lambda \) in the fourth-order term. Similarly to the 1D case, where the relative contribution of mixing is given by the ratio of coefficients \( \beta/\sqrt{\alpha} \approx 0.27 \), the inclusion of this mixing here will not affect convergence but will slightly change the numerical values of the coefficients. For all \( \lambda_i \neq 0 \), the second-order result (36) is sufficient, hence we perform fourth-order expansion only for the subspace of eigenstates with \( \lambda_0 = 0 \). The contribution from the \( \lambda_0 = 0 \) eigenstate to the density-density correlation function can be expressed as:

\[
g_0(\vec{r}_1, \vec{r}_2) = \frac{1}{Z_0} \sum_{\bar{k}_1} \sum_{\bar{k}_2} \cdots \int a_{0\bar{k}_1} a_{0\bar{k}_2} \psi^*_{0\bar{k}_1}(\vec{r}_1) \psi^*_{0\bar{k}_2}(\vec{r}_2) \exp\{-\mathcal{H}[\rho_0 + \sum_{\bar{k}_3} a_{0\bar{k}_3} \psi^*_{0\bar{k}_3}]\} \prod_{\bar{k}_4} da_{0\bar{k}_4},
\]

Using the orthogonality conditions for \( \xi_k(z, y) \) and Eq. (18) we obtain

\[
g_0(\vec{r}_1, \vec{r}_2) = \frac{1}{Z_0} \sum_{\bar{k}_1} \sum_{\bar{k}_2} \cdots \int a_{0\bar{k}_1}^2 \psi^*_{0\bar{k}_1}(\vec{r}_1) \psi^*_{0\bar{k}_1}(\vec{r}_2) \exp\{-2 \sum_{\bar{k}_3} \frac{a_{0\bar{k}_3}^2 k_3^2}{\alpha \sum_{\bar{k}_3} a_{0\bar{k}_3}^2} \} \prod_{\bar{k}_4} da_{0\bar{k}_4},
\]

\[
Z_0 = \int \cdots \int \exp\{-2 \sum_{\bar{k}_3} \frac{a_{0\bar{k}_3}^2 k_3^2}{\alpha \sum_{\bar{k}_3} a_{0\bar{k}_3}^2} \} \prod_{\bar{k}_4} da_{0\bar{k}_4},
\]

where \( \alpha \) is defined by (22). Direct evaluation of the functional integrals in (38) is impossible; however, a simple approximation will allow us to obtain a physically reasonable expression for \( g_0(\vec{r}_1, \vec{r}_2) \). The main contribution to the integral in (38) comes from \( a_{0\bar{k}} \) with small \( |\bar{k}| \), so in the first approximation it is natural to introduce an upper cutoff \( C \) in sums on \( \bar{k} \). In particular, we replace the infinite limits in all the sums and products on \( n_x \) and \( n_y \) in (38) by the finite cutoff, \( |n_x, n_y| \leq \sqrt{CL}/2 \). It corresponds to a system-size-independent cutoff for a wavevector \( \bar{k} \) with
|$k_{x,y}| \leq \sqrt{C\pi}$. We select $C$ in such a way that the term $-2\sum_k a_{0k}^2 k^2$, quadratic in $a_{0k}$, can be neglected in the exponent, which decouples the integration over $da_{0k}$ from the summation on $n_x,n_y$. Besides neglecting the quadratic term, we remove the functions $\psi_{0k}(\vec{r})$ from (38), and call the remaining expression $A$.

\[
A = \sum_{k_1} \cdots \int \frac{\exp\{-\frac{\alpha}{L^2} \sum_{k_1=1}^{N} a_{k_1}^2 \} \prod a_{k_3}}{\cdots \int \exp\{-\frac{\alpha}{L^2} \sum_{k_4=1}^{N} a_{k_4}^2 \} \prod a_{k_5}} \cdots
\]

with $N = CL^2$. This expression can be evaluated by using $N$-dimensional spherical coordinates, $\sum_k a_k^2 \equiv R^2$

\[
A = \int \frac{\int \frac{R^2 \exp\{-\frac{\alpha}{L^2} R^4 \} R^{N-1} \Omega_N dR}{\int \exp\{-\frac{\alpha}{L^2} R^4 \} R^{N-1} \Omega_N dR}}{\sqrt{\alpha \Gamma(N/2)}} = \frac{L}{2} \left[ \sqrt{\frac{N}{\alpha}} + O\left(\frac{1}{\sqrt{N}}\right)\right]
\]

Here $\Omega_N = 2\pi^{N/2}/\Gamma(N/2)$ is the area of the $N$-dimensional sphere. By inspection, one can identify $A$ as the sum of the first $N$ terms of $\langle a^2 \rangle$, $A = \sum_{i=1}^{N} \langle a^2 \rangle$. Therefore

\[
\langle a^2 \rangle = \frac{A}{N} = \frac{1}{2} \sqrt{\frac{1}{\alpha C}}
\]

Now we return to Eq. (38) and replace one sum in the fourth-order term in the exponential by $\sum_{i=1}^{N} \langle a^2 \rangle$:

\[
\frac{\alpha}{L^2} \sum_{k} a_{0k}^2 \approx \frac{\alpha}{L^2} \sum_{k} a_{0k}^2 \langle a^2 \rangle = \frac{\sqrt{\alpha C}}{2} \left[ \sum_{k} a_{0k}^2 \right]
\]

After this substitution, Eq. (38) becomes a product of Gaussian integrals and its evaluation becomes trivial:

\[
g_0(\vec{r}_1, \vec{r}_2) \approx \phi_0(z_1)\phi_0(z_2) \sum_k \tilde{a}_k^2 \exp\left[i(k_x x + k_y y)\right],
\]

where the “improved” average values $\tilde{a}_k^2$ are given by

\[
\tilde{a}_k^2 = \frac{\int a_k^2 \exp\left[-a_k^2(2k^2 + \sqrt{\alpha C}/2)\right] da_k}{\int \exp\left[-a_k^2(2k^2 + \sqrt{\alpha C}/2)\right] da_k} = \frac{1}{4k^2 + \sqrt{\alpha C}}
\]

Taking the limit $L \to \infty$ and replacing the summation $\sum_{n_x,n_y}$ in (43) by the integration $\int d\vec{k} \int d\vec{k}$, we obtain

\[
g_0(\vec{r}_1, \vec{r}_2) \approx \phi_0(z_1)\phi_0(z_2) \frac{1}{(4\pi)^2} \int_0^\infty \frac{k dk}{k^2 + \sqrt{\alpha C}/4} J_0(k r_\perp) = \phi_0(z_1)\phi_0(z_2) \frac{1}{(4\pi)^2} K_0\left[\frac{(\alpha C)^{1/4} r_\perp}{2}\right].
\]

Here $J_0$ and $K_0$ are Bessel and Modified Hankel functions of zero order and $r_\perp \equiv \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}$. For large positive $q$ one has $K_0(q) = \sqrt{\pi/2q} \exp(-q)[1 + O(1/q)]$. Consequently, we can identify $(\alpha C)^{1/4}/2$ with the previously introduced upper cutoff for the wavevector $k$, i.e., with $\sqrt{C\pi}$. It allows us to express the constant $C$ through the known parameters of the system, $C = \alpha/(4\pi)^3$. Finally, we write for the zero-eigenstate contribution to the correlation function:

\[
g_0(\vec{r}_1, \vec{r}_2) \approx \phi_0(z_1)\phi_0(z_2) \frac{1}{(4\pi)^2} K_0\left[\frac{\sqrt{\alpha}}{4\pi} \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}\right].
\]

The contribution from other eigenstates, $\tilde{g}(\vec{r}_1, \vec{r}_2)$, is obtained by straightforward integration,

\[
\tilde{g}(\vec{r}_1, \vec{r}_2) = \sum_{j=1}^{N} \phi_j(z_1)\phi_j(z_2) \frac{1}{2(2\pi)^2} K_0\left[\frac{\sqrt{\lambda_j}}{2} \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}\right]
\].
V. CONCLUSION

We show that taking into account the fourth-order terms in the expansion of the Hamiltonian in the calculation of the density-density correlation function makes the previously divergent (for $D \leq 3$) zero-eigenstate term convergent. We also note that the macroscopic shifts of the interfacial profile are described not by the zero and other bound eigenstates, but by the combination of low-lying continuum eigenstates of the Hamiltonian second-derivative matrix. The inclusion of the convergent zero-order term allows us to improve the accuracy of the calculation of the correlation function in the vicinity of the interface. Our approach could be relevant for the experimental results obtained in the microgravity conditions using a local analytical method, e.g., scattering with a narrow beam, focused on the interface.

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