

Molecular fields and statistical field theory of fluids: Application to interface phenomena

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Using the integral transformation, the field-theoretical Hamiltonian of the statistical field theory of fluids is obtained along with the microscopic expressions for the coefficients of the Hamiltonian. Applying this approach to the liquid-vapor interface, we derive an explicit *analytical* expression for the surface tension in terms of temperature, density, and parameters of the intermolecular potential. We also demonstrate that a clear physical interpretation may be given to the formal statistical field arising in the integral transformation—it may be associated with the one-body local microscopic potential. The results of the theory, lacking any *ad hoc* or fitting parameters are in good agreement with available simulation data.

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The growing popularity of the field theoretical (FT) methods in statistical physics reflects recognition of the power and flexibility of such methods [1,2]. In most of the FT approaches, the configuration integral, associated with a thermodynamic potential (free energy, Gibbs free energy, etc.) is expressed in terms of a functional integral over one or a few space-dependent fluctuating fields, emerging in the Kac-Siegert-Stratonovich-Hubbard-Edwards (KSSHE) transformation [3–9]. Commonly, this field for simple fluids is treated as a formal mathematical object facilitating the analysis. The query, whether a physical interpretation to this field may be given, is explained here.

Once the functional integral representation is obtained, one can apply standard field-theoretical techniques to find the configuration integral and space correlation functions. These tools comprise the mean-field (MF) (or saddle-point) approximation, e.g., Refs. [1,2,10–14], random phase approximation, e.g., Refs. [15–19], Gaussian equivalent representation, e.g., Refs. [20,21], many-loop expansion, e.g., Ref. [22], variation method, e.g., Ref. [23], and renormalization group theory (RG), e.g., Refs. [24,25].

The field-theoretical methods are successfully applied to describe thermodynamic and structural properties of simple and complex fluids, nonhomogeneous fluids, and fluid interfaces and have already a half-century history [6–8,10–14,20,26–30]. In the pioneering paper [26], Storer outlined the derivation of the equation of state of simple fluid, treating

separately the repulsive (short-range) and attractive parts of the interaction potential. He expressed the grand partition function in terms of the functional integral with the coefficients depending on the thermodynamic and structural properties of the reference fluid with the short-range potential. The properties of the reference fluid, such as the equation of state and structure factor, were supposed to be known. The functional integration has been then performed under the random phase approximation. The approach was close to the one developed by Edwards [8] for ionic fluids where the excluded volume interactions between ions were taken into account to improve the Debye-Hueckel theory.

A similar field theory of simple fluids has been proposed by Hubbard and Schofield (HS) [6]. They also divided the total intermolecular potential into repulsive and attractive parts and recast the grand partition function into the form of a functional integral [6]. The exponential factor in the functional integral was written as an effective magneticlike Hamiltonian, expressed in terms of functional series of a fluctuating field $\phi(\mathbf{r})$. The latter mimics the magnetization field in magnetics. The coefficients of the effective Hamiltonian were, in their turn, written as multiparticle correlation functions of the reference fluid with purely repulsive interactions.

Using this effective Hamiltonian, the authors further discussed, whether Wilson's theory of criticality was applicable to fluid criticality. They demonstrated that the modified RG analysis applied to the magneticlike Hamiltonian, proved the Ising-like criticality of simple fluids. Although the main focus of the study [6] was the fluid criticality, the authors also

showed that the coefficients of the field-theoretical Hamiltonian could be related to the microscopic properties of the reference system. This was in a sharp contrast to the phenomenological theories, see, e.g., Refs. [31–33] where such Hamiltonians, used to analyze the near-critical behavior of fluids and interface phenomena, had phenomenological coefficients.

The derivation of the effective field-theoretical Hamiltonian has been completed in Ref. [13]. Here, all the coefficients have been found and explicitly expressed in terms of the thermodynamic and structural characteristics of the reference hard-core fluid, namely, in terms of its compressibility and zero moments of multiparticle correlation functions. The microscopic expression for the Gizburg criterion [32] for fluid criticality has been also reported [13]. Somewhat alternative approaches for the field-theoretical description of simple fluids and liquid-vapor interface have been developed in Refs. [10,12,14,28]. Although the microscopic expressions for the coefficients of the field-theoretical Hamiltonian could be, in principle, obtained in such approaches, this was beyond the scope of the above studies; the physical nature of the field was not also addressed.

As has been already mentioned, the KSSHE integral transformation yields the Hamiltonian that depends on the statistical field, which mimics the magnetization field in magnetics [13]. The magneticlike form of the Hamiltonian is very convenient to analyze critical and interface phenomena [24,33]. In particular, one can find an equilibrium space distribution of the magnetization with an interface. Finding, then, the free energy per unit area of the interface, one obtains the surface tension. Still, this purely phenomenological approach does not provide surface tension in terms of molecular parameters but rather the expressions in terms of the phenomenological coefficients of the magneticlike Hamiltonian [32]. It seems also interesting to find a possible physical interpretation of the formal field in the field-theoretical Hamiltonian.

In the present paper, we provide the microscopic molecular expressions for the parameters of the magneticlike field-theoretical Hamiltonian and reveal the physical nature of the stochastic field exploited in the field theories of fluids. Using these microscopic relations and general theory of interface phenomena for magnetics, we obtain an explicit expression for the surface tension which is in good agreement with simulation data. The rest of the article is organized as follows. In Sec. II, we outline the Hubbard-Schofield transformation and derivation of the microscopic expressions for the effective magneticlike Hamiltonian. In Sec. III, we discuss the application of the effective Hamiltonian to the liquid-vapor interface and compute the surface tension; we also compare the theoretical results with the available simulation data. Finally, in Sec. IV, we summarize our findings.

II. HUBBARD-SCHOFIELD TRANSFORMATION AND MAGNETICLIKE HAMILTONIAN

A. Hubbard-Schofield transformation

There is a variety of approaches to perform integral transformations that result in field-theoretical Hamiltonian. We outline here the derivation of Ref. [6], which has been further

developed in Ref. [13], making focus on the derivation detail that will help to understand the nature of the stochastic field. In what follows, we will use the reference system with only repulsive interactions [34].

We start from the fluid Hamiltonian $H = H_R + H_A + H_{ex}$,

$$H = \sum_{i < j} v_r(\mathbf{r}_{ij}) - \sum_{i < j} v(\mathbf{r}_{ij}) + \sum_j g(\mathbf{r}_j), \quad (1)$$

where $v_r(r)$ denotes the repulsive part of the interaction potential, $-v(r)$ —the attractive part and $g(\mathbf{r})$ —the external potential; \mathbf{r}_i are the coordinates of the i th particle, $i = 1, \dots, N$ and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The last two terms of the Hamiltonian (1) may be written using the Fourier transforms of the density fluctuations,

$$n_{\mathbf{k}} = \frac{1}{\sqrt{\Omega}} \sum_{j=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_j},$$

of the attractive potential, $v_{\mathbf{k}} = \int v(r)e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$ and of the external potential $g_{\mathbf{k}} = \Omega^{-1/2} \int g(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$ as

$$-\frac{1}{2} \sum_{\mathbf{k}} v_{\mathbf{k}} n_{\mathbf{k}} n_{-\mathbf{k}} + \frac{1}{2} v(0)N + \sum_{\mathbf{k}} g_{\mathbf{k}} n_{-\mathbf{k}}, \quad (2)$$

where $\Omega = L^3$ is the volume of the system and summation over $k_l = 2\pi n_l/L$ with $l = x, y, z$, and $n_l = 0, \pm 1, \dots$ is implied. Let μ be the chemical potential of the system with the complete Hamiltonian (1) and μ_R be the chemical potential of the reference system with the Hamiltonian H_R , which has only repulsive interactions. If $\langle N \rangle = \partial \Xi / \partial \mu$ is the average number of particles in the system so that $\rho = \langle N \rangle / \Omega$ is the average number density, we choose the reference system with such chemical potential μ_R , that the average density ρ is the same in both systems.

Following Hubbard and Schofield [6], we express the grand partition function $\Xi(\mu, \Omega, T)$ in terms of the grand partition function $\Xi_R(\mu_R, \Omega, T)$ of the reference fluid as:

$$\Xi = \Xi_R \left\langle \exp \left\{ \beta \mu' N + \beta \sum_{\mathbf{k}} \left[\frac{v_{\mathbf{k}}}{2} n_{\mathbf{k}} n_{-\mathbf{k}} - n_{\mathbf{k}} g_{-\mathbf{k}} \right] \right\} \right\rangle_R. \quad (3)$$

Here, $\beta = (k_B T)^{-1}$ with k_B being the Boltzmann constant, $\mu' = \mu - \mu_R + \frac{1}{2}v(0)$, and $\langle \rangle_R$ denotes the average over the reference system with the chemical potential μ_R . Using the identity,

$$e^{(1/2)a^2x^2 - bx} = \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{\infty} e^{-(y+b)^2/(2a^2) + xy} dy$$

for each \mathbf{k} in (3), we obtain, after some algebra, the ratio $Q = \Xi / \Xi_R$,

$$Q \propto \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \left\langle \exp \left\{ \sum_{\mathbf{k}} \phi_{\mathbf{k}} n_{-\mathbf{k}} \right\} \right\rangle_R \exp \left\{ \frac{\mu'}{v_0} \Omega^{1/2} \phi_0 \right\} \times \exp \left\{ -\frac{1}{2\beta} \sum_{\mathbf{k}} v_{\mathbf{k}}^{-1} (\phi_{\mathbf{k}} + \beta g_{\mathbf{k}})(\phi_{-\mathbf{k}} + \beta g_{-\mathbf{k}}) \right\}. \quad (4)$$

The integration in Eq. (4) is to be performed under the constraint $\phi_{-\mathbf{k}} = \phi_{\mathbf{k}}^*$, and a factor which does not affect the

subsequent analysis is omitted. Applying the cumulant theorem to the factor, $\langle \exp \{ \sum_{\mathbf{k}} \phi_{\mathbf{k}} n_{-\mathbf{k}} \} \rangle_R$ we arrive at [6]

$$Q \propto \int \prod_{\mathbf{k}} d\phi_{\mathbf{k}} \exp(-\beta\mathcal{H}),$$

$$\beta\mathcal{H} = -\tilde{h}\Omega^{1/2}\phi_0 + \sum_{n=2}^{\infty} \Omega^{1-n/2} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} \tilde{u}_n \phi_{\mathbf{k}_1} \cdots \phi_{\mathbf{k}_n}, \quad (5)$$

where the coefficients of the effective magneticlike Hamiltonian \mathcal{H} read for $g(\mathbf{r}) = 0$ [13],

$$\tilde{h} = \mu' v_0^{-1} + \rho,$$

$$\tilde{u}_2(\mathbf{k}_1, \mathbf{k}_2) = \frac{1}{2!} \delta_{\mathbf{k}_1+\mathbf{k}_2,0} \{ \beta^{-1} v_{\mathbf{k}_1}^{-1} - \langle n_{\mathbf{k}_1} n_{-\mathbf{k}_1} \rangle_{cR} \},$$

$$\tilde{u}_n(\mathbf{k}_1, \dots, \mathbf{k}_n) = -\frac{\Omega^{n/2-1}}{n!} \langle n_{\mathbf{k}_1} \cdots n_{\mathbf{k}_n} \rangle_{cR} \quad n \geq 3. \quad (6)$$

Here $\langle \rangle_{cR}$ denotes the *cumulant* average calculated in the (homogeneous) reference system with density $\rho = \langle N \rangle / \Omega$. According to (5), Q has the form of a partition function of the system with the field-theoretical Hamiltonian \mathcal{H} , which depends on the order parameter $\phi(\mathbf{r})$ ($\phi_{\mathbf{k}}$ are the Fourier components of the order parameter).

Let us analyze the physical meaning of the order parameter $\phi(\mathbf{r})$. From Eq. (3) directly follows:

$$\frac{\partial \ln \Xi}{\partial g_{-\mathbf{k}}} = \frac{\partial \ln Q}{\partial g_{-\mathbf{k}}} = -\beta \langle n_{\mathbf{k}} \rangle.$$

On the other hand Eq. (4) yields for $g \rightarrow 0$,

$$\frac{\partial \ln Q}{\partial g_{-\mathbf{k}}} = -v_k^{-1} \langle \phi_{\mathbf{k}} \rangle,$$

where the averaging is to be understood as the integration over all distributions of the order parameter. Thus, we conclude that $\langle \phi_{\mathbf{k}} \rangle = \beta v_k \langle n_{\mathbf{k}} \rangle$, which may be written in terms of the space-dependent field as

$$\langle \phi(\mathbf{r}) \rangle = \beta \int \rho(\mathbf{r}_1) v(\mathbf{r} - \mathbf{r}_1) d\mathbf{r}_1 + \bar{\phi}, \quad (7)$$

where $\rho(\mathbf{r}) = \langle n(\mathbf{r}) \rangle$ is the average density and we add an arbitrary constant, $\bar{\phi}$. This equation suggests the following physical interpretation of the order parameter: $\phi(\mathbf{r})$ gives the microscopic one-body molecular potential at point \mathbf{r} (in units of $k_B T = \beta^{-1}$) emerging due to the attractive part of interaction potential $-v(r)$ from particles distributed in space with microscopic density $n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$. Equation (7) relates the average quantities. This microscopic potential is associated with the microscopic force acting on a particle, which may be written for the average values as

$$\beta \langle f(\mathbf{r}) \rangle = \nabla \langle \phi(\mathbf{r}) \rangle = \beta \int \nabla \rho(\mathbf{r} - \mathbf{r}_1) v(\mathbf{r}_1) d\mathbf{r}_1.$$

This force is zero in a uniform system with $\rho(\mathbf{r}) = \text{const}$ and is directed along the density gradient for nonuniform systems. In particular, such a force arises at an interface, pulling the molecules towards a more dense phase, thus, manifesting the interphase surface tension. This illustrates that the stochastic field that formally appears in the KSSHE and HS transformations has a clear physical meaning.

B. Microscopic expressions for the coefficients of the magnetic Hamiltonian

As is seen from Eq. (6), the coefficients of \mathcal{H} depend on the correlation functions of the reference fluid having only repulsive interactions. Using the definition of l -particle correlation functions $g_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ [35,36], one can express the cumulant averages $\langle n_{\mathbf{k}_1} \cdots n_{\mathbf{k}_n} \rangle_{cR}$, and, thus, the coefficients $\tilde{u}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$ in terms of the Fourier transforms of g_l . Actually, \tilde{u}_n depends on the *connected* correlation functions h_1, h_2, \dots, h_n , defined as [13]

$$h_1(\mathbf{r}_1) = \delta(\mathbf{r}_1),$$

$$h_2(\mathbf{r}_1, \mathbf{r}_2) = g_2(\mathbf{r}_1, \mathbf{r}_2) - 1, \quad (8)$$

$$h_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g_2(\mathbf{r}_1, \mathbf{r}_2) - g_2(\mathbf{r}_1, \mathbf{r}_3) - g_2(\mathbf{r}_2, \mathbf{r}_3) + 2, \quad (9)$$

etc. For instance, $\tilde{u}_2(\mathbf{k}_1, \mathbf{k}_2)$ depends on $\tilde{h}_2(\mathbf{k}_1)$ (\tilde{h}_l is the Fourier transforms of h_l) as

$$\tilde{u}_2 = \frac{1}{2!} [(\beta v_k)^{-1} - \rho(1 + \rho \tilde{h}_2(\mathbf{k}_1))] \delta_{\mathbf{k}_1+\mathbf{k}_2,0}. \quad (10)$$

Similarly, \tilde{u}_3 depends on $\tilde{h}_2(\mathbf{k}_1/2/3)$ and $\tilde{h}_3(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$, and \tilde{u}_4 depends on \tilde{h}_2, \tilde{h}_3 , and \tilde{h}_4 , and so on [13].

For the subsequent analysis, it is instructive to use in the effective Hamiltonian the space-dependent order parameter $\phi(\mathbf{r})$, instead of its Fourier components $\phi_{\mathbf{k}}$. Writing \mathcal{H} in terms of $\phi(\mathbf{r})$, we assume that $\phi(\mathbf{r})$ varies smoothly in space and make the gradient expansion. This corresponds to small \mathbf{k} expansion of the coefficients $\tilde{u}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$. We keep only the square-order gradient terms $\sim (\nabla \phi)^2$ which correspond to $\sim k^2 \phi_{\mathbf{k}} \phi_{-\mathbf{k}}$ and omit high-order gradient terms and cross-terms $\sim (\nabla \phi)^2 \phi^k$ with $k > 0$. In the square gradient approximation, \tilde{u}_2 should be expanded as $\tilde{u}_2 = \tilde{u}_2(0) - \tilde{u}_2''(0)k^2 + \dots$ since $(\nabla \phi)^2 \sim k^2 \phi_{\mathbf{k}} \phi_{-\mathbf{k}}$. The other coefficients \tilde{u}_n , where $n \geq 3$ are to be taken at zero wave vectors as $\tilde{u}_n(0, 0, \dots, 0)$ since the terms $\sim (\nabla \phi)^2 \phi^k$ should be omitted. Thus, as follows from Eq. (10) and the discussion below (10), only $\tilde{h}_2''(0)$ and $\tilde{h}_l(0) \equiv \tilde{h}_l(0, 0, \dots, 0)$ with $l \geq 2$, are needed. Using the expansions $v_k = v_0 - v_0''k^2 + \dots$ and $\tilde{h}_2(k) = \tilde{h}_2(0) - \tilde{h}_2''(0)k^2 + \dots$ (the functions v_k and \tilde{h}_2 are even), we obtain for the coefficients,

$$\tilde{u}_2 = \left[\frac{k_B T}{v_0} - \rho - \rho^2 \tilde{h}_2(0) + k^2 \left(\frac{k_B T}{v_0^2} v_0'' - \rho^2 \tilde{h}_2''(0) \right) \right] \delta_{1,2,0},$$

$$\tilde{u}_3 = -\rho [1 + 3\rho \tilde{h}_2(0) + \rho^2 \tilde{h}_3(0)] \delta_{1,2,3,0},$$

$$\tilde{u}_4 = -\rho [1 + 7\rho \tilde{h}_2(0) + 6\rho^2 \tilde{h}_3(0) + \rho^3 \tilde{h}_4(0)] \delta_{1,2,3,4,0}, \quad (11)$$

where we apply the shorthand notation $\delta_{1,2,\dots,n,0} \equiv \delta_{\mathbf{k}_1+\mathbf{k}_2+\dots+\mathbf{k}_n,0}/n!$. In what follows, we will use the relation for the isothermal compressibility $\chi_R = \rho^{-1}(\partial \rho / \partial P_R)_T$ of the reference fluid (P_R is the pressure of the reference fluid),

$$1 + \rho \tilde{h}_2(0) = \rho k_B T \chi_R \equiv z_0. \quad (12)$$

We will also use the general relation between the successive l -particle correlation function $g_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ [35],

$$\chi \rho^2 \frac{\partial}{\partial \rho} \rho^l g_l = \beta \rho^l \left[l g_l + \rho \int d\mathbf{r}_{l+1} (g_{l+1} - g_l) \right].$$

With Eq. (8), one can express the l -particle correlation functions g_l in terms of the *connected* correlation functions h_l . Applying the Fourier transform to the resulting equations for h_l , we finally arrive at the following relation for the Fourier transforms of the functions \tilde{h}_l , taken at zero wave-vectors $\mathbf{k}_1 = \mathbf{k}_2 = \dots = \mathbf{k}_l = 0$ [13]:

$$z_0 \rho \frac{\partial}{\partial \rho} \rho^l \tilde{h}_l(\mathbf{0}) = \rho^l [l \tilde{h}_l(\mathbf{0}) + \tilde{h}_{l+1}(\mathbf{0})]. \quad (13)$$

Equation (13) will be applied for the reference system, where z_0 as defined by Eq. (12), is the reduced compressibility of the reference fluid.

Equation (13) allows to express $\tilde{h}_{l+1}(\mathbf{0})$ in terms of $\tilde{h}_l(\mathbf{0})$ and its density derivative. Using this equation iteratively along with $\tilde{h}_1(\mathbf{0}) = 1$, one can express all functions $\tilde{h}_l(\mathbf{0})$ in terms of the reduced compressibility z_0 and its density derivatives. With Eq. (11), we obtain for the coefficients of the effective Hamiltonian,

$$\begin{aligned} \tilde{u}_3 &= -\rho z_0 (z_0 + z_1) \delta_{1-3} \equiv u'_3 \delta_{1,2,3,0}, \\ \tilde{u}_4 &= -\rho z_0 [z_1^2 + z_0(z_0 + 4z_1 + z_2)] \delta_{1,2,3,4,0} \equiv u'_4 \delta_{1,2,3,4,0}, \end{aligned} \quad (14)$$

where $z_1 = \rho(\partial z_0 / \partial \rho)$ and $z_2 = \rho^2(\partial^2 z_0 / \partial \rho^2)$. Similarly, one can obtain all coefficients \tilde{u}_n of the magneticlike Hamiltonian.

For a reference system with only repulsive interactions, one can use the hard-sphere fluid with an appropriately chosen diameter [35,36]. For soft (not impulsive) repulsive forces, a simple Barker-Henderson relation [36],

$$d = \int_0^R \{1 - \exp[-\beta v_r(r)]\} dr \quad (15)$$

gives the effective diameter of the hard-sphere system, corresponding to a repulsive potential $v_r(r)$ vanishing at $r \geq R$. The fairly accurate Carnahan-Starling equation of state for this system [35,36] yields for the reduced compressibility,

$$z_0 = (1 - \eta)^4 / (1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4), \quad (16)$$

with the packing fraction $\eta = \pi d^3 \rho / 6$. For the hard-sphere reference system, one can also find $\tilde{h}_2''(0)$. This may be performed expressing $\tilde{h}_2(k)$ in terms of the direct correlation function $\tilde{c}_2(k)$ as $\tilde{h}_2(k) = \tilde{c}_2(k) / [1 - \rho \tilde{c}_2(k)]$ [35,36] and expanding $\tilde{c}_2(k)$ as $\tilde{c}_2(k) = \tilde{c}_2(0) - \tilde{c}_2''(0)k^2 + \dots$,

$$\tilde{h}_2(k) = \tilde{h}_2(0) - z_0^2 \tilde{c}_2''(0)k^2 + \dots, \quad (17)$$

where we use Eq. (12) for $\tilde{h}_2(0)$. Hence, $\tilde{h}_2''(0) = z_0^2 \tilde{c}_2''(0)$. The value of $\tilde{c}_2''(0)$ may be found from the the Wertheim-Thiele solution for the direct correlation function of a hard-sphere fluid [35,36],

$$\tilde{c}_2''(0) = \frac{\pi d^5 (16 - 11\eta + 4\eta^2)}{120 (1 - \eta)^4}. \quad (18)$$

Substituting $\tilde{h}_2''(0)$, expressed through $\tilde{c}_2''(0)$ from Eq. (18), into Eq. (11), we recast \tilde{u}_2 into the form

$$\begin{aligned} \tilde{u}_2 &= (a'_2 + b'_2 k^2) \delta_{1,2,0}, \\ a'_2 &= (\beta v_0)^{-1} - \rho z_0, \\ b'_2 &= (\beta v_0)^{-1} (v_0'' / v_0) + \rho^2 z_0^2 \tilde{c}_2''(0). \end{aligned} \quad (19)$$

Now, we perform a transformation from the variables $\phi_{\mathbf{k}}$ to the space-dependent field $\phi(\mathbf{r})$. Under this transformation, the integration over the set $\{\phi_{\mathbf{k}}\}$ in Eq. (5) converts into integration over the field $\phi(\mathbf{r})$ and the term $\sim k^2 \phi_{\mathbf{k}} \phi_{-\mathbf{k}}$ transforms into $\sim (\nabla \phi_{\mathbf{k}})^2$. As the result, we obtain

$$\beta \mathcal{H}[\phi] = \int d\mathbf{r} \left[\frac{1}{2} \kappa (\nabla \phi)^2 + W(\phi) \right], \quad (20)$$

where

$$W(\phi) = -h' \phi(\mathbf{r}) + \frac{a'_2}{2!} \phi^2(\mathbf{r}) + \frac{u'_3}{3!} \phi^3(\mathbf{r}) + \frac{u'_4}{4!} \phi^4(\mathbf{r}) + \dots, \quad (21)$$

and we keep only terms up to the fourth order in $\phi(\mathbf{r})$. In Eq. (21), $h' = \tilde{h}$ is defined by Eq. (6), a'_2 is defined by Eq. (19), and u'_3 and u'_4 are defined by Eq. (14). The coefficient at the gradient term reads

$$\kappa = \frac{3}{40\pi d} \left[\frac{\lambda_{\text{eff}}^2}{\beta \epsilon_{\text{eff}}} - B \right], \quad (22)$$

where $B = 4\eta^2(1 - \eta)^4(16 - 11\eta + 4\eta^2) / (1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4)^2$ and the constants ϵ_{eff} and λ_{eff} characterize the effective depth and effective width of the attractive potential $v(r)$,

$$\epsilon_{\text{eff}} = \frac{3}{4\pi d^3} \int v(r) d\mathbf{r}, \quad (23)$$

$$\lambda_{\text{eff}}^2 = \frac{5}{3v_0 d^2} \int v(r) r^2 d\mathbf{r}. \quad (24)$$

To obtain κ , we use Eqs. (19) and (18) for b'_2 and $\tilde{c}_2''(0)$, respectively.

The cubic term in the potential $W(\phi)$ may be removed by the shift of the field $\phi \rightarrow \phi + \bar{\phi}$ with the constant field $\bar{\phi}$, chosen to make the term $\sim \phi^3$ vanish. This results in the celebrated Landau-Ginzburg-Wilson (LGW) Hamiltonian (20) with

$$V(\phi) = -h\phi(\mathbf{r}) + \frac{a_2}{2!} \phi^2(\mathbf{r}) + \frac{u_4}{4!} \phi^4(\mathbf{r}), \quad (25)$$

and renormalized coefficients,

$$\begin{aligned} u_4 &= -\rho z_0 [z_1^2 + z_0(z_0 + 4z_1 + z_2)], \\ a_2 &= (\beta v_0)^{-1} - \rho [z_0 + z_3^2 / (2\rho u_4)], \\ h &= \mu' v_0^{-1} + [a_2 + z_3^2 / (6u_4)] (z_3 / u_4) + \rho, \end{aligned} \quad (26)$$

where z_0 , z_1 , and z_2 have been defined above and $z_3 \equiv -\rho z_0(z_0 + z_1)$. The coefficient κ is not affected by the field transformation.

The free energy of system F with the LGW Hamiltonian may be written in terms of the functional integral over the statistical field as

$$\beta F = -\ln \left(\int \mathcal{D}[\phi(\mathbf{r})] e^{-\beta H(\phi)} \right), \quad (27)$$

where $H[\phi(\mathbf{r})]$ is given by Eq. (20) and $\mathcal{D}[\phi]$ denotes the functional (field) integration. For brevity, we skip in (27) the normalization constant.

III. SURFACE TENSION OF LIQUID-VAPOR INTERFACE

To illustrate some practical application of our approach, we calculate the surface tension of the liquid-vapor interface within the MF approximation. In the MF approximation, only the extremal field $\phi^*(\mathbf{r})$, which minimizes the free energy, $\delta F[\phi^*(\mathbf{r})]/\delta\phi(\mathbf{r}) = 0$ is taken into account. Using Eq. (27), we obtain for the mean-field free energy (see also Refs. [24,33]),

$$F_{\text{mf}} = \mathcal{H}[\phi^*] = \int d\mathbf{r} \left[\frac{\kappa}{2} (\nabla\phi^*)^2 + V(\phi^*) \right] \\ = \int d\mathbf{r} f(\phi^*, \nabla\phi^*),$$

where $f(\phi^*, \nabla\phi^*) = \kappa(\nabla\phi^*)^2/2 + V(\phi^*)$ is the free energy density for a general geometry.

For a flat interface with $\nabla = d/dx$, the equation for the extremal field reads [24,33]

$$\kappa \frac{d^2\phi^*}{dx^2} = \frac{dV(\phi^*)}{d\phi^*}. \quad (28)$$

In the bulk of the two phases, i.e., far from the surface, the order parameter takes constant values, ϕ_1^* at $x \rightarrow -\infty$, and ϕ_2^* at $x \rightarrow \infty$, which are related to the mean densities of these phases—of the liquid ρ_l and of the vapor ρ_g density, respectively. As stated above and follows from Eq. (7), the extremal fields $\phi_{1,2}^*$ in the bulk of the phases are linearly related to the densities of the phases $\phi_{1,2}^* = \beta v_0 \rho_{l,g} + \bar{\phi}$. Hence, the standard phase equilibrium conditions for the free energy density $f'(\rho_l) = f'(\rho_g)$ and $f(\rho_l) + \rho_l f'(\rho_l) = f(\rho_g) + \rho_g f'(\rho_g)$ for two bulk phases may be written as

$$V'(\phi_1^*) = V'(\phi_2^*), \\ V(\phi_1^*) + \phi_1^* V'(\phi_1^*) = V(\phi_2^*) + \phi_2^* V'(\phi_2^*),$$

which is the double-tangent construction for fields ϕ_1^* and ϕ_2^* .

If we choose the interface located at $x = 0$, the first integral of Eq. (28) yields

$$\frac{1}{2}\kappa \left(\frac{d\phi^*}{dx} \right)^2 = \begin{cases} V(\phi^*) - V(\phi_1^*), & x \leq 0, \\ V(\phi^*) - V(\phi_2^*), & x > 0. \end{cases} \quad (29)$$

The surface tension γ is equal to the difference per unit area between the free energy, calculated for the space-dependent $\phi^*(\mathbf{r})$ and that for ϕ_1^* for $x < 0$ and ϕ_2^* for $x > 0$. If the order parameter at the interface equals ϕ_0^* , which may be chosen from the condition $\phi_1^* < \phi_0^* < \phi_2^*$, $V'(\phi_0^*) = 0$, straightforward calculations yield for the surface tension with $V_{1,2} = V(\phi_{1,2}^*)$ (see also Refs. [24,33]),

$$\beta\gamma = \int_{\phi_1^*}^{\phi_0^*} \sqrt{2\kappa[V(\phi) - V_1]} d\phi + \int_{\phi_0^*}^{\phi_2^*} \sqrt{2\kappa[V(\phi) - V_2]} d\phi. \quad (30)$$

Now, we choose the system for which the coefficient h in (26) vanishes, that is, $V = \frac{1}{2}a_2\phi^{*2} + \frac{1}{4!}u_4\phi^{*4}$. For this system, $\phi_{1,2}^* = \pm(-6a_2/u_4)^{1/2}$, $\phi_0^* = 0$, and the solution to Eq. (28) reads

$$\phi^*(x) = (-6a_2/u_4)^{1/2} \tanh(x/\xi_0),$$

with the interface width $\xi_0 = (-\kappa/2a_2)^{1/2}$ [24,33]. The solution is symmetric and has zero volume average $\bar{\phi}^* \equiv \Omega^{-1} \int \phi^*(\mathbf{r}) d\mathbf{r} = 0$.

Averaging Eq. (7) over the volume yields $\bar{\phi}^* = \beta\bar{\rho}v_0 + \bar{\phi} = 0$, implying that $\bar{\phi} = -\beta v_0 \bar{\rho}$, where $\bar{\rho} = \Omega^{-1} \int \rho(\mathbf{r}) d\mathbf{r} = N/\Omega$ is averaged over the volume density. Since $\phi_1^* = -\phi_2^*$ and, simultaneously, $\phi_{1,2}^* = \pm\beta v_0 \rho_{l,g} + \bar{\phi}$, we conclude that $\bar{\rho} = (\rho_l + \rho_g)/2$, i.e., that the averaged density of our system is the mean between the liquid and the vapor density. Naturally, this is the density of our homogeneous reference system with the same volume and number of particles. With the above values of $\phi_{1,2}^*$ and ϕ_0^* , the integration in (30) is easily performed yielding

$$\gamma/k_B T = 4 \left(-2\kappa a_2^3/u_4^2 \right)^{1/2}, \quad (31)$$

where microscopic expressions for the constants a_2 , u_4 , and κ , are given by Eqs. (22) and (26) where the density $\rho = (\rho_l + \rho_g)/2$ of the reference fluid is to be used.

Not far from the critical point (ρ_c, T_c) , one can approximate $(\rho_l + \rho_g)/2 \simeq \rho_c$ and, thus, use ρ_c as the reference density. In particular, one can write for a_2 : $a_2 \simeq a_2(\beta, \rho_c) = (\beta v_0)^{-1} - \rho_c [z_0 + z_3^2/(2\rho u_4)]_c$ [see (26)]. If we, then, use the mean-field condition for the critical point $a_2(\beta_c, \rho_c) = 0$ [1], we obtain $a_2 = (\beta v_0)^{-1} - (\beta_c v_0)^{-1} = -\alpha\tau$, and finally, for the surface tension,

$$\frac{\gamma}{k_B T} = 4 \left(\frac{2\kappa_c \alpha^3}{u_{4c}^2} \right)^{1/2} \tau^{3/2}, \quad (32)$$

where $\alpha = (\beta_c v_0)^{-1}$, $\tau = (T_c - T)/T_c$, and the coefficients $u_{4,c}$ and κ_c are to be calculated at $\rho = \rho_c$, $T = T_c$. Equation (32) is the main result of the present paper. It gives an explicit analytical expression for the surface tension in terms of temperature, density, and parameters of the interaction potential. It is worth noting that Eq. (32) demonstrates (as expected for the mean-field analysis), the classical critical exponent $3/2$, that is, $\gamma \sim \tau^{3/2}$, as was first observed by Widom [32,37].

The theoretical predictions, Eq. (32), have been compared with the available data of numerical experiments for the Lennard-Jones (LJ) and hard-core Yukawa (HCY) fluids. For these systems, the standard Weeks-Chandler-Andersen partition (see, e.g., Ref. [36]) of the potential into attractive and repulsive parts has been applied [13]. The numerical data have been obtained for the LJ fluid by means of molecular dynamics (MD) [38,39] and Monte Carlo [40]. For the HCY fluid the MC and MD [41] have been also applied. The critical parameters for the LJ fluid were taken from Ref. [40]. For the HCY fluid, we used the critical parameters from Ref. [42] for the curves 2–4 and parameters from Ref. [43] for the curve 2'. The values of σ and ϵ for the LJ potential were taken from Ref. [40] and σ , ϵ , and λ for the HCY potential from Ref. [41].

As follows from Fig. 1, our theory is in good agreement with the numerical experiments. It is expected, however, that the agreement would be worse in the very close vicinity of the critical point where the mean-field theory loses its accuracy. The accuracy of numerical simulations also decreases in the vicinity of the critical point [44]. Equation (32) is quite sensitive to the critical parameters ρ_c and T_c . Although these are known rather accurately for the LJ fluid, they are

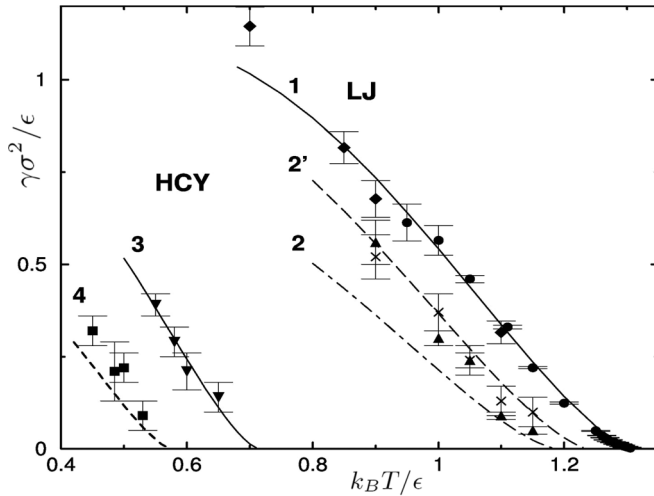


FIG. 1. Reduced surface tension $\gamma\sigma^2/\epsilon$ as a function of the reduced temperature $k_B T/\epsilon$. Curves: theory Eq. (32); points: numerical data. LJ fluid: curve 1, diamonds [38,39] and circles [40]. HCY fluid: curves 2, 2', 3, and 4, stars and triangles up ($\lambda = 1.8$ [41]), triangles down ($\lambda = 3.0$, [41]), and squares ($\lambda = 4.0$, [41]). Critical parameters and σ , ϵ , and λ are taken from Refs. [40–43], see the text for details.

estimated with much larger uncertainty for the HCY fluid. This is demonstrated in Fig. 1 where two theoretical curves (2 and 2') correspond to the same HCY fluid but with ρ_c and T_c taken from different sources (ρ_c and T_c differ by about 4%).

IV. CONCLUSION

We develop a theory of inhomogeneous simple fluids based on the microscopic one-body potential in fluid, which naturally emerges in the HS transformation. We demonstrate that the “technical” field variable $\phi(\mathbf{r})$, associated with the HS transformation, possesses a clear physical meaning. It gives the molecular potential at point \mathbf{r} (in units of $k_B T$) from the attractive part of the interparticle potential of molecules located in the vicinity of \mathbf{r} . Hence, $\phi(\mathbf{r})$ depends on both the particle

density $\rho(\mathbf{r})$ and the attractive potential $v(r)$, being the convolution of $\rho(\mathbf{r})$ and $v(r)$. As the result, the microscopic field $\phi(\mathbf{r})$ varies much more smoothly, even in the interface region than the local density $\rho(\mathbf{r})$ itself. The smooth variation of $\phi(\mathbf{r})$ guarantees the accuracy of the small gradient expansion, applied for the field-dependent Hamiltonian. Moreover, any additional smoothing procedure is not required. This makes the approach more simple and presumably more reliable. In contrast, the density functional theory, based on the local density, see, e.g., Ref. [45], exploits the smoothing of $\rho(\mathbf{r})$ due to its sharp variation at the interface. The smoothing weight function is commonly chosen *ad hoc*, see, e.g., Refs. [45–47].

Using the microscopic molecular field approach, which stems from the HS transformation, we calculate the surface tension γ for the liquid-vapor interface. Here, we apply the mean-field approximation which considers only the average molecular field and ignores the field fluctuations. We obtain an explicit analytical result for γ , which expresses this quantity in terms of temperature and density of the system and parameters of the intermolecular potential. The theoretical predictions for the surface tension are in good agreement with the results of numerical experiments. The mean-field approach loses, however, its accuracy in the very close vicinity to the critical point where the near-critical fluctuations become important. The account of the critical fluctuation for γ is straightforward and may be performed applying the technique developed in Ref. [24]. Our paper reports a simple analytical expression for the surface tension that agrees well with the numerical experiments.

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