The $\phi^4$ Theory Hamiltonian for Fluids:
Application to the surface tension near the critical point

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We show that the coefficients of the Hamiltonian for the $O(N)$ symmetric $\phi^4$ field theory in $N = 1$ limit, may be expressed in terms of the known properties of the reference (hard-core) system: the compressibility and its derivatives with respect to density. We consider the fluid Hamiltonian with microscopic expressions for its coefficients when it is taken in the approximation up to second order of interaction term i.e. in the form of Landau-Ginzburg-Wilson Hamiltonian and explicitly demonstrate that it is equivalent to the Hamiltonian of the $\phi^4$ field theory model. We propose a rigorous generalization of known results for the critical interfacial tension to the microscopic case. Based on the renormalization group approach the analytical microscopic expression for the surface tension of liquids near the critical point is obtained which is in a good agreement with numerical experiments.

I. INTRODUCTION

The behavior of many systems with short range interactions, in the critical domain, can be reproduced by an effective local field theory which is described by Landau-Ginzburg-Wilson (LGW) Hamiltonian [1-8]:

$$\beta \mathcal{H} = \int d\mathbf{r} \left[ \kappa (\nabla \phi)^2 / 2 + V(\phi) \right],$$

where, $\beta$ is the reciprocal of Boltzmann’s constant times the temperature $T$, and $V(\phi)$ is chosen to mimic a possibility of the two-phase coexistence:

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

The coefficients $\kappa, a_2, u_4$ are functions of $T$, and $h$ is the applied magnetic field. The order parameter $\phi(\mathbf{r})$ may be of any physical nature: density, composition of the fluid mixture, magnetization, etc. [1]. The vicinity of the critical point can be also described by a continuum model with the Hamiltonian of $\phi^4$ field theory written in terms of the order parameter $\phi \equiv \phi(x)$ in an arbitrary external field $h \equiv h(x)$:

$$\beta H = \int d^d x \left[ \frac{1}{2} (\nabla \phi)^2 - \tau_0 \phi^2 / 2! + g_0 \phi^4 / 4! - h \phi \right].$$

The universality of the transition at the critical point allows to consider a mapping of the system under consideration on a continuous scalar real $\phi^4$ field model. The field-theoretical methods, elaborated especially for the $\phi^4$ field theory may be then applied to describe the critical fluctuations. We note that many systems to which the renormalization group (RG) predictions based on the $\phi^4$ field theory apply are non-magnetic [1]. Several types of such systems are of special interest because they allow precise comparisons between RG results, experiments and simulations [1]. The critical properties of these systems are related to the $N$-component $\phi^4$ field theory: $N = 0$ describes the statistical properties of polymer chains asymptotically when the length becomes large, $N = 1$ and $N = 2$ the universal properties of liquid-vapor and Helium-4 superfluid transitions, respectively. We focus on the case when the field $\phi$ has one component. The liquid-vapor transition does not have the $O(1) = Z_2$ symmetry which is present in magnetic systems: for the liquid-vapor critical point the order parameter does not have the inversion symmetry. However, there exist several methods for establishing a connection between the liquid-vapor transition and the $O(1) \phi^4$ theory: one can either start from a true gas model in the continuum, or a lattice gas model, and by a number of approximations, obtain directly a $\phi^4$ field theory [1,4,6]. Hubbard and Schofield [9] derived the effective LGW-Hamiltonian for fluids by an exact mapping, based on the transformation of variables. They argued that fluids belong to the Ising universality class. Later, an important progress in the development of the effective LGW Hamiltonian approach was achieved by expressing the coefficients of the effective LGW fluid Hamiltonian in terms of the properties of the reference system [10]. These studies of the fluid criticality by means of the LGW Hamiltonian approach were performed for the case of the hard spheres reference system. Recently, the case when the reference system in addition to the hard-sphere repulsion includes also the short range attraction was considered in [11]. Still, it was not explicitly demonstrated that the effective LGW Hamiltonian with its coefficients expressed in terms of the known properties of the reference system, is equivalent to the Hamiltonian of the $\phi^4$ field theory model. Meanwhile, in the $\phi^4$ field theory model, the choice of
the coefficients of the Hamiltonian is to a great extent arbitrary; they are considered as some model parameters for which microscopic expressions are not provided. Thus, in this regard the $\phi^4$ field theoretical approach is not now, strictly speaking, a microscopic theory. The present study is addressed to overcome this flaw.

In this paper, we consider the Hamiltonian for the fluid, and demonstrate how to map it on the Hamiltonian of the $\phi^4$ field theory. We express the coefficients of the $\phi^4$ theory Hamiltonian in terms of the compressibility of the reference system and its derivatives with respect to density. Further, we illustrate the obtained results by applying them to the study of behavior of the surface tension near the critical point. In the mean field (MF) approximation we derive an analytical microscopic expressions for the surface tension which allows to obtain this quantity for the given temperature, density, and interaction potential. Based on Wilson’s epsilon expansion we show that in the one-loop approximation the expression for the surface tension gives a good agreement with numerical experiments in the near-critical region.

II. METHOD AND MODEL

In this section we demonstrate how to obtain the mapping of the liquid-vapor system on the $\phi^4$ theory with microscopic expressions for the parameters of the corresponding Hamiltonian.

We consider the one-component system of classical particles interacting via a pairwise potential $w(r)$. Here, $w(r)$ is supposed to be short-range ($r^{d+2}w(r) \to 0$ in $d$ dimensions as $r \to \infty$), such that the system possesses a thermodynamic limit and a liquid-vapor critical point, and has in addition properties implied by the assumptions below. We assume that the interaction potential $w(r)$ may be resolved into an attractive part $-v(r) \leq 0$ and the repulsive part $\phi(r) \geq 0$ in such a way that $v(r)$ is bounded and has a positive Fourier transform $v_k > 0$ with the property $v_k = V_0 - v''_n k^2 + ...$, for $k$ small; $\phi(r)$ is to be as short-range as possible consistent with these conditions.

We start from the fluid Hamiltonian

$$H^f = \sum_{i<j} \phi(r_{ij}) - \sum_{i<j} v(r_{ij}) = H_R + H_A,$$  (4)

here $r_i$ are coordinates of the particles, and $r_{ij} = r_i - r_j$. According to the identity: $2 \sum_{i<j} = \sum_{i,j} - \sum_{i=j}$, the attractive part of the Hamiltonian, $H_A$ may be written in terms of the Fourier components of the density $n_k = V^{-1/2} \sum_{j=1}^N e^{-ikr_j}$, and the Fourier transform of the attractive potential $v_k = \int v(r)e^{-ikr}dr$, as [9]

$$H_A = -\sum_{i<j} v(r_{i,j}) = -\frac{1}{2} \sum_k v_k n_k n_{-k} + \frac{1}{2} v_0 N,$$  (5)

where $N$ is the number of particles, $V = L^3$ is the volume of the system, and summation over the following set of $k$ is implied: $k_l = \frac{2\pi}{L} n_l$ with $l = x, y, z$, and $n_l = 0, \pm 1, \pm 2, ...$; the thermodynamic limit $L \to \infty$ is assumed. Let $\mu$ be the chemical potential of the system with the total Hamiltonian $H_R$, and $\mu_R$ the chemical potential in the reference system having the Hamiltonian $H_R$ which includes only repulsive interaction. Then the grand partition function, $Z_G$, may be expressed in terms of that of the reference fluid, $Z_R$ as [9]

$$Z_G = Z_R \left\langle \exp \left\{ \frac{\beta \mu'}{N} + \frac{1}{2} \beta \sum_k v_k n_k n_{-k} \right\} \right\rangle_R,$$  (6)

here we used the notation: $\left\langle A \right\rangle_R = \frac{1}{Z_R} \sum_C A e^{\beta H_R(C)}$ - an average over configurations $C$ of the reference system, at the temperature $T$ with chemical potential $\mu_R$. In Eq. (6), $\mu' = \mu - (\mu_R + v_0/2)$. Note that the reference system with only repulsive interactions does not possess a liquid-vapor transition; i.e. its grand partition function $Z_R$ is regular in the vicinity of the critical point of the fluid of interest. Using the identity: $\exp \left( \frac{1}{2} a^2 x^2 - bx \right) = \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{+\infty} dy \exp \left[ -\frac{1}{2} (y + b)^2/a^2 + xy \right]$, for the ratio $Q \sim Z_G/Z_R$ we obtain [9]

$$Q \sim \prod_k d\phi_k \left\langle \exp \left\{ \sum_k \phi_k n_{-k} \right\} \right\rangle_R \times \exp \left\{ \frac{\mu'}{V_0} V^{1/2} \phi_0 - \frac{1}{2} \beta^{-1} \sum_k v_{-1}^{-1} \phi_k \phi_{-k} \right\};$$  (7)

here the integration is to be performed under the constrain $\phi_{-k} = \phi_k^*$, and a factor which does not affect the subsequent analysis is omitted. Applying the cumulant theorem [12] to the factor $\left\langle \exp \left\{ \sum_k \phi_k n_{-k} \right\} \right\rangle_R$ one can write [9]

$$Q \propto \prod_k d\phi_k \exp(-\beta \mathcal{H}),$$  (8)

with the effective field theoretical Hamiltonian

$$\beta \mathcal{H} = -\hbar V^{1/2} \phi_0 + \sum_{n=2}^{\infty} V^{1-n/2} \sum_{k_1,...,k_n} \tilde{u}_n \phi_{k_1} \cdots \phi_{k_n}. \quad (9)$$
The coefficients of the Hamiltonian $\mathcal{H}$ read as $\tilde{h} = \mu' v_0^{-1} + \rho$, and
\begin{align*}
\tilde{u}(k_1, k_2) &= \frac{1}{2!} \delta_{k_1 + k_2, 0} \left[ \beta^{-1} v_{0}^{-1} - \langle n_{k_1} n_{k_2} \rangle_{\mathcal{R}} \right], \\
\tilde{u}_n(k_1, \ldots, k_n) &= -\frac{V^{n-2}}{n!} \langle n_{k_1} \cdots n_{k_n} \rangle_{\mathcal{R}}, \text{ for } n \geq 3.
\end{align*}

Here, $\rho = V^{-1/2} \langle n_0 \rangle_{\mathcal{R}} = N/V$ is the fluid density, and $(\ldots)_{\mathcal{R}}$ denotes the cumulant average calculated in the (homogeneous) reference system. The cumulant average of a product excludes all products of cumulant averages of all subsets \cite{12, 13}. Thus, in Eq. (10) $Q$ is written in the same way as the partition function for a ferromagnetic system with the number of spin components $n = 1$ that described by Ising-like Hamiltonian: $\phi_k$ are the Fourier components of the "spin field", and $h'$ is the "magnetic field". Now, we apply the integral transformation that maps the fluid Hamiltonian (4) onto the LGW Hamiltonian \[1\]. As it follows from Eq. (10) the coefficients of $\mathcal{H}$ depend on the correlation function of the reference fluid having only repulsive interactions. Using definitions of cumulants \cite{12, 13} and definitions of the particle correlation functions of fluids \cite{14, 15} one can express the cumulant averages $\langle n_{k_1} \cdots n_{k_n} \rangle_{\mathcal{R}}$ and thus the coefficients $\tilde{u}_n(k_1, \ldots, k_n)$ in terms of the Fourier transforms of the connected correlation functions $h_{k_1} h_{k_2} \ldots h_{k_n}$ of the reference system. These are defined as $h_{k}(r_1) \equiv \delta(r_1), h_{k}(r_1, r_2) \equiv g_{2}(r_1, r_2) - 1$, $h_{k}(r_1, r_2, r_3) \equiv g_{3}(r_1, r_2, r_3) - g_{2}(r_1, r_2) - g_{2}(r_1, r_3) - g_{2}(r_2, r_3) + 2$, etc., where $g_{l}(r_1, \ldots, r_l)$ are $l$-particle correlation functions \cite{14}. In particular, the first few coefficients read \cite{10}
\begin{align*}
\tilde{u}_2 &= \frac{1}{2!} \left[ (\beta v_0)^{-1} - \rho - \rho^2 \tilde{h}_2(k_{1}) \right] \delta_{k_1 + k_2, 0} \\
\tilde{u}_3 &= -\frac{1}{3!} \left[ \rho + \rho^2 \tilde{h}_2(k_{1}) + \rho^2 \tilde{h}_2(k_{2}) + \rho^3 \tilde{h}_2(k_{3}) \right] + \rho^3 \tilde{h}_3(k_{1}; k_{2}) \delta_{k_1 + k_2 + k_3, 0},
\end{align*}

where $\tilde{h}_l$ are the Fourier transforms of $h_l$.

To obtain the conventional square gradient form of the effective Hamiltonian we perform the small-$k$ expansion of the coefficients $\tilde{u}_n(k_1, \ldots, k_n)$. First, we note that the function $\tilde{h}_2(k)$ may be expressed in terms of the Fourier transform of the direct correlation function, $\tilde{c}_2(k)$, as $h_{2}(k) = \tilde{c}_2(k)/(1 - \rho \tilde{c}_2(k))$, and its zero-$k$ value can be given in terms of the isothermal compressibility $\chi_R = \rho^{-1} (\partial \rho / \partial P)_R$, (where $P_R$ is the pressure of the reference fluid) as $1 + \rho \tilde{h}_2(0) = \beta^{-1} \rho \chi_R \equiv z_0$. Using the expansions $v_k = v_0 + v_0' k^2 + \ldots$ \cite{9} and $\tilde{c}_2(k) = \tilde{c}_2(0) - \tilde{c}_2(0)'' k^2 + \ldots$ (with $k = |k|$) for the direct correlation function, one obtains for $u'_2$ up to $O(k^4)$ terms
\begin{align*}
\tilde{u}_2' &= \frac{1}{2!} \left[ u_2' + b'_2 k^2 + \ldots \right] \delta_{k_1 + k_2, 0} \\
\tilde{u}_3' &= (\beta v_0)^{-1} - \rho z_0 \\
b'_2 &= \rho^2 \left[ z_0 v_0''(0) + \beta v_0''(\rho \beta v_0)^{-2} \right]
\end{align*}

From the structure of the LGW Hamiltonian \[1\], which has the only gradient term $(\nabla \phi)^2 \sim k^2 \phi_k \phi_{-k}$, follows that only $\tilde{u}_2$ should be expanded as $\tilde{u}_2 = \tilde{u}_2(0) - \tilde{u}_2(0)'' k^2 + \ldots$, while the other coefficients $\tilde{u}_n$ for $n \geq 3$ should be taken at zero wave vectors, as $\tilde{u}_n(0, 0, \ldots, 0)$ \cite{10}. Thus, as it is seen from \cite{11} only $\tilde{h}_2(0), \tilde{h}_2(0)''$, and $\tilde{h}_4(0) = \tilde{h}_4(0), \tilde{h}_4(0)$, $l > 2$ are needed. Hence we may write the contribution of such terms using this approximation:
\begin{align*}
u_3' &= -\frac{1}{3!} \left[ \rho + 3 \rho^2 \tilde{h}_2(0) + \rho^3 \tilde{h}_3(0) \right] \delta_{k_1 + k_2 + k_3, 0} \\
u_4' &= -\frac{1}{4!} \left[ \rho + 7 \rho^2 \tilde{h}_2(0) + 6 \rho^3 \tilde{h}_3(0) + \rho^4 \tilde{h}_4(0) \right] \delta_{k_1 + k_2 + k_3 + k_4, 0}
\end{align*}

From a relation between successive correlation functions \cite{14}
\begin{equation}
z_0 \rho \frac{\partial}{\partial \rho} \rho' g_l = \rho' \left[ l g_l + \rho \int d x_{l+1} (g_{l+1} - g_l) \right]
\end{equation}
a chain relation between the functions $\tilde{h}_l(0)$ follows \cite{10}
\begin{equation}
z_0 \rho \frac{\partial}{\partial \rho} \rho' \tilde{h}_l(0) = \rho' \left[ \tilde{h}_l(0) + \rho \tilde{h}_{l+1}(0) \right]
\end{equation}
expressing each $\tilde{h}_{l+1}(0)$ in terms of $\tilde{h}_l(0)$ and density derivative. Using the Eq. (15) iteratively, one finally finds each $\tilde{h}_l(0)$ expressed in terms of the reference system compressibility $\chi_R$ and its derivatives with respect to density. Explicitly, we obtain:
\begin{align*}
u_3' &= \frac{1}{3!} \rho \rho_3 \delta_{k_1 + k_2 + k_3, 0} = \\
&= -\frac{1}{3!} \rho z_0 (z_0 + z_l) \delta_{k_1 + k_2 + k_3, 0} \\
u_4' &= \frac{1}{4!} \rho \rho_4 \delta_{k_1 + k_2 + k_3 + k_4, 0} = \\
&= -\frac{1}{4!} \rho z_0 \left[ z_0 + 2 z_0 + 4 z_1 + z_2 \right] \delta_{k_1 + k_2 + k_3 + k_4, 0},
\end{align*}
defining $u_n$ as the critical density, $z_0 \equiv \beta^{-1} \rho \chi_R$ as before, $z_1 \equiv \rho \partial z_0 / \partial \rho$, and $z_2 \equiv \rho^2 \partial^2 z_0 / \partial \rho^2$. In this way, one can evaluate all the coefficients of the effective LGW Hamiltonian of the fluid and express them in terms of the compressibility of the reference system and its derivatives with respect to density. The compressibility, in its turn, can be related with the intermolecular interaction potential as we show here. Further, to recast the effective Hamiltonian \[9\] into conventional form \[1, 2\] we i) perform transformation from variables $\phi_k$ to the space-dependent field $\phi(r)$; ii) remove the cubic term with respect to the field, which $V(\phi)$ does not contain; iii) omit all terms in \[9\] with powers of the field higher than four. The second item may be realized by the shift $\phi \rightarrow \phi + \phi_0$ with $\phi_0$ chosen to make the cubic term vanish. Regarding the last item, it was shown \[2, 16, 17\] that all odd terms of higher orders are strongly irrelevant at the
specify the reference system. This solves the problem of $\rho$ would be present in the vapor and broken in the liquid \[2\].

The paramagnetic to ferromagnetic transition, in the case that, if the breaking of a symmetry is well apparent in conditions are set up appropriately. We want to recall of an Ising ferromagnets, or equivalently below the critical point of the liquid, the two pure phases coexist (the ical exponent \(\gamma\)) by the field theoretical methods.

Here, we want to mention that below the Curie point ical point (\(p, T\)) plane ending at the critical point \((p_c, T_c)\). The liquid-vapor transition for \(T < T_c\) is thus accompanied in jump from \(p_c\) to \(p_L\) when the pressure \(p\) increases from a value smaller that \(p_{\text{coexistence}}(T)\) to an infinitesimally larger value. This is analogous to the transition for \(T < T_c\) between the down and the up spin phase of a ferromagnet when applied field goes from a negative to a positive value, and the magnetization from \(-m_s(T)\) to \(+m_s(T)\). At the critical point, this jump vanishes and one defines a characteristic critical exponent \(\beta\) as \(\Delta \rho = \rho_c(T) - \rho_L(T) \sim (T_c - T)^\beta\) or \(m_s(T) \sim (T_c - T)^\beta\). Above \(T_c\) there is only one phase: the fluid phase above the liquid-vapor transition, the paramagnetic phase for magnets. For the definiteness, we consider a sample contained in a vertical cylinder of height \(L\) and cross-sectional area \(A\); if the spins point down in the \(z = -L/2\) plane and up in the \(z = L/2\) plane, an interface appears between two pure phases of opposite magnetization.

Now, we will consider in some detail the epsilon expansion introduced by Wilson and Fisher \[18\] and later developed by many authors \[1,2,21,22\]. We demonstrate how it is applied to our results; from now on \(\epsilon\) will denote the difference \(4 - d\), with \(d\) being the dimension of space.

The partition function for the system with the $\phi^4$ Hamiltonian \[3\]:

\[
\exp W[\tilde{h}] = \int D\phi e^{-\beta H},
\]

and the Legendre transform $\Gamma[\phi]$ of $W[\phi]$ defined by

\[
\phi = \frac{\delta W}{\delta \tilde{h}},
\]

\[
\Gamma[\phi] = -W[\tilde{h}] + \int d^d x h(x) \phi(x).
\]

In zero field the free energy is given by

\[
\beta F = \Gamma[\phi^c],
\]

here $\phi^c(x)$ is the solution of

\[
h(x) \equiv \frac{\delta \Gamma}{\delta \phi(x)} = 0.
\]

The Eq. \[21\] must be supplemented by boundary conditions. For up-up or down-down boundary conditions at $z = -L/2$ and $z = L/2$, respectively, $\phi^c(x)$ is uniform and equal to the spontaneous magnetization $M_0$. For down-up boundary conditions, $\phi^c(z, \vec{x}_{||})$ is independent of $\vec{x}_{||}$ but vary with $z$ between $-M_0$ and $M_0$.

In order to go beyond the mean-field theory, we use the renormalized perturbation theory \[1,3\]. The theory with Hamiltonian \[3\] is regularized by considering its extension in dimension $d = 4 - \epsilon$. Divergences are removed by expressing all bare couplings in terms of renormalized ones. Thus, in terms of renormalized parameters we have \[1\]

\[
\beta H = \int d^d x \left[ Z(\nabla \varphi)^2 \frac{2}{2} - \tau \frac{Z_2 \varphi^2}{2} + \lambda' g \frac{Z_1 \varphi^4}{4!} \right],
\]

where $\lambda$ is an arbitrary inverse length scale, so that $g$ is dimensionless. We use the minimal subtraction renormalization scheme in which $Z$’s are power series in $g$ with coefficients containing only multiple poles in $\epsilon$, but no finite part \[1\].

First, we consider a simpler model (mean-field) in which the lowest approximation, in which we neglect all fluctuations of the order parameter around its most likely value, reduces to the Landau theory. Thus, at the MF level ($\epsilon = 0$) for the free energy we have \[1\]

\[
\Gamma^{MF}[\varphi] = \int d^d x \left[ \frac{(\nabla \varphi)^2}{2} - \tau \frac{\varphi^2}{2} + g \frac{\varphi^4}{4!} \right].
\]

This gives the spontaneous magnetization

\[
M^{MF} = \sqrt{\frac{\beta \gamma}{g}},
\]

\[23\]
and for the coexistence problem, the equation for $\varphi_c^{MF}$ is

$$- \frac{d^2 \varphi_c^{MF}}{dz^2} - \tau \varphi_c^{MF} + g (\varphi_c^{MF})^3  = 0,$$

(25)

The solution of (25) supplemented with the boundary condition: $\varphi_c^{MF}(\pm\infty) = \pm M^{MF}$ is a kink

$$\varphi_c^{MF} = M^{MF} \tanh[\sqrt{\tau/2}(z - z_0)],$$

(26)

where $z_0$ is free parameter due to translational invariance, that specifies the location of the kink.

The renormalized critical free-energy (at one-loop order) is

$$\Gamma^{(1)}[\varphi] = \int d^d x \left[ \frac{Z(\nabla \varphi)^2}{2} - \tau \frac{Z_2 \varphi^2}{2} + A' \frac{Z_1 \varphi^4}{4!} \right] + \frac{1}{2} \text{Tr} \ln K,$$

$$+ \frac{1}{2} \text{Tr} \ln K,$$

with $K = \delta(x - y) \left[ -Z \nabla^2 - \tau Z_2 + \frac{1}{2} A' g Z_1 \varphi^2 \right].$

III. THE SURFACE TENSION NEAR THE CRITICAL POINT

There are several physical observables that might be drawn from (27); they would all lead to a similar analysis of the critical behavior. One of such observables is the critical interfacial tension that enters into theoretical descriptions of nucleation and wetting. [19–27], topics of broad fundamental and applied interests.

The surface tension near criticality in the thermodynamic limit for a $l^d$ cubic lattice system vanishes as $\sigma(\tau, l \to \infty) = \sigma_0 l^{\eta_4}$, where $\tau \equiv (T_c - T)/T_c$, and $\tau > 0$, is the critical interfacial tension critical exponent, and $\sigma_0$ is the amplitude. Below $T_c$ there is the surface tension $\sigma$ that appears in an interface between two pure phases of opposite magnetization, defined in terms of the free energy $F$ per unit area $A$ as

$$\sigma = (F_{\uparrow \uparrow} - F_{\uparrow \downarrow})/A,$$

(28)

where the arrows specify the boundary conditions in the planes $z = L/2$ and $z = -L/2$ correspondingly. Noting that

$$\Gamma^{MF}_{\uparrow \uparrow} - \Gamma^{MF}_{\uparrow \downarrow} = A \int_{-\infty}^{+\infty} dz \left[ \frac{1}{2} \left( \frac{d \varphi_c}{dz} \right)^2 + \frac{1}{4!} g (\varphi_c^2 - (M^{MF})^2)^2 \right],$$

(29)

in the MF approximation we obtain

$$\frac{\sigma^{MF}}{kT} = \frac{4\sqrt{2}}{g} \varphi^{3/2},$$

(30)

which yields the van der Waals surface tension exponent $\mu = 3/2$. Using the Eq. (27) the one-loop corrections to the MF expression (30) (the first order in $\epsilon$) give [20]

$$\frac{\sigma}{kT} = \frac{4\sqrt{2}}{g} \varphi^{3/2},$$

$$+ \frac{u}{\epsilon} \int_{-\infty}^{+\infty} dz \left( -\frac{1}{4} \tau (\varphi_c^2 - M^2) + \frac{9}{16} (\varphi_c^4 - M^4) \right) \ln (\sqrt{\tau^2 + \varphi_c^2}),$$

(31)

with $u \equiv g K_d \equiv g \frac{2\pi^{d/2}}{\Gamma(d/2)} (2\pi)^{d/2}$, and $K_d$ is the ‘area’ of the unit sphere in dimension $d$, divided by $(2\pi)^d$. Again, following Brézin [20] for the surface tension in the one-loop approximation, we have

$$\frac{\sigma(\tau)}{kT} = \frac{4\sqrt{2}}{g^*} \left[ 1 + \frac{\epsilon}{4} \left( 1 - \ln 2 - \frac{\pi \sqrt{3}}{9} \right) \right] \varphi^{3/2 - \epsilon/4},$$

(32)

with $g^*$ - the renormalized coupling constant fixed point.

Still, we need further analysis, in order to apply our results to the case of a specific reference system. Namely, for the reference system with the only repulsive interactions we use the hard-sphere system with an appropriately chosen diameter [14]. For soft (not impulsive) repulsive forces a simple relation [14];

$$d = \int_0^{\sigma} [1 - \exp(-\beta \phi(r))]$$

(33)

gives the effective diameter of the hard-sphere system, corresponding to a repulsive potential $\phi(r)$ vanishing at $r \geq \sigma$. The fairly accurate Carnahan-Starling equation of state for this system [28, 29] yields for the reduced compressibility

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

(34)

where the packing fraction $\eta = \frac{1}{6} \pi \rho d^3$. For the hard-sphere reference system one can also find $\tilde{h}_2(0)^\nu$. This may be done by expressing $\tilde{h}_2(0)$ in terms of the direct correlation function $\tilde{c}_2(k)$ as $\tilde{h}_2(k) = \tilde{c}_2(k)/(1 - \tilde{c}_2(k))$ [14], expanding $\tilde{c}_2(k)$ as $\tilde{c}_2(k) = \tilde{c}_2(0) - \tilde{c}_2(0)\nu^2 k^2 + \ldots$, and using that $\tilde{c}_2(0)^\nu = -(\pi d^3/120)(16 - 11\eta + 4\eta^2)(1 - \eta)^{-4}$ which may be obtained from Wertheim-Thiele solution [14] for the direct correlation function [10]. Following these lines the coefficient $\kappa$ in Eq. (17) reads

$$\kappa = \frac{3}{40\pi d} \left[ \frac{\lambda_{eff}}{3\varepsilon_{eff}} - B \right],$$

(35)

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 constants $\varepsilon_{eff}$ and $\lambda_{eff}$ that appear due to the expansion of $\tilde{c}_2$, characterize the effective depth and the effective width of the attractive part.
v(r): \( \varepsilon_{\text{eff}} = \left(4\pi d^3/3\right)^{-1} \int v(r)\,dr = \left(4\pi d^3/3\right)^{-1} v_0 \), and
\[\lambda_{\text{eff}}^2 = \frac{3v_0 d^2}{5}\int v(r)^2\,dr = \frac{3v_0 d^2}{5}\, v_0^\prime.\]
In this way, we find the explicit expressions for all coefficients \(17\) of the \(\phi^4\) Hamiltonian \(3\) in the case of the hard-sphere reference system.

At the critical point the two phases lose their separate identities and merge into one homogeneous phase (see e.g. Fig.1, Top). The averaged density \(\bar{\rho} = (\rho_L + \rho_G)/2 \simeq \rho_c\) of our system is the mean between the liquid density \(\rho_L\) and vapor density \(\rho_G\).

Now, we show how the results \(30\) and \(32\) for the surface tension are expressed in terms of the coefficients \((\kappa, a_2, u_4)\) of the LGW Hamiltonian \(H(\phi)\). Based on \(11\) from \(30\), for the surface tension in the MF approximation we obtain
\[
\frac{\gamma_{\text{MF}}}{kT} = \frac{4\sqrt{2}}{u_4} \kappa^{1/2} a_2^{3/2},
\]
where \(\alpha = (\beta\nu_0\rho_c)^{-1}\) and the coefficients \(u_{4c}\) and \(\kappa_c\) are to be calculated at \(\rho = \rho_c\), \(T = T_c\).

At last, carrying out the same analysis for the surface tension in the one-loop approximation, from \(32\) we obtain
\[
\gamma(\tau) = \frac{4\sqrt{2} \kappa_c^2}{u_{4c}} \times \left[ 1 + \frac{\epsilon}{4} \left(1 - \ln 2 - \frac{\pi \sqrt{3}}{9}\right) \right] \left(\kappa^{-1}\Lambda^2 \alpha \tau\right)^{3/2 - \epsilon/4}.
\]

IV. RESULTS

In this section, we apply the analytical expressions \(37\) and \(38\) to the case of space dimension \(d = 3\), by using the extrapolation \(\epsilon \rightarrow 1\) in the one-loop case, and compare the results with the available data of numerical experiments for the Lennard-Jones (LJ) fluid. The Weeks-Chandler-Andersen (WCA) partition \(32\) of the LJ potential \(u_{\text{LJ}}(r) = 4\epsilon_{\text{LJ}}\left[\left(\sigma/r\right)^{12} - \left(\sigma/r\right)^6\right]\) into attractive and repulsive parts, gives for the attractive part,
\[
v(r) = \begin{cases} 
\epsilon_{\text{LJ}}, & r \leq \sigma^{1/6} \sigma \\
-u_{\text{LJ}}(r), & r > \sigma^{1/6} \sigma,
\end{cases}
\]
which is perfectly smooth in the core region. The repulsive part \(\phi(r) = u_{\text{LJ}}(r) + v(r)\) is then used to find the effective hard-core diameter using the expression \(33\).

This partition gives the best estimates for the thermodynamic functions in the WCA perturbation scheme \(32\) and satisfies all the conditions desirable for the interparticle interactions assumed in the beginning of the first section.

Normally \(1\), at critical temperatures, the distances are measured in some arbitrary unit much larger than the lattice spacing and corresponding to the typical distances at which correlations are measured. Thus, in \(38\) we measure \(\Lambda\) in \(\rho_c^{-1/3}\) units. Here, we consider the variables that reduced as follows: the temperature \(T^* = kT/\varepsilon\), the density \(\rho^* = \rho\sigma\), and the surface tension \(\gamma^* = \gamma\sigma^2/\varepsilon\), where \(\sigma, \varepsilon\) are parameters of the LJ potential.

In Fig.1 (Bottom) we show the plane of parameters \((g_0, \tau_0)\) of the \(\phi^4\) Hamiltonian calculated for the reduced temperatures and the reduced densities obtained in \(24\) and shown in diagram Fig.1 (Top). In Fig.2 (Top) we show the temperature dependence of the parameter \(\kappa\) and in Fig.2 (Bottom) we show the plane of parameters \((a_2, u_4)\) of the LGW Hamiltonian.
calculated for the reduced temperatures and the reduced densities from Fig. 1 (Top).

In Fig. 2 we compare the estimates of MF theory and its one-loop correction with experimental results. As follows from Fig. 2 (Top) our theoretical prediction within MF approach is close to results of the numerical MC and MD experiments, except for the very close vicinity of the critical point, where the mean field theory loses its accuracy. We note that, the Fig. 2 (Top) reproduces the analogous mean-field dependence of the surface tension from the temperature obtained in [20]. In Fig. 2 (Bottom) we see that in the very close vicinity of the critical point our results for the one-loop approximation converge better to experimental data than in the MF case.

V. CONCLUSION

In conclusion, in our work, we show that the microscopic Hamiltonian with the short-range interactions can be described by a renormalizable \( \phi^4 \) theory. Namely, based on the conjecture that the fluid with the liquid-vapor transition at the critical point belongs to the Ising universality class, we described the liquid-vapor transition in terms of the \( \phi^4 \) field theory model. For this, we considered the effective magnetic Hamiltonian for fluids with the microscopic expressions for its coefficients. Following the analysis of Hubbard and Schofield [9] we demonstrated how a LGW Hamiltonian with all powers of \( \phi \) can be derived for the fluid system. Furthermore, the \( \phi^4 \) term can be removed by a change of variable \( \phi \rightarrow \phi + \phi_0 \) with a proper choice of the constant \( \phi_0 \), and the powers beyond the fourth could be safely dropped. Eliminating the \( \phi^4 \) term also eliminates the difference between the RG analysis of the liquid-vapor
system and that of the magnetic system. Then, using the results obtained in [10], we showed how to map the LGW Hamiltonian on the Hamiltonian of the $\phi^4$ field theory model. We obtained the microscopic expressions (17) for the parameters of the $\phi^4$ Hamiltonian, and demonstrated how Wilson’s epsilon expansion is applied to the problem. Further, based on the analysis conducted in [20], we illustrated the obtained results by applying them to the study of behavior of the surface tension near the critical point. In the MF and the one-loop approximation we derived an analytical expressions (37) and (38) for the surface tension which allows to obtain this quantity for the given temperature, density, and interaction potential. Finally, we have shown that our results are in a good agreement with numerical experiments.

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