

FIELD THEORY ANALYSIS OF CRITICAL BEHAVIOR OF A SYMMETRIC BINARY FLUID

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A method is elaborated for constructing an effective field theory Hamiltonian of the Landau–Ginzburg–Wilson type for off-lattice models of binary fluids. We show that all coefficients of the effective Hamiltonian for a symmetric binary fluid can be expressed in terms of some known characteristics of the model hard-sphere fluid, namely, compressibility and its derivatives with respect to density. Application of the effective Hamiltonian is demonstrated by an example of determining the curve of critical layering points in the mean-field approximation. This curve agrees well with numerical experiment results for symmetric binary fluids.

1. Introduction

The modern theory of critical phenomena, which is based on the universality hypothesis and (technically) on the renormalization group (RG) method, is successfully applied in many divisions of physics ranging from magnetic systems and solutions to processes of self-avoiding walks and percolation [1], [2]. Application of the RG method to critical phenomena was initially developed for magnetic systems (see, e.g., [3] and [4]). The majority of investigations were devoted to these systems. The RG method was also used to investigate critical properties of fluids, and a number of effective algorithms were elaborated for calculating thermodynamic quantities in the domain where critical fluctuations play a dominant role [5]–[9]. These approaches are based on the direct application of the Kadanoff–Wilson recursive scheme (see, e.g., [4]). But this does not permit the general analysis of critical behavior as visually and simply as do the methods based on using the system Hamiltonian in the Landau–Ginzburg–Wilson (LGW) form. This Hamiltonian is written as

$$H = \int d\mathbf{r} [a_2\sigma^2 + B_4\sigma^4 + B_6\sigma^6 + \dots + b_2(\nabla\sigma)^2],$$

where σ is the magnetization or the order parameter or, as it is also called, the “critical field,” and the coefficients a_2 , B_4 , B_6, \dots and b_2 characterize the respective dependence of the Hamiltonian (or free energy [4]) on the degree of the field and its spatial gradient. A Hamiltonian of this type is also called a “field theory” Hamiltonian. Knowing such an effective Hamiltonian of a system, one can draw conclusions about the character of its critical behavior and universality class, determine the domain of influence and the magnitude of the contribution of critical fluctuations to thermodynamic functions, derive simple mean-field estimates for the position of the critical point, and so on. It is therefore very important to find the field theory Hamiltonian for a system possessing critical behavior.

Effective field Hamiltonians for fluids were constructed by different methods in a number of works. For example, in [10], the Hamiltonian of a fluid was reduced to a field Hamiltonian by coarsening the

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spatial scale. In [11], the coefficients of the effective Hamiltonian were found by comparing the values of compressibility, correlation length, and critical amplitudes of the order parameter calculated in the framework of the generalized mean-sphere approximation with the same quantities calculated using the LGW Hamiltonian. In [12], a functional generalization of the Mayer expansion was used. In this case, attractive interactions were considered at the level of the second virial coefficient, and a number of different approximations were used for repulsive interactions. The indicated approximations were used in [12] to calculate the coefficients of the effective LGW Hamiltonian for a one-component fluid. A similar approach, but in combination with somewhat different approximations, was used to calculate the coefficients of the effective Hamiltonian for the so-called restricted primitive electrolyte model [12]–[14].

In contrast to all these approaches, which use some approximations, Hubbard and Schofield [15] suggested an exact method for constructing an effective field Hamiltonian of a “real,” off-lattice fluid using an integral transformation of the Hubbard–Stratonovich type. Although no coefficients of the effective Hamiltonian were calculated in [15], they convincingly argued that critical behavior of fluids relates to the same universality class as Ising magnets. A further development of the Hubbard–Schofield method was suggested in [16] and [17], and it was shown that all coefficients of the effective LGW Hamiltonian for a one-component fluid can be expressed via some known characteristics of the model hard-sphere fluid, namely, compressibility and its derivatives with respect to density. In [18], this method was used to find the LGW Hamiltonian for Coulomb fluids. In particular, using the RG method, it was shown that the unusual critical behavior of such systems is related to the negativity of the coefficient B_4 . In this case, it was established that the lattice and off-lattice models have different types of critical behavior in these systems. We note that the Hubbard–Schofield method is much simpler than the collective variables method, which is also an exact method for finding the effective Hamiltonian of a fluid [19].

Unlike one-component systems, two-component fluids can show both the ordinary critical behavior corresponding to the liquid–gas transition and the critical behavior related to the layering into two phases, one enriched by the A component and the other by the B component. In the first case, the order parameter is the difference between the densities of the liquid and gas phases (with uniform compositions), and in the second case, it is the difference between the concentrations of the A and B components in the phases. In the first case, the liquid–gas coexistence curve in the temperature–density plane ends at a single critical point, and in the second case, an entire line of critical layering points, usually called a λ -line,² appears in this plane. The λ -line ends at its point of intersection with the liquid–gas coexistence curve (see Fig. 1), and this point is called the final critical point (FCP).

The critical behavior of systems whose phase diagram has a λ -line and an FCP has been actively investigated in recent years. The main questions here relate to the universality class and the character of critical behavior along the λ -line and at the FCP [20]–[23]. For example, the nonclassical character of critical behavior near the FCP was revealed in the framework of the spherical model [20]. Similar behavior on the λ -line was established theoretically [21], [22] and numerically using the Monte Carlo method [23]. In [24], the phase behavior of a symmetric binary fluid (i.e., a fluid consisting of identical A and B components differing only in the interaction potentials for particles of different types) was investigated both numerically and with the phenomenological expansion of the free energy with respect to the order parameter. In this case, the dependence of phase diagrams on the parameter ϵ equal to the ratio of the interaction energy for particles of one type to that for particles of different types was studied.

A qualitative field theory analysis of the critical behavior of a system with a Hamiltonian depending on two fluctuating fields (one of which is regular at the critical point) was performed in [25], where the Hubbard–

²For mixtures, it is also necessary to introduce the axis of relative concentrations in addition to density and temperature. Then a coexistence curve in the density–composition coordinates with the related critical point corresponds to each temperature. This precisely leads to the appearance of the line of critical layering points (the λ -line).

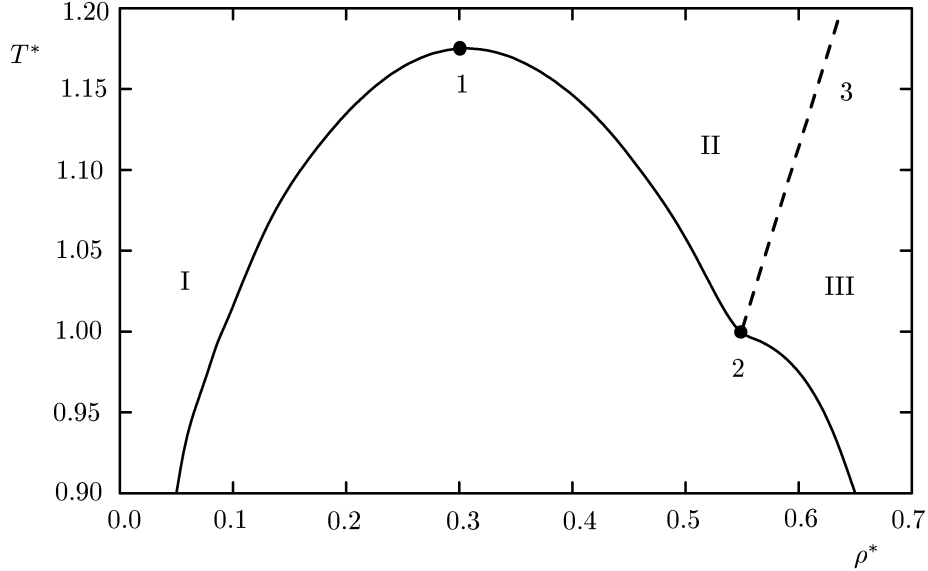


Fig. 1. Typical structure of phase diagrams for two-component systems having a λ -line (3) and an FCP (2). Point 1 is the critical gas–liquid transition point. The respective domains I, II, and III correspond to the gas phase, the homogeneous mixture of particles of types A and B , and the coexisting phases enriched by one (A) or the other (B) component.

Stratonovich transformation for the spin Hamiltonian corresponding to the lattice gas of a symmetric binary mixture was used. It was shown that the critical behavior near the FCP is equivalent to that along the λ -line. In [26], the collective variables method was used to study the critical liquid–gas transition point for a binary fluid.

In this paper, the critical behavior of a symmetric binary fluid is investigated by constructing an effective field theory Hamiltonian of the LGW type. We use the Hubbard–Schofield transformation of the original Hamiltonian of the fluid [16], [17]. In contrast to the similar Hubbard–Stratonovich transformation, this transformation does not require the existence of the inverse operator for the part of the interaction potential corresponding to the interactions of the impenetrable particle cores. In particular, this permits using off-lattice models. The singular part of this potential is considered separately and is a basis for calculating the coefficients of the effective Hamiltonian. In the framework of this approach, an effective field theory Hamiltonian can be constructed with explicit expressions for the coefficients for field powers of any order.

As an example of applying the effective Hamiltonian, we determine the curve of critical layering points (the λ -line), which agrees well with numerical experiment results [24].

2. Derivation of the effective LGW Hamiltonian

The particle interaction potential $U(r)^{ab}$ in a binary mixture can be represented as a sum of two parts, $U(r)^{ab} = U_r(r)^{ab} + J(r)^{ab}$, where U_r^{ab} and J^{ab} describe the respective purely repulsive and purely attractive interactions, $a = A, B$, and $b = A, B$.

The suggested approach is valid for any interaction potential representable as a sum of repulsive and attractive parts. To simplify the presentation of the material and also to make it possible to compare predictions of our theory with numerical experiment results [24], we consider an interaction potential of the type of a rectangular potential well. Moreover, we assume that the repulsive interactions in the binary

mixture under study are the same for all types of particles,

$$U_r^{AA} = U_r^{BB} = U_r^{AB} = U_{\text{hs}}(r) = \begin{cases} \infty & \text{for } r < d, \\ 0 & \text{for } r \geq d, \end{cases}$$

where d is the diameter of the hard cores of the particles, and the attractive part of the potential has the form

$$J^{AA} = J^{BB} = J(r) = \begin{cases} -J & \text{for } r \leq \lambda d, \\ 0 & \text{for } r > \lambda d, \end{cases} \quad J^{AB} = \begin{cases} -\epsilon & \text{for } J \leq \lambda d, \\ 0 & \text{for } r > \lambda d. \end{cases}$$

Here, λd is the width of the rectangular potential well, J describes the attraction between the particles (the depth of the potential well), and we introduce the parameter $\epsilon = J^{AB}/J \leq 1$ determining the relative interaction force for the particles of one type and different types. We consider the Hamiltonian of the above system (omitting its ideal part),

$$H = H_{\text{hs}} - \frac{1}{2} \sum_{a,b} \sum_{\mathbf{k}} J_{\mathbf{k}}^{ab} n_{\mathbf{k}}^a n_{-\mathbf{k}}^b + \frac{1}{2} N_A J(0) + \frac{1}{2} N_B J(0). \quad (1)$$

Here, H_{hs} characterizes the repulsive interaction between the hard cores of the particles, and all the other terms in the right-hand side of (1) relate to the attractive part H_a of the Hamiltonian represented via the collective variables,

$$n_{\mathbf{k}}^{a,b} = \frac{1}{\sqrt{V}} \sum_{j=1}^{N_{a,b}} e^{-i\mathbf{k}\mathbf{r}_j^{a,b}}, \quad (2)$$

where \mathbf{r}_j are the coordinates of the j th particle. (The parameters N_a and N_b are the numbers of particles of each of the types, $a = A, B$, and $b = A, B$.) Here, V is the volume of the system and $J_{\mathbf{k}} = \int J(r) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}$. The summation in (1) ranges the wave vectors $\mathbf{k} = \{k_x, k_y, k_z\}$ with $k_i = 2\pi l_i/L$ ($i = x, y, z$), where l_i are integers and $L^3 = V$. We introduce the new variables

$$q_{\mathbf{k}} = n_{\mathbf{k}}^a - n_{\mathbf{k}}^b, \quad s_{\mathbf{k}} = n_{\mathbf{k}}^a + n_{\mathbf{k}}^b, \quad (3)$$

for which the attractive part of the Hamiltonian has the form³

$$H_a = -\frac{1}{2} \sum_{\mathbf{k}} \left\{ \frac{J_{\mathbf{k}}}{2} (1 - \epsilon) q_{\mathbf{k}} q_{-\mathbf{k}} + \frac{J_{\mathbf{k}}}{2} (1 + \epsilon) s_{\mathbf{k}} s_{-\mathbf{k}} \right\} + \frac{1}{2} N_A J(0) + \frac{1}{2} N_B J(0). \quad (4)$$

Then it becomes possible to write the configuration integral of the system in question [15], [16],

$$Q = \left\langle \exp \left\{ \frac{\beta}{2} \sum_{\mathbf{k}} \frac{J_{\mathbf{k}}}{2} [(1 - \epsilon) q_{\mathbf{k}} q_{-\mathbf{k}} + (1 + \epsilon) s_{\mathbf{k}} s_{-\mathbf{k}}] \right\} \right\rangle_r Q_r e^{-\beta J(0)(N_A + N_B)/2}, \quad (5)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant, and T is the temperature. The expression Q_r is the configuration integral of the base system of hard spheres, and $\langle (\cdot) \rangle_r = Q_r^{-1} \int d\mathbf{r}^N (\cdot)$ denotes the average

³In the general case of a binary system with an attractive potential of an arbitrary form (for which it is not allowable to write $J^{AB} = \epsilon J^{AA}$, $\epsilon \leq 1$), the expressions $J_{\mathbf{k}}(1 \pm \epsilon)$ in (4) should be replaced with $J_{\mathbf{k}}^{AA} \pm J_{\mathbf{k}}^{AB}$.

over this system. We note that the configuration integral Q_r is a regular function in the phase-space domain under consideration because the base hard-sphere system has no critical layering points; therefore, only the first term in (5) determines the critical behavior of the system. In accordance with the Hubbard–Schofield scheme [15], i.e., using the identity

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

we bring the configuration integral Q to the form [16]

$$Q \sim \int \prod_{\mathbf{k}} d\sigma_{\mathbf{k}} \prod_{\mathbf{p}} d\gamma_{\mathbf{p}} \exp\left\{-\frac{1}{\beta} \sum_{\mathbf{k}} \frac{\sigma_{\mathbf{k}}\sigma_{-\mathbf{k}}}{(1-\epsilon)J_{\mathbf{k}}} - \frac{1}{\beta} \sum_{\mathbf{p}} \frac{\gamma_{\mathbf{p}}\gamma_{-\mathbf{p}}}{(1+\epsilon)J_{\mathbf{p}}}\right\} \times \left\langle \exp\left\{\sum_{\mathbf{k}} \sigma_{\mathbf{k}}q_{-\mathbf{k}} + \sum_{\mathbf{p}} \gamma_{\mathbf{p}}s_{-\mathbf{p}}\right\}\right\rangle_r, \quad (6)$$

where the factor that is regular at the critical point and does not affect the further analysis has been omitted. The integration in (6) is performed under the condition that $\sigma_{-\mathbf{k}} = \sigma_{\mathbf{k}}^*$ and $\gamma_{-\mathbf{p}} = \gamma_{\mathbf{p}}^*$. (Here, $\sigma_{\mathbf{k}}^*$ and $\gamma_{\mathbf{p}}^*$ are the respective complex conjugates of $\sigma_{\mathbf{k}}$ and $\gamma_{\mathbf{p}}$.)

We assume that the critical point for the gas–liquid transition lies sufficiently far from the line of critical layering points (see Fig. 1). It is clear that in this case, only the field $\sigma_{\mathbf{k}}$ conjugate to the variable $q_{\mathbf{k}} = n_{\mathbf{k}}^a - n_{\mathbf{k}}^b$ is critical, whereas the field $\gamma_{\mathbf{p}}$ conjugate to $s_{\mathbf{p}} = n_{\mathbf{p}}^a + n_{\mathbf{p}}^b$ is regular.⁴ Therefore, applying the cumulant expansion for $\langle \exp\{\sum_{\mathbf{k}} \sigma_{\mathbf{k}}q_{-\mathbf{k}} + \sum_{\mathbf{p}} \gamma_{\mathbf{p}}s_{-\mathbf{p}}\} \rangle_r$ [28], we retain the terms up to the fourth degree with respect to the field variable σ in resulting expression (6) (because the coefficient in σ^2 vanishes in the neighborhood of the λ -line) and up to the second degree with respect to γ (because the coefficient of γ^2 is always nonzero in the domain under consideration). This results in the relation

$$Q \sim \int \prod_{\mathbf{k}} d\sigma_{\mathbf{k}} \prod_{\mathbf{p}} d\gamma_{\mathbf{p}} \exp\left\{-\frac{1}{\beta} \sum_{\mathbf{k}} \frac{\sigma_{\mathbf{k}}\sigma_{-\mathbf{k}}}{(1-\epsilon)J_{\mathbf{k}}} + \sum_{\mathbf{p}} \frac{F(\mathbf{p})}{\sqrt{V}} \gamma_{\mathbf{p}} + \sum_{n=1}^4 \frac{1}{V^{n/2-1}} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} u_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \sigma_{\mathbf{k}_1} \cdots \sigma_{\mathbf{k}_n} + \sum_{\mathbf{p}_1, \mathbf{p}_2} \frac{G(\mathbf{p}_1, \mathbf{p}_2)}{V} \gamma_{\mathbf{p}_1} \gamma_{\mathbf{p}_2}\right\} \quad (7)$$

with the expressions for the coefficients F and G

$$\begin{aligned} \frac{F(\mathbf{p})}{V} &= v_1(\mathbf{p}) + 2 \sum_{\mathbf{k}} \frac{w_{11}(\mathbf{k}, \mathbf{p})}{\sqrt{V}} \sigma_{\mathbf{k}} + 3 \sum_{\mathbf{k}_1, \mathbf{k}_2} \frac{w_{21}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{p})}{V} \sigma_{\mathbf{k}_1} \sigma_{\mathbf{k}_2} + \\ &+ 4 \sum_{\mathbf{k}_1, \dots, \mathbf{k}_3} \frac{w_{31}(\mathbf{k}_1, \dots, \mathbf{k}_3, \mathbf{p})}{V^{3/2}} \sigma_{\mathbf{k}_1} \cdots \sigma_{\mathbf{k}_3} + \\ &+ 5 \sum_{\mathbf{k}_1, \dots, \mathbf{k}_4} \frac{w_{41}(\mathbf{k}_1, \dots, \mathbf{k}_4, \mathbf{p})}{V^2} \sigma_{\mathbf{k}_1} \cdots \sigma_{\mathbf{k}_4}, \end{aligned}$$

⁴It was shown in [27] that the order parameter and its conjugate field in the corresponding integral transformation have the same critical behavior.

$$\begin{aligned}
\frac{G(\mathbf{p}_1, \mathbf{p}_2)}{V} &= -\frac{1}{\beta(1+\epsilon)J_{\mathbf{p}}} + v_2(\mathbf{p}_1, \mathbf{p}_2) + 3 \sum_{\mathbf{k}} \frac{w_{12}(\mathbf{k}, \mathbf{p}_1, \mathbf{p}_2)}{\sqrt{V}} \sigma_{\mathbf{k}} + \\
&+ 6 \sum_{\mathbf{k}_1, \mathbf{k}_2} \frac{w_{22}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{p}_1, \mathbf{p}_2)}{V} \sigma_{\mathbf{k}_1} \sigma_{\mathbf{k}_2} + \\
&+ 10 \sum_{\mathbf{k}_1, \dots, \mathbf{k}_3} \frac{w_{32}(\mathbf{k}_1, \dots, \mathbf{k}_3, \mathbf{p}_1, \mathbf{p}_2)}{V^{3/2}} \sigma_{\mathbf{k}_1} \dots \sigma_{\mathbf{k}_3} + \\
&+ 15 \sum_{\mathbf{k}_1, \dots, \mathbf{k}_4} \frac{w_{42}(\mathbf{k}_1, \dots, \mathbf{k}_4, \mathbf{p}_1, \mathbf{p}_2)}{V^2} \sigma_{\mathbf{k}_1} \dots \sigma_{\mathbf{k}_4},
\end{aligned}$$

where

$$\begin{aligned}
u_n(\mathbf{k}_1, \dots, \mathbf{k}_n) &= \frac{V^{n/2-1}}{n!} \langle q_{\mathbf{k}_1}, \dots, q_{\mathbf{k}_n} \rangle_{c,r}, \\
v_m(\mathbf{p}_1, \dots, \mathbf{p}_m) &= \frac{V^{m/2-1}}{m!} \langle s_{\mathbf{p}_1}, \dots, s_{\mathbf{p}_m} \rangle_{c,r}, \\
w_{nm}(\mathbf{k}_1, \dots, \mathbf{k}_n, \mathbf{p}_1, \dots, \mathbf{p}_m) &= \frac{V^{(n+m)/2-1}}{(n+m)!} \langle q_{\mathbf{k}_1}, \dots, q_{\mathbf{k}_n}, s_{\mathbf{p}_1}, \dots, s_{\mathbf{p}_m} \rangle_{c,r}.
\end{aligned}$$

Here $\langle \cdot \rangle_{c,r}$ denotes the cumulant mean calculated for the base system. Using the definitions of equilibrium correlation functions of a fluid [29] and of cumulant means [28], we can express the coefficients of the powers of σ and γ in (7) explicitly in terms of the Fourier transforms of the correlation functions h_1, h_2, \dots, h_n of the base hard-sphere system, which are defined as

$$\begin{aligned}
h_1(\mathbf{r}) &\equiv \delta(\mathbf{r}), & h_2(\mathbf{r}_1, \mathbf{r}_2) &\equiv g_2(\mathbf{r}_1, \mathbf{r}_2) - 1, \\
h_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &\equiv g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g_2(\mathbf{r}_1, \mathbf{r}_2) - g_2(\mathbf{r}_1, \mathbf{r}_3) - g_2(\mathbf{r}_2, \mathbf{r}_3) + 2, & \dots,
\end{aligned} \tag{8}$$

where $g_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ are the l -particle equilibrium correlation functions of the base system. As the simplest example, we consider the main stages in calculating the function $w_{11}(\mathbf{k}, \mathbf{p})$. Using the definitions of cumulant means [28],

$$w_{11}(\mathbf{k}, \mathbf{p}) = \frac{1}{2!} \langle q_{\mathbf{k}} s_{\mathbf{p}} \rangle_{c,r} = \frac{1}{2!} (\langle q_{\mathbf{k}} s_{\mathbf{p}} \rangle_r - \langle q_{\mathbf{k}} \rangle_r \langle s_{\mathbf{p}} \rangle_r), \tag{9}$$

we obtain

$$\begin{aligned}
\langle q_{\mathbf{k}} s_{\mathbf{p}} \rangle_{c,r} &= \langle n_{\mathbf{k}}^a n_{\mathbf{p}}^a \rangle_r - \langle n_{\mathbf{k}}^a \rangle_r \langle n_{\mathbf{p}}^a \rangle_r + \langle n_{\mathbf{k}}^a n_{\mathbf{p}}^b \rangle_r - \langle n_{\mathbf{k}}^a \rangle_r \langle n_{\mathbf{p}}^b \rangle_r - \\
&- \langle n_{\mathbf{k}}^b n_{\mathbf{p}}^a \rangle_r + \langle n_{\mathbf{k}}^b \rangle_r \langle n_{\mathbf{p}}^a \rangle_r - \langle n_{\mathbf{k}}^b n_{\mathbf{p}}^b \rangle_r + \langle n_{\mathbf{k}}^b \rangle_r \langle n_{\mathbf{p}}^b \rangle_r
\end{aligned} \tag{10}$$

for the variables $q_{\mathbf{k}}$ and $s_{\mathbf{p}}$ using expressions (2) and (3). The definition of a binary symmetric fluid implies that the averaging in calculating means of the form $\langle n_{\mathbf{k}_1}^\alpha, n_{\mathbf{k}_2}^\beta, \dots, n_{\mathbf{k}_n}^\gamma \rangle$, where $\alpha, \beta, \dots, \gamma = A, B$, is performed with respect to the Hamiltonian of the base system of hard-sphere particles of diameter d . (This system is the same for particles of types A and B .) We now take representation (2) and the definition of equilibrium correlation functions [29] into account. For example, this gives

$$\begin{aligned}
\langle n_{\mathbf{k}}^a n_{\mathbf{p}}^a \rangle_r - \langle n_{\mathbf{k}}^a \rangle_r \langle n_{\mathbf{p}}^a \rangle_r &= \frac{\rho_a}{V} \int e^{-i\mathbf{k}\mathbf{r}_1 - i\mathbf{p}\mathbf{r}_1} d\mathbf{r}_1 + \frac{\rho_a^2}{V} \int e^{-i\mathbf{k}\mathbf{r}_1 - i\mathbf{p}\mathbf{r}_2} g_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - \\
&- \frac{\rho_a^2}{V} \int e^{-i\mathbf{k}\mathbf{r}_1} d\mathbf{r}_1 \int e^{-i\mathbf{p}\mathbf{r}_2} d\mathbf{r}_2 = \\
&= \delta_{\mathbf{k}+\mathbf{p},0} \{ \rho_a^2 \tilde{h}_2(\mathbf{k}) + \rho_a \}
\end{aligned}$$

for the Fourier transform, where $\rho_a = N_A/V$ and $\rho_b = N_B/V$ are the respective particle densities for types A and B , \tilde{h}_l denotes the Fourier transform of h_l , and the relation $\delta_{\mathbf{k},0}V = \int e^{i\mathbf{k}\mathbf{r}} d\mathbf{r}$ expressing the Kronecker delta for a discrete argument is used. Calculating analogously for the other terms in (10), we obtain the final expression for $w_{11}(\mathbf{k}, \mathbf{p})$ (see (9)),

$$w_{11}(\mathbf{k}, \mathbf{p}) = \frac{\delta_{\mathbf{k}+\mathbf{p},0}}{2!} \{ \tilde{h}_2(\mathbf{k})(\rho_a + \rho_b)(\rho_a - \rho_b) + (\rho_a - \rho_b) \}.$$

The coefficients in (7) can be calculated similarly up to an arbitrary order. For example,

$$\begin{aligned} u_1 &= \delta_{\mathbf{k}_1,0} \{ \rho_a - \rho_b \}, \\ u_2 &= \frac{\delta_{\mathbf{k}_1+\mathbf{k}_2,0}}{2!} \{ \tilde{h}_2(\mathbf{k}_1)(\rho_a - \rho_b)^2 + (\rho_a + \rho_b) \}, \\ u_3 &= \frac{\delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3,0}}{3!} \{ \tilde{h}_3(\mathbf{k}_1, \mathbf{k}_2)(\rho_a - \rho_b)^3 + (\rho_a - \rho_b) + \\ &\quad + [\tilde{h}_2(\mathbf{k}_1) + \tilde{h}_2(\mathbf{k}_2) + \tilde{h}_2(\mathbf{k}_3)](\rho_a^2 - \rho_b^2) \}, \\ w_{21} &= \frac{\delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{p}_1,0}}{3!} \{ \tilde{h}_3(\mathbf{k}_1, \mathbf{k}_2)(\rho_a - \rho_b)^2(\rho_a + \rho_b) + (\rho_a + \rho_b) + \\ &\quad + [\tilde{h}_2(\mathbf{k}_1) + \tilde{h}_2(\mathbf{k}_2)](\rho_a - \rho_b)^2 + \tilde{h}_2(\mathbf{p}_1)(\rho_a + \rho_b)^2 \}, \end{aligned}$$

and so on. It follows from the structure of the coefficients that all coefficients of odd powers of the field variable σ are identically zero for a symmetric system (where the average number of type- A particles is equal to the average number of type- B particles, i.e., $\rho_a = \rho_b$).

Integrating with respect to the set of variables $\{\gamma_{\mathbf{p}}\}$ in (7), we obtain the relation for the configuration integral of the system:

$$\begin{aligned} Q &\sim \int \prod_{\mathbf{k}} d\sigma_{\mathbf{k}} \exp \left\{ -\frac{1}{\beta} \sum_{\mathbf{k}} \frac{\sigma_{\mathbf{k}} \sigma_{-\mathbf{k}}}{(1-\epsilon)J_{\mathbf{k}}} + \sum_{n=1}^4 \frac{1}{V^{n/2-1}} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n} u_n(\mathbf{k}_1, \dots, \mathbf{k}_n) \sigma_{\mathbf{k}_1} \cdots \sigma_{\mathbf{k}_n} \right\} \times \\ &\quad \times \exp \left\{ -\sum_{\mathbf{p}_1, \mathbf{p}_2} \frac{1}{4} F(\mathbf{p}_1) G^{-1}(\mathbf{p}_1, \mathbf{p}_2) F(\mathbf{p}_2) - \log[\det G(\mathbf{p}_1, \mathbf{p}_2)] \right\}, \end{aligned} \quad (11)$$

where $G^{-1}(\mathbf{p}_1, \mathbf{p}_2)$ is the inverse matrix of $G(\mathbf{p}_1, \mathbf{p}_2)$. Assuming that the critical liquid-gas transition point is located far from the λ -line, we can neglect the fluctuations of the full density $\rho = \rho_a + \rho_b$ of the fluid and keep only the terms corresponding to $\mathbf{p}_1 = 0$ and $\mathbf{p}_2 = 0$ in (11). We next expand the functions $F(0)$ and $G(0,0)$ in (11) up to the fourth-order terms with respect to the field variable $\sigma_{\mathbf{k}}$, which corresponds to the usual LGW representation in analyzing the critical behavior of a system in the three-dimensional space. Then collecting the terms in like powers of $\sigma_{\mathbf{k}}$, we find

$$Q \sim \int \prod_{\mathbf{k}} \sigma_{\mathbf{k}} e^{-H}$$

with the effective Hamiltonian H given by the formula

$$H = \sum_{\mathbf{k}_1, \mathbf{k}_2} B'_2 \sigma_{\mathbf{k}_1} \sigma_{\mathbf{k}_2} + \sum_{\mathbf{k}_1, \dots, \mathbf{k}_4} \frac{B'_4}{V} \sigma_{\mathbf{k}_1} \cdots \sigma_{\mathbf{k}_4} + \sum_{\mathbf{k}_1, \mathbf{k}_2} \frac{D'_4}{V} \sigma_{\mathbf{k}_1} \sigma_{\mathbf{k}_2} \sum_{\mathbf{k}_3, \mathbf{k}_4} \sigma_{\mathbf{k}_3} \sigma_{\mathbf{k}_4}. \quad (12)$$

(The expressions for the coefficients in the effective Hamiltonian are given below.)

We are interested in the behavior of the system in the vicinity of the curve of critical layering points (the λ -line), i.e., in the domain where the major role is played by large-scale fluctuations of the density difference, which corresponds to fluctuations with small wave vectors. We therefore consider the expansion of the Hamiltonian coefficients for small k . We note that the LGW Hamiltonian written in terms of the Fourier transforms of field variables contains no terms with powers of k higher than k^2 . (This is equivalent to the absence of gradient terms of an order higher than two in the LGW Hamiltonian [4].) Moreover, the only term of the order of k^2 is proportional to $k^2\sigma_{\mathbf{k}}\sigma_{-\mathbf{k}}$. Hence, for $n > 2$, only the zeroth-order terms should be kept in expansion (12) for the coefficients of the effective Hamiltonian, and we represent the coefficient B'_2 in the form $B'_2 = a'_2 + b'_2k^2$.

We use the expansion for the correlation functions $\tilde{h}_l(k) = \tilde{h}_l(0) - k^2\tilde{h}_l''(0)$ with small k . (In this case, $\tilde{h}_l(0) = \tilde{h}_l(0, \dots, 0)$.) The value of $\tilde{h}_2(0)$ can be expressed via the isothermal compressibility $\chi_r = \rho^{-1}(\partial\rho/\partial P_r)_\beta$ of the base hard-sphere system in the form $1 + \rho\tilde{h}_2(0) = \rho k_B T \chi_r \equiv z_0$, where z_0 is the reduced density and P_r and $\rho = \rho_a + \rho_b$ are the corresponding pressure and density in the base system. Using the well-known formulas relating the correlation functions of different orders [29]

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

we derive a formula for the zeroth moments of the functions $\tilde{h}_l(0)$ [16],

$$\chi\rho^2\frac{\partial}{\partial\rho}\rho^l \tilde{h}_l(0) = \beta\rho^l [l\tilde{h}_l(0) + \rho\tilde{h}_{l+1}(0)]. \quad (13)$$

Recursive application of Eq. (13) to itself can give an expression for each of the functions $\tilde{h}_l(0)$ in terms of the reduced compressibility z_0 and its derivatives with respect to density, for example,

$$\begin{aligned} \tilde{h}_2(0) &= \rho^{-1}(z_0 - 1), \\ \tilde{h}_3(0) &= \rho^{-2}(z_0^2 - 3z_0 + 2 + z_0 z_1), \\ \tilde{h}_4(0) &= \rho^{-3}(z_0^3 - 6z_0^2 + 11z_0 - 6 + 4z_0^2 z_1 - 6z_0 z_1 + z_0 z_1^2 + z_0^2 z_2), \end{aligned}$$

where $z_1 = \rho\partial z_0/\partial\rho$ and $z_2 = \rho^2\partial^2 z_0/\partial\rho^2$. We thus reach the conclusion that all coefficients of effective Hamiltonian (12) can also be expressed in terms of the isothermal compressibility χ_r of the base system and its derivatives with respect to density. Using the very exact Carnahan–Starling state equation [30] for the hard-sphere system,

$$\frac{\beta F_{\text{ex,hs}}}{N} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2},$$

where $\eta = (\pi/6)\rho d^3$ is the packing coefficient, and differentiating twice with respect to density, we obtain

$$z_0 = (1 - \eta)^4 (1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4)^{-1}.$$

Next, we express the effective Hamiltonian via the field depending on the spatial coordinate. For this, it is necessary to transform the variables $\sigma_{\mathbf{k}}$ to the field variables $\sigma(\mathbf{r})$. Under this transformation, integration with respect to the set of variables $\{\sigma_{\mathbf{k}}\}$ is replaced with integration with respect to the field

$\sigma(\mathbf{r})$, and the term proportional to $k^2\sigma_{\mathbf{k}}\sigma_{-\mathbf{k}}$ becomes the one proportional to $[\nabla\sigma(\mathbf{r})]^2$. We introduce the new variables $a'_2 = \rho_c a_2$, $b'_2 = \rho_c^{1/3} b_2$, $B'_4 = \rho_c B_4$, and $D'_4 = \rho_c D_4$, where ρ_c is the critical density at the FCP. We use $\rho_c^{-1/3}$ as the length-scale factor. Performing all the necessary transformations, we obtain the final expression for the effective LGW Hamiltonian of a symmetric binary fluid in the neighborhood of the λ -line,

$$H = \int d\mathbf{r} [a_2\sigma^2 + B_4\sigma^4 + D_4\sigma^2\langle\sigma^2\rangle + b_2(\nabla\sigma)^2],$$

where $\langle\sigma^2\rangle = V^{-1} \int \sigma^2(x) d\mathbf{x}$ and the coefficients a_2 , b_2 , B_4 , and D_4 have the forms

$$\begin{aligned} a_2\rho_c &= \frac{3\rho w_{21}(0)}{2G_0} + \frac{1}{(1-\epsilon)\beta J_0} - \frac{3\rho^2 w_{22}(0)}{2G_0^2} - u_2(0), \\ b_2\rho_c^{1/3} &= \frac{3\rho^2}{2G_0^2} w_{22}''(0) - \frac{3\rho}{2G_0} w_{21}''(0) + \frac{J_0''}{(1-\epsilon)\beta J_0^2}, \\ B_4\rho_c &= \frac{5\rho w_{41}(0)}{2G_0} - \frac{15\rho^2 w_{42}(0)}{4G_0^2} - u_4(0), \\ D_4\rho_c &= \frac{9}{4G_0} \left[w_{21}(0) - \frac{2\rho}{G_0} w_{22}(0) \right]^2. \end{aligned} \tag{14}$$

In (14), we have

$$\begin{aligned} G_0 &= -\frac{1}{\beta(1+\epsilon)J_0} + v_2(0), \\ v_2(0) &= \frac{\rho}{2!}(\rho h_2(0) + 1), \\ u_2(0) &= \frac{\rho}{2!}, \\ u_4(0) &= \frac{\rho}{4!}(3\rho\tilde{h}_2(0) + 1), \\ w_{41}(0) &= \frac{\rho}{5!}(3\rho^2\tilde{h}_3(0) + 7\rho\tilde{h}_2(0) + 1), \\ w_{42}(0) &= \frac{\rho}{6!}(3\rho^3\tilde{h}_4(0) + 16\rho^2\tilde{h}_3(0) + 15\rho\tilde{h}_2(0) + 1), \end{aligned} \tag{15}$$

and b_2 has been calculated using the representation $v_2 = v_2(0) - k^2 v_2''(0)$, $w_{nm} = w_{nm}(0) - k^2 w_{nm}''(0)$, and $J_k = J_0 - k^2 J_0''$. The zeroth and second moments of the attractive part of the interaction potential are found from the relations

$$\begin{aligned} \beta J_0 &= \int J(r) d\mathbf{r} = \frac{4\pi d^3 \lambda^3}{3T^*}, \\ \beta J_0'' &= \frac{1}{6} \int r^2 J(r) d\mathbf{r} = \frac{\lambda^2 d^2}{10} \beta J_0 \end{aligned} \tag{16}$$

with the effective temperature $T^* = k_B T/J$.

The zeroth and second moments of w_{21} and w_{22} can be expressed in terms of those of the correlation functions $\tilde{h}_l(0)$,

$$\begin{aligned} w_{21}(0) &= \frac{\rho}{3!}(\rho\tilde{h}_2(0) + 1), \\ w_{21}''(0) &= \frac{\rho^2}{3!}\tilde{h}_2''(0), \\ w_{22}(0) &= \frac{\rho}{4!}(\rho^2\tilde{h}_3(0) + 3\rho\tilde{h}_2(0) + 1), \\ w_{22}''(0) &= \frac{\rho}{4!}(\rho^2\tilde{h}_3''(0) + 3\rho\tilde{h}_2''(0)). \end{aligned}$$

The function $\tilde{h}_2(\mathbf{k})$ is representable via the Fourier transform of the direct correlation function $c_2(\mathbf{k})$ of the base system, $\tilde{h}_2(\mathbf{k}) = \tilde{c}_2(\mathbf{k})/(1 - \rho\tilde{c}_2(\mathbf{k}))$. Expanding the Fourier transform $\tilde{c}_2(\mathbf{k})$ as a Taylor series, $\tilde{c}_2(\mathbf{k}) = \tilde{c}_2(0) - \tilde{c}_2''(0)k^2 + \dots$, we obtain

$$\tilde{h}_2(\mathbf{k}) = \tilde{h}_2(0) - k^2\tilde{c}_2''(0)(1 + \rho\tilde{h}_2(0))^2,$$

whence follows the relation $\tilde{h}_2''(0) = \tilde{c}_2''(0)(1 + \rho\tilde{h}_2(0))^2$. To calculate $\tilde{c}_2''(0)$, we use the Wertheim–Thiele analytic solution of the Percus–Yevick equation for the direct correlation function of the hard-sphere system.⁵ This results in the expression

$$\tilde{c}_2''(0) = \frac{1}{6} \int r^2 c_2(r) d\mathbf{r} = -\frac{\pi d^5}{120}(16 - 11\eta + 4\eta^2)(1 - \eta)^{-4}$$

for $\tilde{c}_2''(0)$.

In contrast to $\tilde{h}_2''(0)$, the expression $\tilde{h}_3''(0)$ cannot be written in terms of the compressibility of the base system. For $\tilde{h}_3''(0)$, we have the formula

$$\tilde{h}_3''(0)k^2 = \int h_3(r_1, r_2, r_{12}) \left[\frac{(\mathbf{kr}_1)^2}{2} + \frac{(\mathbf{kr}_2)^2}{2} - (\mathbf{kr}_1)(\mathbf{kr}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2, \quad (17)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Formula (17) shows that to calculate $\tilde{h}_3''(0)$, it is required to know the second (rather than the zeroth) moment of the three-particle correlation function. By (8), the expression $h_3(r_1, r_2, r_{12})$ can be written in terms of the three-particle function $g_3(r_1, r_2, r_{12})$, whose analytic representation is unknown. But the calculations can be performed using some approximations, e.g., the superpositional approximation

$$g_3(r_1, r_2, r_{12}) = g_2(r_1)g_2(r_2)g_2(r_{12}). \quad (18)$$

⁵According to [31] and [32], the direct correlation function of the hard-sphere system has the form $c_2(r^*) = 0$ for $r^* \geq 1$ and $c_2(r^*) = (1 - \eta)^{-4} \{ -(1 + 2\eta)^2 + 6\eta(1 + \eta/2)^2 r^* - \eta(1 + 2\eta)^2 r^{*3}/2 \}$ for $r^* < 1$, where $r^* = r/d$ and d is the diameter of the hard spheres.

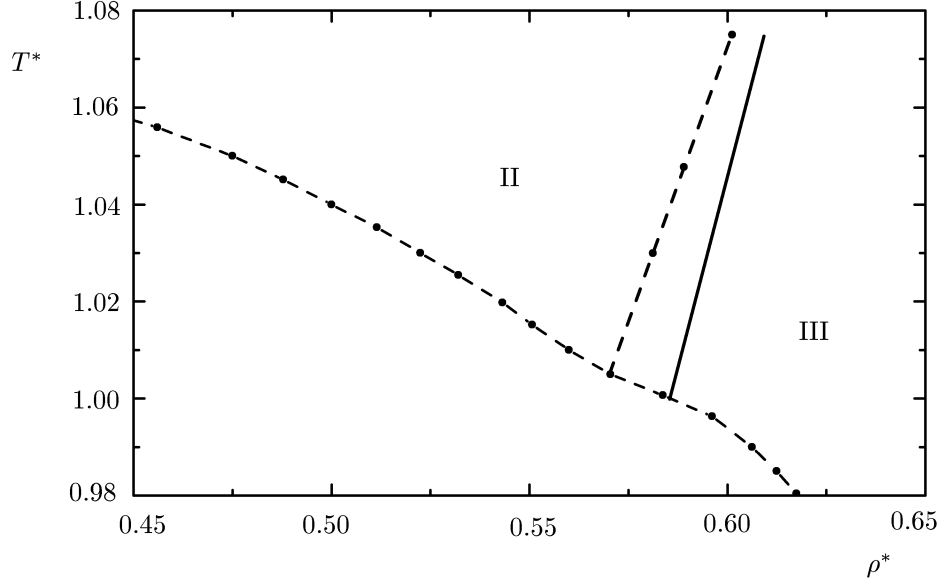


Fig. 2. Comparison of the data obtained for the λ -line theoretically (solid line) with the results of experimental numerical calculation using the Monte Carlo method (dashed lines). The parameter values are $\epsilon = 0.72$ and $\lambda = 1.5$.

Numerical calculations of the coefficient b_2 using approximation (18) showed that b_2 is positive in the domain we are interested in for any values of the system parameters.

We have thus constructed the effective LGW Hamiltonian for a symmetric binary fluid. Using a similar argument, we can obtain analytic expressions for the coefficients of an arbitrary order with respect to the field variable. We note that the resulting Hamiltonian involves two different fourth-order terms with respect to the field variable that are proportional to the corresponding expressions σ^4 and $\sigma^2\langle\sigma^2\rangle$.

As an example of applying the effective field theory Hamiltonian, we consider the mean-field condition for the critical point according to which the coefficient in the second power with respect to the field must vanish as the temperature tends to the critical value, i.e., $a_2 = 0$. We rewrite expression (14) for a_2 as

$$\frac{3\rho}{2G_0} \left[w_{21}(0) - \frac{\rho}{G_0} w_{22}(0) \right] = \rho - \frac{1}{(1-\epsilon)\beta J_0}. \quad (19)$$

Formula (19) corresponds to the actual mean-field condition under which the field is assumed to be constant throughout the system volume, i.e., $\sigma(x) = \sigma_0$ and $\langle\sigma^2\rangle = \sigma_0^2$. In this case, the Hamiltonian (or the free-energy density [4]) has the form $H = a_2\sigma_0^2 + (B_4 + D_4)\sigma_0^4$. Use can also be made of a more complicated self-consistent condition imposed on the critical point taking the field fluctuation in the Gaussian approximation, $a_2 + D_4\langle\sigma^2\rangle_c = 0$, into account. (Here $\langle\sigma^2\rangle_c$ is calculated at the critical point.) But this approximation is not as simple and convenient as (19). Using (19), (15), and (16), we calculated the dependence of the critical density on the critical temperature along the critical layering curve, i.e., the λ -line, in the case of particle interaction described by a rectangular potential well. The calculation results are presented in Fig. 2, where the λ -line found numerically by the Monte Carlo method for the parameter values $\epsilon = 0.72$ and $\lambda = 1.5$ [24] is also shown. As is seen, resulting mean-field relation (19) agrees well with the numerical experiment. It turned out that the coefficient B_4 can take both positive and negative values along the λ -line. In this case, the coefficient B_6 is always positive. (We do not present the analytic expression for this coefficient because it is very cumbersome.)

3. Conclusion

In this paper, a method is suggested for constructing an effective field theory Hamiltonian of the LGW type for off-lattice models of binary fluids. It is based on using an integral transformation of variables of the Hubbard–Stratonovich type. In contrast to the Hubbard–Stratonovich transformation, however, this method does not require the existence of the inverse operator for the singular part of the potential describing the interaction between the impenetrable particle cores. This permits considering off-lattice fluid models with a specific form of the interaction potential for hard cores.

We have shown that for a symmetric binary fluid, all coefficients of the effective Hamiltonian can be expressed in terms of the compressibility and its derivatives with respect to the density of the “support” system possessing only repulsive interactions. In the case of repulsive interactions modeled using hard-sphere interactions, there exist very accurate analytic expressions for these derivatives. Calculations were performed for a symmetric binary mixture with an interaction potential of the type of a rectangular potential well, and several first coefficients were determined for the effective LGW Hamiltonian. The curve of critical layering points (the λ -line) was found in the mean-field approximation, and it turned out to agree well with the numerical experiment results obtained using the Monte Carlo method.

Acknowledgments. This work was supported in part by INTAS-OPEN (Grant No. 97-1094).

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