

Investigation of a Homogeneous Many-Particle System in the Vicinity of the Critical Point

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A theory based on a separate account of short-range repulsion and long-range attraction between particles is applied to the description of the liquid–gas critical point in the classical fluid case. The collective variables method with a reference system (RS) is used. Detailed investigation of the properties of RS cumulants makes it possible to transform the grand partition function into a functional form defined on the effective block lattice. The functional corresponds to the partition function of the Ising model in an external field. Then the collective variables method is used to calculate the Ising-model partition function in the vicinity of the phase transition point, which was developed in our previous papers. As a result one can separate reference system and long-range subsystem variables, which makes possible the quantitative solution of the liquid–gas critical point problem. The equation for the parameters of the critical point is obtained, as are explicit expressions for the equation of state both above and below T_c ; the chemical potential of the system is investigated.

KEY WORDS: Expanded phase space; reference system; partition function; liquid–gas critical point; cumulants; Ising model in external field; chemical potential isotherm.

1. INTRODUCTION

During recent decades the problem of the liquid–gas critical point has been a field of intensive investigation, but is still far from complete solution. Different approaches treating interparticle attraction as a perturbation with respect to short-range repulsion^(1–6) have helped to understand the connections between the structure of the system and the character of the interaction and to reproduce approximately the experimental data. The

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renormalization group method and its combination with computer simulation has provided the possibility for calculation of the critical exponents and allowed the approach to a quantitative description of the thermodynamic properties.

Nevertheless, the derivation of an *ab initio* theory of the critical point, in which the order parameter is introduced in a natural way, and the Ginsburg–Landau–Wilson (GLW) functional explicitly related to the microscopic properties is obtained, remains an unresolved problem.

Important ideas concerning the problem were offered in refs. 15–17. In particular, in ref. 15 a GLW-type Hamiltonian was formally introduced, its connections with a reference system were pointed out, and a scheme for the calculation of the partition function was described. However, the authors were not engaged in a derivation of explicit expressions for coefficients of the Hamiltonian, and hence the calculation of the partition function and of the free energy was not their aim.

The calculation in the renormalization group approach and the structure of the GLW Hamiltonian were considered in detail in ref. 16. However, the treatment is rather formal concerning calculations of the initial values of the GLW Hamiltonian coefficients and their relations with microscopic properties of the system.

An original approach was developed by Parola *et al.* (see ref. 17 and their following papers on the same subject) which in principle leads to the derivation of a quantitative theory of a fluid in the vicinity of the critical point. The difficulties of this approach consist in the apparent convergence near the critical point of the perturbation series by means of which the differential generator of the reference system hierarchy has been constructed, and in cumbersome calculations as well.

Our method is based on taking account of the long-range attraction effects using the collective variables method, while the short-range repulsion is included in the reference system. The long-range attraction is related to direct and indirect interactions and results in collective effects, in particular in phase transitions and critical behavior. The short-range repulsion describes the impenetrability of particles, removes a formal divergence at short distances, and modulates the distribution and dispersion of the fluctuation processes. Both types of interaction are considered in the expanded phase space consisting of a subspace of Cartesian coordinates, in which the short-range repulsion is described, and of a subspace of collective variables $\rho_{\mathbf{k}}$, in which the effects of the long-range attraction are taken into account.

A transition operator which has the form of an analytic functional removes the phase space overflow.

In our approach, all properties of the structural functions of the system used as the reference system (RS) are supposed to be known. In this

paper we use the hard-sphere system, but in principle it is possible to use another system with known structural and thermodynamic functions; we shall consider this case elsewhere. In the present paper we demonstrate how knowledge of the general properties of the RS facilitates the actual solution of the critical point problem.

The structure functions of the RS (cumulants) were calculated in our previous papers.^(27,30) The expression for the grand partition function was obtained in the form of a functional integral in which the coefficients are cumulants depending on wave vector.⁽¹⁴⁾

Application of the mathematical techniques of the collective variables connected with the fluctuation modes of the number density $\hat{\rho}_{\mathbf{k}} \approx \sum_i \exp(i\mathbf{k}\mathbf{r}_i)$, where \mathbf{r}_i are the coordinates of a particle, allows one to reduce in the problem of taking into account a long attraction "tail" at long distances to the calculation of its influence in a certain finite interval of the wave vectors $|\mathbf{k}| \in [0, B]$.

Let us outline the main results of the paper:

(a) The dependence of RS cumulants on wave vector in a certain interval $|\mathbf{k}| \in [0, B]$, typical for the Fourier transform of the attractive forces, is proved to be rather weak.

(b) Taking into account the basic properties of pairwise attraction potentials allows one to transform the configuration integral into a functional defined on a certain effective block lattice. In such a representation the grand partition function corresponds to that of the Ising model in an external field, for which the method of calculation developed in refs. 7-16 is used here.

(c) A method of calculation of the partition function at $T < T_c$ and $T > T_c$ by integration over the collective-variable (CV) phase space is proposed. The grand partition function is reduced to a single integral over the collective variable ρ_0 , which is connected with the order parameter.

(d) It is shown how a definition of the critical point emerges in this approach, and its coordinates are calculated. In particular, for the critical fraction density we find $\eta_c = 0.130443$.

(e) An analysis of an explicit expression for a single integral over ρ_0 is carried out. The nonanalytic dependence of the Hamiltonian coefficients $E(\rho_0)$ on temperature is shown, and possibilities for one- or two-phase states below the critical point T_c are examined.

(f) An explicit expression for the chemical potential isotherm is obtained, and a density jump is calculated. The boundaries of the transition region, density jump region, and thermodynamic instability region are determined.

Table I. Values of Critical Indexes and Critical Amplitude Ratios for Heat Capacity (A^\pm) and Magnetic Susceptibility (Γ^\pm) for 3D Ising Model

	CV method ρ^6 model ⁽¹⁰⁾	Refs. 11–13
ν	0.637	0.630; 0.638
α	0.088	0.110; 0.125
β	0.319	0.325; 0.312
γ	1.275	1.241; 1.250
η	0.018 ^a	0.031
A^+/A^-	0.675	0.550; 0.48; 0.51
Γ^+/Γ^-	9.253	4.8; 5.07

^a ρ^4 model.

It is clear that universal characteristics such as the critical exponents have in this case values in common with the class of Ising-like systems because both the liquid–gas critical point and the Ising model belong to the same universality class. Detailed calculations of the critical exponents using the CV method were performed in refs. 7–10; therefore here we restrict ourselves to the presentation of some exponents from these papers (see Table I).

In the present paper we deliberately avoid extensive consideration of results connected with the Ising problem. Instead, we call the reader's attention to refs. 7 and 8, where this problem was carefully investigated. The main points of the present paper are the demonstration of the possibility to describe quantitatively the liquid–gas critical point, the development of a method for calculating the grand partition function in the vicinity of the critical point, and the calculation of an explicit expression for the equation of state and chemical potential. With these results, [see (25), (26), and (29) at $T > T_c$ and (46) and (61) at $T < T_c$], one can find other thermodynamic characteristics, for example, the heat capacity or entropy.

2. FUNCTIONAL REPRESENTATION OF THE GRAND PARTITION FUNCTION IN THE VICINITY OF THE CRITICAL POINT

Consider a system of N pairwise interacting particles in volume V at temperature T . According to the concept of the reference system, we express the full pairwise potential of two particles located at points \mathbf{r}_i and \mathbf{r}_j , $U_{ij} = U(|\mathbf{r}_i - \mathbf{r}_j|)$, as a sum

$$U_{ij} = \psi_{ij} + \Phi_{ij} \quad (1)$$

The main problem of the paper, namely the calculation of the grand partition function in the vicinity of the liquid-gas critical point, will be solved in the expanded phase space composed of the subspace of Cartesian coordinates of the particles $\mathbf{r}_1, \dots, \mathbf{r}_N$ and the collective-variables subspace. The behavior of the particles, conditioned by short-range repulsion, is described in the coordinate space, and that caused by attraction effects is described in the CV subspace.

The grand partition function

$$\Xi = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \exp \left\{ -\beta \sum_{i < j=1}^N [\psi_{ij} + \Phi_{ij}] \right\} (d\mathbf{r})^N \tag{2}$$

where $z = \exp(-\beta\mu) (2\pi mk_B T)^{3N/2}$ is the activity, μ denotes the chemical potential, $\beta = (k_B T)^{-1}$ is the inverse temperature, k_B is Boltzmann's constant, and m is the mass of the particle, can be represented in the form⁽¹⁴⁾

$$\Xi = \Xi_0 \int \exp \left\{ N^{1/2} \beta \rho_0 \left[\tilde{\mu} + \frac{1}{2} \tilde{\Phi}(0) \right] - \frac{1}{2} \beta \frac{N}{V} \sum_{\mathbf{k}} \tilde{\Phi}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right\} J(\rho) (d\rho) \tag{3}$$

where $\tilde{\mu} = \mu - \mu_0$; and

$$J(\rho) = \Xi_0^{-1} \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \exp \left\{ -\beta \sum_{i < j=1}^N \psi(|\mathbf{r}_i - \mathbf{r}_j|) \right\} J(\rho \mathbf{r}) (d\mathbf{r})^N$$

is the Jacobian of the transition from Cartesian coordinates to the collective variables ρ . Here

$$J(\rho \mathbf{r}) = \delta(\rho_0 - \hat{\rho}_0) \prod_{\mathbf{k} \neq 0}' \delta(\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}); \quad \hat{\rho}_{\mathbf{k}} = N^{-1/2} \int \hat{n}(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}$$

The collective variable $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}^c - \rho_{\mathbf{k}}^s$ is related to the real and imaginary parts of the Fourier transform of the particle density $\hat{\rho}_{\mathbf{k}} = \hat{\rho}_{\mathbf{k}}^c - \hat{\rho}_{\mathbf{k}}^s$ by

$$\begin{aligned} \hat{\rho}_{\mathbf{k}'}^c &= N^{-1/2} \sum_{i=1}^N \cos(\mathbf{k}'\mathbf{r}_i) = \int \rho_{\mathbf{k}'}^c J(\rho \mathbf{r}) (d\rho) \\ \hat{\rho}_{\mathbf{k}'}^s &= N^{-1/2} \sum_{i=1}^N \sin(\mathbf{k}'\mathbf{r}_i) = \int \rho_{\mathbf{k}'}^s J(\rho \mathbf{r}) (d\rho) \\ (d\rho) &= d\rho_0 \prod_{\mathbf{k} \neq 0} d\rho_{\mathbf{k}}^c d\rho_{\mathbf{k}}^s \end{aligned}$$

In the above,

$$\Xi_0 = \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \exp \left\{ -\beta \sum_{i < j=1}^N \psi(|\mathbf{r}_i - \mathbf{r}_j|) \right\} (d\mathbf{r})^N$$

is the RS grand partition function, which we suppose is known; $\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$ is the density of particles at the point \mathbf{r} ; $\tilde{\Phi}(k) = \int \Phi(r) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}$ is the Fourier transform of the potential $\Phi(r)$; μ_0 is the chemical potential of the reference system; and μ is the total chemical potential.

Inserting the integral representation for δ -functions in the Jacobian and performing the integration over Cartesian coordinates in the expression for the Jacobian, we obtain for the grand partition function

$$\begin{aligned} \Xi &= \Xi_0 \int \exp \left\{ hN^{1/2} \rho_0 - \frac{1}{2} \sum_{\mathbf{k}} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} - i2\pi N^{1/2} \mathfrak{M}_1 \omega_0 \right\} \\ &\times \exp \left\{ -\frac{(2\pi)^2}{2!} \sum_{\mathbf{k}} \mathfrak{M}_2(k) \omega_{\mathbf{k}} \omega_{-\mathbf{k}} \right\} \\ &\times \exp \left\{ \sum_{m \geq 3} \frac{(-i2\pi)^m}{m!} N^{-(m-2)/2} \right. \\ &\left. \times \sum_{\mathbf{k}_1, \dots, \mathbf{k}_m} \mathfrak{M}_m(k_1, \dots, k_m) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_m} \right\} (d\omega) (d\rho) \end{aligned} \quad (4)$$

where $h = \beta[\tilde{\mu} + \frac{1}{2}\tilde{\Phi}(0)]$; $\alpha(k) = \beta(N/V) \tilde{\Phi}(k)$; $\omega_{\mathbf{k}}$ is the Fourier-conjugate variable to the collective variable $\rho_{\mathbf{k}}$; $\mathfrak{M}_m(k_1, \dots, k_m) = \langle \hat{\rho}_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_m} \rangle_c$ is the m th-order RS cumulant, which can be expressed in terms of the RS correlation functions;⁽²²⁾ and $\langle \dots \rangle_c$ means cumulant average by the RS.

It is well known that the main features of the behavior of the system at the critical point are connected with the long-range fluctuations of the density.

We classify the density fluctuation modes into short-range and long-range modes based on the properties of $\tilde{\Phi}(k)$ —the Fourier transform of the potential $\Phi(r)$,

$$\Phi(r) = \frac{1}{V} \sum_{\mathbf{k}} \tilde{\Phi}(k) e^{-i\mathbf{k}\mathbf{r}}$$

The potential $\tilde{\Phi}(k)$ is negative at $0 \leq |\mathbf{k}| \leq B$, $\tilde{\Phi}(B) = 0$, and at $k > B$ it may be positive or oscillating and vanishes at $|\mathbf{k}| \rightarrow \infty$ (see Fig. 1). In this paper we use as an attractive potential $\Phi(r)$ the negative branch of the Morse potential [see (15)]. As one can see from Fig. 1, the value of $|\tilde{\Phi}(k)|$ at

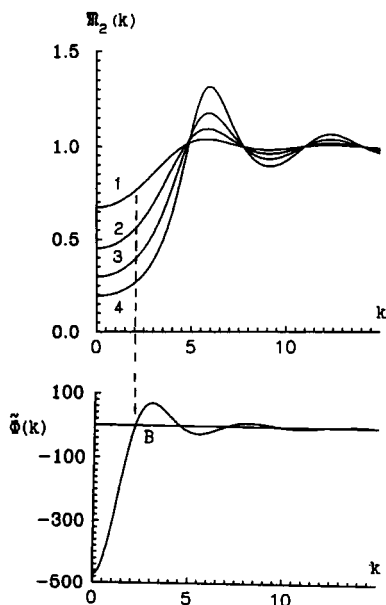


Fig. 1. Plots of (a) second cumulants $\mathfrak{M}_2(k)$ and (b) the Fourier transform $\tilde{\Phi}(k)$ of the attractive part of the interaction potential. The point B separates long- and short-wave fluctuations of the density. Curves 1-4 correspond to values $\eta=0.05, 0.1, 0.15,$ and $0.2,$ respectively.

$k > B$ is small. This allows us to describe the short-wave fluctuations, corresponding to $\omega_{\mathbf{k}}$ and $\rho_{\mathbf{k}}$ for $|\mathbf{k}| > B$, with a Gaussian basic density measure. The variables $\omega_{\mathbf{k}}$ and $\rho_{\mathbf{k}}$ for $|\mathbf{k}| \leq B$ are connected with long-wave fluctuations. The Gaussian approximation cannot be used here because it leads to a divergence in the vicinity of the critical point. This is the main difficulty in the calculation of the integral (4).

After integration over the short-wave modes of the density fluctuation $\omega_{\mathbf{k}}$ and $\rho_{\mathbf{k}}, |\mathbf{k}| > B$, we find the following expression for the grand partition function:

$$\Xi = \Xi_0 \Xi_G \Xi_L \tag{5}$$

Here Ξ_L is a functional of the long-wave fluctuations and will be described below. Ξ_G is the part of the grand partition function connected with the short-wave density fluctuations distributed according to the Gaussian law.

The expression for Ξ_G and a way of calculating it are given in Appendix A.

Integration over $\omega_{\mathbf{k}}$ and $\rho_{\mathbf{k}}$, $|\mathbf{k}| > B$, leads to renormalization of the cumulants, the new values of which are denoted below as $\tilde{\mathfrak{M}}_n(k_1, \dots, k_n)$; for example,

$$\tilde{\mathfrak{M}}_2(k) \approx \mathfrak{M}_2(k) + \frac{1}{4N} \sum_{\mathbf{k}_1, |\mathbf{k}_1| > B} \mathfrak{M}_4(k, -k, k_1, -k_1) \langle \omega_{\mathbf{k}_1} \omega_{-\mathbf{k}_1} \rangle + \dots \quad (6)$$

Expressions (A4) and (6) describe the contribution of the short-wave density fluctuations. We have evaluated its value in the case of argon, taking for the interaction between particles the Morse potential (see below). For the "long-range" attraction its negative branch was employed.

In particular, at the critical point at $k=0$ we obtain from expression (6) in zeroth approximation

$$\tilde{\mathfrak{M}}_2(0) \approx \mathfrak{M}_2(0)(1 - 0.271 \times 10^{-6}) \quad (6')$$

In this way, the influence of short-wave fluctuations is negligible here. This is conditioned by the behavior of $\alpha(k)$ at $k > B$ and by the small value of $\mathfrak{M}_4(0, 0, k, -k) \approx 0.1$.

Taking into account the estimate (6'), in the zeroth approximation we may neglect the renormalization of cumulants \mathfrak{M}_n in the region $|\mathbf{k}_i| \leq B$ due to integration over the variables $\rho_{\mathbf{k}}$ and $\omega_{\mathbf{k}}$, $|\mathbf{k}| > B$, setting $\tilde{\mathfrak{M}}_n \approx \mathfrak{M}_n$.

The investigation of the cumulants is the most important part of the preliminary discussion of the initial form of the partition function. In Fig. 1a, the curves for $\mathfrak{M}_2(k)$ are plotted for values of the fraction density $\eta = (\pi/6)(N/V) \sigma^3$. The RS structure factor $\mathfrak{M}_2(k)$ was calculated in ref. 25. An essential property of $\mathfrak{M}_2(k)$ is the way in which it depends on k at small k , namely, the presence of an almost horizontal "shoulder" of the curve $\mathfrak{M}_2(k)$ (see Fig. 1). The length of the shoulder depends on η . As one can see from Fig. 1, the region $0 \leq |\mathbf{k}| \leq B$ of negative values of $\tilde{\Phi}(k)$ almost coincides with the "shoulder" region. Using Schofield's equation for the correlation functions,⁽²⁸⁾ expressions for the cumulants $\mathfrak{M}_3(k, -k, 0)$ and $\mathfrak{M}_4(k, -k, 0, 0)$ with a reduced dependence on wave vector were obtained in ref. 27 (see also Appendix B).

Plots of $\mathfrak{M}_3(k, -k, 0)$ and $\mathfrak{M}_4(k, -k, 0, 0)$ are given in Fig. 2. One can see that a weak dependence on k at small k is common to all the cumulants we have considered here. This allows us to replace the functions $\mathfrak{M}_n(k_1, \dots, k_n)$ at $|\mathbf{k}_i| \leq B$ by a constant value $\mathfrak{M}_n(0, \dots, 0)$.

Values of $\mathfrak{M}_2(0)$ through $\mathfrak{M}_5(0)$ are listed in Table II.

The main part of the partition function in view of the present consideration is \mathcal{E}_L , for which we found in refs. 14 and 26 the expression

$$\mathcal{E}_L = \int (1 + D_4 + \dots) W_4(\rho; \omega) (d\omega)^{N_B} (d\rho)^{N_B} \quad (7)$$

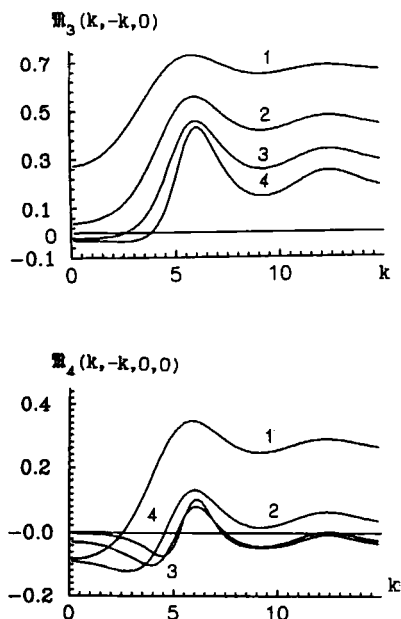


Fig. 2. Dependence of cumulants $\mathfrak{M}_3(k, -k, 0)$ and $\mathfrak{M}_4(k, -k, 0, 0)$ on k . Curves 1-4 correspond to values $\eta = 0.05, 0.1, 0.15,$ and $0.2,$ respectively.

Here

$$D_4 = \sum_{m>4} \frac{(-2i\pi)^m}{m!} N^{1-m/2} \sum_{\substack{k_1, \dots, k_m \\ |k_i| \leq B}} \mathfrak{M}_m(0) \omega_{k_1} \dots \omega_{k_m} \quad (8)$$

$W_4(\rho; \omega)$ is a basic measure density in the vicinity of the critical point.

Table II. Dependence on the Fraction Density of Cumulants $\mathfrak{M}_n(k_1, \dots, k_n)$ at Zero Values of Arguments k_i

η	$\mathfrak{M}_2(0)$	$\mathfrak{M}_3(0)$	$\mathfrak{M}_4(0)$	$\mathfrak{M}_5(0)$
0.05	0.673	0.275	7.81×10^{-2}	-0.18×10^{-5}
0.10	0.456	4.61×10^{-2}	-8.66×10^{-2}	2.04×10^{-2}
0.15	0.309	-1.59×10^{-2}	-2.83×10^{-2}	2.74×10^{-2}
0.20	0.208	-2.49×10^{-2}	-3.96×10^{-2}	9.64×10^{-3}
0.25	0.141	-1.98×10^{-2}	-2.16×10^{-3}	1.81×10^{-3}

It was shown in ref. 19 that

$$\begin{aligned}
 W_4(\rho; \omega) = \exp \left\{ hN^{1/2}\rho_0 - \frac{1}{2} \sum_{\mathbf{k}, |\mathbf{k}| \leq B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + i2\pi \sum_{\mathbf{k}, |\mathbf{k}| \leq B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right. \\
 \left. + \sum_{n=1}^4 \frac{(-i2\pi)^n}{n!} N^{1-n/2} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_n \\ |\mathbf{k}_i| \leq B}} \mathfrak{M}_n(0) \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n} \right\} \tag{9}
 \end{aligned}$$

We keep in the exponent of the function $W_4(\rho; \omega)$ only terms up to the fourth power in the variable $\omega_{\mathbf{k}}$. Following the above arguments, we have neglected in (8) and (9) the dependence of $\mathfrak{M}_n(k_1, \dots, k_n)$ on k_i , as well as the renormalization of \mathfrak{M}_n due to integration over $d\rho_{\mathbf{k}}, d\omega_{\mathbf{k}}, |\mathbf{k}| > B$, and replaced $\mathfrak{M}_n(k_1, \dots, k_n)$ for $k_i \leq B$ by $\mathfrak{M}_n(0)$.

It is essential that all odd cumulants $\mathfrak{M}_1, \mathfrak{M}_3, \mathfrak{M}_5, \dots$ in (7) possess the factor i . The convergence of the integrals in (7) is ensured by the term containing \mathfrak{M}_4 .

Then the shift

$$\begin{aligned}
 \omega_0 &= \omega'_0 - \frac{iN^{1/2}\mathfrak{M}_3(0)}{2\pi\mathfrak{M}_4(0)} \\
 \rho_0 &= \rho'_0 + \mathfrak{M}_1
 \end{aligned} \tag{10}$$

where

$$\mathfrak{M}_1 = N^{1/2} \left(1 + \frac{\mathfrak{M}_2(0) \mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|} + \frac{\mathfrak{M}_3^3(0)}{3\mathfrak{M}_4^2(0)} \right)$$

transforms W_4 into a form containing terms $\mathfrak{M}_1, \mathfrak{M}_2$, and \mathfrak{M}_4 only. Such an expression for W_4 corresponds to the Ising model in an external field. In fact, at this point, the critical point problem is basically solved. The CV method was earlier applied to the Ising problem.^(7,8) Having introduced the collective variables related to the Fourier transforms of the spin density, one obtains after summation over all spin configurations an expression for the partition function which has just the same structure as (4), but instead of the cumulants $\mathfrak{M}_1, \mathfrak{M}_2, \mathfrak{M}_4$ one has 0, 1, -2 . The value h in (9) corresponds to an external field in the case of the Ising model. Integration over $\omega_{\mathbf{k}}$ in (7) transforms it [see (13)] to a known form, which was investigated, for example, in ref. 29. Notice that application of functional methods to the Ising problem leads to a density measure in the expression for the free energy similar to (9).

After integration over $\rho_{\mathbf{k}}, \omega_{\mathbf{k}}, |\mathbf{k}| > B$, the expression for Ξ_L contains only sums over \mathbf{k} with $|\mathbf{k}| \leq B$. We can consider a set of \mathbf{k} vectors, $|\mathbf{k}| \leq B$, as corresponding to sites of a reciprocal lattice conjugated to a certain block lattice $\{r_i\}$ with N_B block sites in a periodicity volume V :

$$N_B = N \frac{(B\sigma)^3}{6\pi^2\eta} \tag{11}$$

One may consider the quantity B as the size of the first Brillouin zone of this block lattice.

Setting for the Kronecker symbol

$$\delta_{\mathbf{k}} = \frac{1}{N_B} \sum_{r_i} e^{i\mathbf{k}r_i}$$

we obtain for W_4

$$\begin{aligned} W_4(\rho; \omega) = \exp \left\{ \mu^* \rho_0 - \frac{1}{2} \sum_{\mathbf{k}, |\mathbf{k}| \leq B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + i2\pi \sum_{\mathbf{k}, |\mathbf{k}| \leq B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right. \\ \left. - i2\pi \mathfrak{M}_1 \omega_0 - \frac{(2\pi)^2}{2} \mathfrak{M}_2(0) \sum_{\mathbf{k}, |\mathbf{k}| \leq B} \omega_{\mathbf{k}} \omega_{-\mathbf{k}} \right. \\ \left. - \frac{(2\pi)^4}{4! N_B} |\mathfrak{M}_4(0)| \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ |\mathbf{k}_i| \leq B}} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4} \right\} \tag{12} \end{aligned}$$

with

$$\mathfrak{M}_2(0) = \mathfrak{M}_2(0) - \frac{\mathfrak{M}_3^2(0)}{2 |\mathfrak{M}_4(0)|}; \quad \mathfrak{M}_4(0) = \frac{N_B}{N} \mathfrak{M}_4(0)$$

Therefore, we have reduced the problem of calculating the partition function of the fluid to that of the Ising-like system.

Integrating W_4 over all $\omega_{\mathbf{k}}$, we finally obtain the following form for the grand partition function:

$$\begin{aligned} \Xi = \Xi_0 \Xi_G^{(1)} Z(\mathfrak{M}_2, \mathfrak{M}_4) \int \exp \left\{ \mu^* \rho_0 - \frac{1}{2} \sum_{\mathbf{k}, |\mathbf{k}| \leq B} d_2(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right. \\ \left. - \frac{\tilde{a}_4}{4!} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ |\mathbf{k}_i| \leq B}} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4} \right\} (d\rho)^{N_B} \tag{13} \end{aligned}$$

Here

$$\mu^* = N^{1/2}h - \tilde{a}_1; \quad \tilde{a}_1 = N^{1/2} \frac{\mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|} + \alpha(0) \mathfrak{M}_1;$$

$$\tilde{a}_2 = (12)^{1/2} |\mathfrak{M}_4(0)|^{-1/2} K(\zeta)$$

$$\tilde{a}_4 = 6 |\mathfrak{M}_4(0)|^{-1} L(\zeta); \quad d_2(k) = \tilde{a}_2 + \alpha(k); \quad \zeta = \frac{3\mathfrak{M}_2^2(0)}{4 |\mathfrak{M}_4(0)|}$$

$$L(\zeta) = 6K^2(\zeta) + 4\zeta^{1/2}K(\zeta) - 1;$$

$$Z(\mathfrak{M}_2, \mathfrak{M}_4) = \frac{1}{2\pi} \left(\frac{144\zeta}{|\mathfrak{M}_4(0)|} \right)^{1/4} e^\zeta K(\zeta)$$

$$K(\zeta) = \zeta^{1/2} [K_{3/4}(\zeta)/K_{1/4}(\zeta) - 1]$$

$K_{1/4}(\zeta)$ and $K_{3/4}(\zeta)$ are Bessel functions of imaginary argument; we have

$$\begin{aligned} \Xi_G^{(1)} = \Xi_G \exp \left\{ -N \left[\frac{\mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|} + \frac{\mathfrak{M}_2(0) \mathfrak{M}_3^2(0)}{2\mathfrak{M}_4^2(0)} + \frac{\mathfrak{M}_3^4(0)}{8 |\mathfrak{M}_4(0)|^3} \right] \right. \\ \left. + \frac{1}{2} \alpha(0) \mathfrak{M}_1^2 + \mu^* \mathfrak{M}_1 \right\} \end{aligned}$$

To finish with the introduction, let us now touch on the question of the separation of the RS potential $\psi(r)$ from the total potential $V(r) = \psi(r) + \Phi(r)$. In the present paper we start with the Morse potential

$$V_m(r) = \varepsilon [e^{-2(r-r_0)/\alpha} - 2e^{-(r-r_0)/\alpha}]$$

with parameters α , ε , and r_0 .⁽²⁰⁾ The potential V_m possesses two branches, a positive one at $r < r_0 - \alpha \ln 2$ and a negative one for the remaining r .

The negative branch will be described by CV. Instead of the positive branch, we shall use an appropriate hard-sphere system and choose the diameter of the spheres to provide a coincidence of the binary correlation functions of the hard spheres with those of the system with the positive branch only. So one can calculate the hard-sphere diameter σ in a way similar to that developed by Weeks *et al.*⁽¹⁾

The equation of state will include a part which corresponds to the hard-sphere system pressure, for which we adopt the Carnahan–Starling equation⁽²¹⁾

$$\frac{P_0 V}{NkT} = z_0 = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (14)$$

Table III. Coefficients a_1, a_2, a_3, a_4 of the Effective LGW Hamiltonian and Coefficient \bar{a}_2 of the Hamiltonian with Reduced a_3 term^a

η	a_1	a_2	a_3	a_4	\bar{a}_2
0.04	-0.1959	0.9405	-0.4542	0.5870	0.7647
0.06	-0.4616	0.9974	-0.3160	0.4133	0.8766
0.08	-0.6355	1.0132	-0.2196	0.2756	0.9257
0.10	-0.7660	1.0113	-0.1350	0.1570	0.9532
0.12	-0.8681	1.0010	-0.0698	0.0796	0.9704
0.14	-0.9518	0.9902	-0.0271	0.0384	0.9807
0.16	-1.0237	0.9825	-0.0024	0.0183	0.9824
0.18	-1.0883	0.9784	0.0103	0.0087	0.9723
0.20	-1.1479	0.9770	0.0158	0.0038	0.9446

^a $\sigma = 3.2 \text{ \AA}$, $B = 0.648 \text{ \AA}^{-1}$.

Here z_0 is the compressibility factor of the RS, and $\eta = (\pi/6)(N/V)\sigma^3$. The diameter σ is a function dependent on both density and temperature. We will neglect this dependence, taking for σ its value at the critical point: $\sigma = \sigma(\eta_c, T_c)$.

Equation (14) can be utilized to calculate the chemical potential μ_0 of the RS. Thus, in our further investigation μ_0 is taken to be known.

For the remaining branch of the interaction $\Phi(r)$ we have

$$\Phi(r) = \begin{cases} 0, & r \leq r^* \\ V_m(r), & r > r^* \end{cases} \quad (15)$$

Its Fourier transform $\tilde{\Phi}(k)$

$$\begin{aligned} \tilde{\Phi}(k) &= \int \Phi(r) e^{-ikr} dr \\ &= \varepsilon \alpha^3 \frac{4\pi}{k} e^{-(r_0 - r^*)/\alpha} \left\{ \frac{e^{(r_0 - r^*)/\alpha}}{4 + k^2 \alpha^2} \right. \\ &\quad \times \left[\left(\frac{2r^*}{\alpha} + \frac{4 - k^2 \alpha^2}{4 + k^2 \alpha^2} \right) \sin kr^* + \left(kr^* + \frac{4kr^*}{4 + k^2 \alpha^2} \right) \cos kr^* \right] \\ &\quad - \frac{2}{1 + k^2 \alpha^2} \left[\left(\frac{r^*}{\alpha} + \frac{1 - k^2 \alpha^2}{1 + k^2 \alpha^2} \right) \sin kr^* \right. \\ &\quad \left. \left. + \left(kr^* + \frac{2k\alpha}{1 + k^2 \alpha^2} \right) \cos kr^* \right] \right\} \quad (16) \end{aligned}$$

is plotted in Fig. 1b. The point B of its intersection with the k axis separates short- and long-wave density fluctuations.

A calculation of the coefficients of the function $W_4(\rho, \omega)$ of Eq. (12), which contains in the exponent an expression of GLW Hamiltonian type, can be performed without making use of the substitution (10). In such a case it will contain all terms of odd and even order in $\rho_{\mathbf{k}}$. Values of the first four coefficients a_1 – a_4 are presented in Table III.

For the partition function Ξ_L we obtain a functional with explicitly defined coefficients.

3. CALCULATION OF THE PARTITION FUNCTION IN THE VICINITY OF THE CRITICAL POINT

Thus, we have transformed the expression for the partition function to the form (13) corresponding to the Ising model in an external field. This allows us to use the method of calculating the partition function using integration over the layers of the phase space (PS) developed in refs. 7–10. Expression 13 contains N_B integrals over $\rho_{\mathbf{k}}(\rho_{\mathbf{k}}^c, \rho_{\mathbf{k}}^s)$, $0 \leq |\mathbf{k}| \leq B$. We will perform a layerwise integration in the PS. Division of the PS into layers is performed as follows.

In the interval $[0, B]$ we choose points $B_1 = B/s$, $B_2 = B_1/s, \dots, B_n = B_{n-1}/s$. Variables $\rho_{\mathbf{k}}(\rho_{\mathbf{k}}^c, \rho_{\mathbf{k}}^s)$ for which the subscript \mathbf{k} satisfies the condition $B_1 < |\mathbf{k}| \leq B$ belong to the first layer. For the second layer one has $B_2 < |\mathbf{k}| \leq B_1$, $B_2 = B/s^2$; for the n th layer one has $B_n < |\mathbf{k}| \leq B_{n-1}$, $B_n = B/s^n$, $B_{n-1} = B/s^{n-1}$.

To factorize the integrals, we replace the Fourier transform of the attraction potential $\tilde{\Phi}(k)$ by its average value in each layer. Hence, instead of $\tilde{\Phi}(k)$ we will have a sequence of values:

$$\begin{aligned} \tilde{\Phi}(k) &\rightarrow \Phi(B_1, B), & B_1 < |\mathbf{k}| \leq B \\ &\Phi(B_2, B_1), & B_2 < |\mathbf{k}| \leq B_1 \\ &\dots \\ &\Phi(B_n, B_{n-1}), & B_n < |\mathbf{k}| \leq B_{n-1} \end{aligned}$$

Here $\Phi(B_1, B)$ is the average value of $\tilde{\Phi}(k)$ over the interval (B_1, B) . The method of averaging is not essential. For example, we take

$$\Phi(B_n, B_{n-1}) = \int_{B_n}^{B_{n-1}} \tilde{\Phi}(k) d\mathbf{k} / \int_{B_n}^{B_{n-1}} d\mathbf{k}$$

or

$$\Phi(B_n, B_{n-1}) = \frac{[\Phi(B_n) + \Phi(B_{n-1})]}{2}$$

for the geometric and arithmetic averages, respectively.

Generally, the division parameter $s > 1$ can take arbitrary values, but as a consequence of the approximations used in the calculations, the highest precision of the results is achieved at some optimal value $s = s^*$ in each case. For example, if the quartic density measure approximation is applied, keeping in the exponent of (13) terms up to the fourth order of ρ_k , the optimal value is $s^* = 3.58$, which provides the coefficient $d_2^{(n)}(0)$ equal to zero at the fixed point: $d_2^{(n)}(0) = d_2^* = 0$.

After the integration over variables ρ_k of the first layer the number of variables under the integral will decrease from N_B to $N_1 = N_B s^{-3}$; and after n layers we have $N_n = N_B s^{-3n}$. The structure of the function under the integral remains unchanged, but instead of initial coefficients a_2, a_4 we have in turn $a_2^{(1)}, a_4^{(1)}; a_2^{(2)}, a_4^{(2)}; \dots; a_2^{(n)}, a_4^{(n)}; \dots$.

After n steps of integration one obtains

$$\begin{aligned} \bar{\mathcal{E}} = & \bar{\mathcal{E}}_0 \bar{\mathcal{E}}_G^{(1)} Z(\bar{\mathfrak{M}}_2, \bar{\mathfrak{M}}_4) Q_0 Q_1 \cdots Q_{n-1} \\ & \times \int \exp \left\{ \mu^* \rho_0 - \frac{1}{2} \sum_{k, |k| \leq B} d_2^{(n)}(k) \rho_k \rho_{-k} \right. \\ & \left. - \frac{\bar{a}_4^{(n)}}{4! N_n} \sum_{\substack{k_1, \dots, k_4 \\ |k_i| \leq B_n}} \rho_{k_1} \cdots \rho_{k_4} \delta_{k_1 + \dots + k_4} \right\} (d\rho)^{N_n} \end{aligned} \quad (17)$$

where $Q_0 \cdots Q_{n-1}$ is the result of integration over the n first layers. We have

$$\begin{aligned} Q_0 &= [Q_{f_0}]^N [Q_{\varphi_0}]^{N_1}; & Q_n &= [Q_{f_0}]^{N_n} [Q_{\varphi_0}]^{N_{n+1}} \\ Q_{\varphi_n} &= \int_{-\infty}^{\infty} \varphi_n(\omega) d\omega; & Q_{f_n} &= \int_{-\infty}^{\infty} f_n(\eta) d\eta \\ \varphi_n(\omega) &= \exp \left\{ -2\pi^2 P_2^{(n)} \omega^2 - \frac{(2\pi)^4}{4!} P_4^{(n)} \omega^4 \right\} \\ f_n(\eta) &= \exp \left\{ -\frac{1}{2} \bar{d}_2^{(n)} \eta^2 - \frac{a_4^{(n)}}{4!} \eta^4 \right\} \\ P_2^{(n)} &= Q_{f_n}^{-1} \int_{-\infty}^{\infty} \eta^2 f_n(\eta) d\eta \\ P_4^{(n)} &= s^{-3} \left\{ Q_{f_n}^{-1} \int_{-\infty}^{\infty} \eta^4 f_n(\eta) d\eta + (3P_2^{(n)})^2 \right\} \end{aligned}$$

$$\begin{aligned} \bar{d}_2^{(n)} &= a_2^{(n)} + \beta \frac{N}{V} \overline{\Phi(B_{n+1}, B_n)} \\ a_2^{(n+1)} &= \beta \frac{N}{V} \overline{\Phi(B_{n+1}, B_n)} + (2\pi)^2 \mathcal{Q}_{\varphi_n}^{-1} \int_{-\infty}^{\infty} \omega^2 \varphi_n(\omega) d\omega \\ a_4^{(n)} &= (2\pi)^4 \left\{ -\mathcal{Q}_{\varphi_n}^{-1} \int_{-\infty}^{\infty} \omega^4 \varphi_n(\omega) d\omega + 3 \left[\mathcal{Q}_{\varphi_n}^{-1} \int_{-\infty}^{\infty} \omega^2 \varphi_n(\omega) d\omega \right]^2 \right\} \end{aligned}$$

The values of $d_2^{(2)}$, $d_2^{(n+1)}$, $a_4^{(n)}$, and $a_4^{(n+1)}$ are linked by the recursion relations

$$\begin{cases} d_2^{(n+1)} = f_1(d_2^{(n)}, a_4^{(n)}) \\ a_4^{(n+1)} = f_2(d_2^{(n)}, a_4^{(n)}) \end{cases} \quad (18)$$

Their explicit form is presented in Appendix C and in Fig. 6.

It was shown in refs. 7, 8, and 23 that for $0 \leq k \leq B$ there exist two main phase-space regions, in which the solutions of the recursion relations (18) and (C1) possess fixed points of different types. These two regions correspond to different fluctuation regimes. The first one holds in the vicinity of the critical point and was named the critical regime. It describes the short-wave fluctuations and corresponds to integration over variables $\rho_{\mathbf{k}}$ with $B_{n_r} < |\mathbf{k}| \leq B$. For a sequence of block Hamiltonians $\{d_2^{(n)}, a_4^{(n)}\}$ the renormalization group symmetry holds and the fixed point is of saddle type.

The second regime describes the long-wave density fluctuations and holds for all $\rho_{\mathbf{k}}$, $|\mathbf{k}| \leq B_{n_r}$. In the case $T > T_c$, that is, above the critical temperature, it was called the limiting Gaussian regime (LGR) and at $T < T_c$ the inverse Gaussian regime (IGR). The recursion relations at both $T > T_c$ and $T < T_c$ possess an unstable node type of fixed point. The measure density under the integral in (17) approaches a Gaussian one with a nonanalytical dependence of dispersion on the temperature.

Fluctuations with $k=0$ should be considered separately, because ρ_0 is a macroscopic variable and its average value is related to the order parameter of the system.

More detailed consideration of all these processes will be given below.

The investigation of the asymptotic behavior of $d_2^{(n)}(0)$ and $a_4^{(n)}$ at $n \rightarrow \infty$ was performed in refs. 7 and 8. By the use of the transformation

$$\begin{aligned} r_n &= d_2^{(n)}(0) s^{2n} \\ u_n &= a_4^{(n)} s^{4n} \end{aligned} \quad (19)$$

Eqs. (C1) were reduced to the form

$$\begin{cases} r_{n+1} = s^2(r_n + q) N(z^{(n)}) - s^2q \\ u_{n+1} = su_n E(z^{(n)}) \end{cases} \quad (20)$$

where

$$\begin{aligned} N(z^{(n)}) &= \left(\frac{\zeta^{(n)}}{z^{(n)}}\right)^{1/2} \frac{U(\zeta^{(n)})}{U(z^{(n)})} \\ E(z^{(n)}) &= \frac{U^2(\zeta^{(n)}) + \frac{2}{3}\zeta^{(n)}U(\zeta^{(n)}) - \frac{2}{3}}{U^2(z^{(n)}) + \frac{2}{3}z^{(n)}U(z^{(n)}) - \frac{2}{3}} \\ q &= \bar{q}\alpha(0); \quad \bar{q} = \frac{3(1-s^{-5})}{5(1-s^{-3})} \end{aligned}$$

Equations (20) have the fixed-point type partial solution $r_n = r^*$, $u_n = u^*$, and relations (19) acquire the properties of a cyclic semigroup. The substitution (19) is equivalent to the scaling transformations $k' = ks$, $\rho'_k = \rho_k/s$ in Wilson's theory.⁽²⁹⁾

The pair of numbers (r_n, u_n) can be considered as coordinates of a point in a parametric space. During the subsequent layer-by-layer integration we shall obtain a trajectory. The character of the trajectory depends on temperature. For the " ρ^4 " model there exists a unique temperature for which the trajectory reduces to a point:

$$(r_n, u_n) \rightarrow (r^*, u^*) \quad n \rightarrow \infty; \quad r^*, u^* > 0$$

The (r^*, u^*) point is the fixed point of the above renormalization group transformation.

In the vicinity of the critical point we can use linear approximations in (20), transforming them to the form

$$\begin{pmatrix} r_{n+1} - r^* \\ u_{n+1} - u^* \end{pmatrix} = R \begin{pmatrix} r_n - r^* \\ u_n - u^* \end{pmatrix} \quad (21)$$

where R is a linearized renormalization group transformation matrix. Expressions for elements of the matrix R are given in Appendix D.

In ref. 7 a general solution of the linearized system (21) was found in the form

$$\begin{aligned} r_n &= r^* + C_1 E_1^n + C_2 \frac{R_{12}}{E_2 - R_{11}} E_2^n \\ u_n &= u^* + C_1 \frac{E_1 - R_{11}}{R_{12}} E_1^n + C_2 E_2^n \end{aligned} \quad (22)$$

Table IV. Values of Some Coefficients of the Solution of the Recursion Relations for $s = 3.58$

E_1	E_2	\bar{r}	\bar{u}	R_{12}^0	R_{21}^0	\bar{q}	R_{11}
8.235	0.377	0.6122	0.8894	3.837	1.174	0.6123	7.613

where E_1, E_2 are the eigenvalues of the matrix R ; $E_1 > 1, E_2 < 1$ (see Table IV); C_1, C_2 are functions depending on temperature, density, and potential of the interaction:

$$C_1 = \left[-a_2 - \beta \frac{N}{V} |\bar{\Phi}(0)| - r^* + (a_4 - u^*) \frac{R_{12}}{R_{11} - E_2} \right] \frac{R_{11} - E_2}{E_1 - E_2}$$

$$C_2 = \left[-\left(a_2 - \beta \frac{N}{V} |\bar{\Phi}(0)| - r^* \right) \frac{E_1 - R_{11}}{R_{12}} + a_4 - u^* \right] \frac{R_{11} - E_2}{E_1 - E_2}$$

The solutions (22) are valid in the vicinity of the critical point, including at the critical point itself. At the critical point the solutions r_n, u_n at $n \rightarrow \infty$ tend to their fixed-point values:

$$\lim_{n \rightarrow \infty} r_n = r^*; \quad \lim_{n \rightarrow \infty} u_n = u^*$$

This is possible [see (22)] only if $C_1 = 0$ and so it coincides with the Wilson definition. Thus, we obtain the definition of “the critical temperature line.” One obtains its explicit form from the solution of the condition $C_1(T, \eta) = 0$:

$$T_c(\eta) = \frac{(N/V) |\bar{\Phi}(0)|}{k_B} \times \frac{2[1 - \bar{r} + R_{12}^0(\bar{u})^{1/2}/(R_{11} - E_2)]}{a_2 + \{a_2^2 + [4a_4 R_{12}^0/\bar{u}^{1/2}(R_{11} - E_2)][1 - \bar{r} + R_{12}^0 \bar{u}^{1/2}/(R_{11} - E_2)]\}} \tag{23}$$

Expression (23) corresponds to a curve on the (T, η) plane and will be used further for the calculation of the critical temperature. However, to determine the critical point one more condition is necessary, which defines another curve in the (T, η) plane. The point of their intersection determines the critical point coordinates. Therefore, at $T = T_c$ the trajectory (r_n, u_n) ends in the saddle-type fixed point (r^*, u^*) .

At $T \neq T_c$ for $n < n_\tau$ the current point (r_n, u_n) stays in the vicinity of the fixed point, approaching it at $n \rightarrow n_\tau$. The limiting number n_τ of the

layer of the collective-variables phase space (CV PS) is a function of reduced temperature $\tau = (T - T_c)/T_c$. At $n > n_\tau$ the current point (r_n, u_n) moves away from (r^*, u^*) . A characteristic feature here is the sign of the coefficient $d_2^{(n)}(k)$ at the quadratic term in ρ_k . At $T > T_c$, $n < n_\tau$, the average value of $d_2^{(n)}(k)$ over the interval $0 \leq k \leq B_{n_\tau}$ is negative; however at $n > n_\tau$ we have $d_2^{(n)}(k) > 0$ moving away from the fixed point (see Fig. 6).

A similar situation obtains at $T < T_c$. Here n_τ is determined as the number of the layer for which $d_2^{(n)}(B_{n_\tau}) = 0$. According to (22), the equation for n_τ is⁽⁸⁾

$$n_\tau = -\frac{\ln \tau}{\ln E_1} + \ln \left(\frac{\bar{u}^{1/2} R_{12}^0}{(E_1 - R_{11}) C_{11}} \right) (\ln E_1)^{-1} \tag{24}$$

where

$$\tilde{C}_{11} = \frac{(1 + \bar{r} + R^0 \bar{u}^{-1/2})(R_{11} - E_2)}{E_1 - E_2}; \quad R^0 = \frac{R_{12}^0}{R_{11} - E_2}$$

As was shown in refs. 7 and 8, n_τ characterizes the correlation-length critical exponent ν :

$$B - B_{n_\tau} = B - B s^{-n_\tau} = B(1 - |\tau|^\nu)$$

The parts of the trajectory corresponding to $n < n_\tau$ and $n > n_\tau$ are related to different regimes of transformation of the coefficients $a_2^{(n)}$ and $a_4^{(n)}$ describing the transformation of the measure density in (17) during subsequent integration. Namely, at $n < n_\tau$ we have

$$z^{(n)} = \frac{[d_2^{(n)}(0)]^2}{a_4^{(n)}} = \frac{r_n^2}{u_n} \leq 1$$

and at $n > n_\tau$, $z^{(n)} \rightarrow \infty$, $n \rightarrow \infty$.

At $T \rightarrow T_c$, where T_c is defined by (23), we have $z^{(n)} \rightarrow z^* = (r^*)^2/u^* = \text{const}$ and, therefore, as follows from (24),

$$n_\tau \rightarrow \infty$$

In this way, the trajectory infinitely approaches the fixed point.

At $n < n_\tau$, the measure density in the configurational integral describes the statistics of the system of correlated effective blocks and is essentially non-Gaussian. We call the corresponding interval (B_{n_τ}, B) the critical regime interval (CR). For $n > n_\tau$, the coefficient $d_2^{(n)}(k)$ is positive, and the distribution by ρ_k is close to Gaussian. The interval $(0, B_{n_\tau})$ is called the limiting Gaussian regime interval (LGR). In the case $T < T_c$, after deviation of the trajectory from the point (r^*, u^*) one has $d_2^{(n)}(k) < 0$ for $n > n_\tau$. Interval $(0, B_{n_\tau})$ at $T < T_c$ is called the inverse Gaussian regime interval

(IGR). For the Ising model the condition $d_2^{(n)}(k) < 0$ indicates the possibility for nonzero average momentum in the corresponding system of effective spin blocks.

It will be shown further that in the considered problem such a condition at $\eta = \eta_c$ leads to a situation in which the coexistence of two values of the particle density is possible in the system.

Performing in (17) the subsequent integrations over the layers of CV PS, we obtain each time a factor Q_n before the integral. Q_n is a partition function of the n th CV PS layer. By summing up the logarithms of Q_n , we obtain the free energy of the system.

We consider the contribution connected with the integral over ρ_0 as a separate term.

A new point in this problem as compared to the case of the Ising model is the dependence of T_c and all coefficients on the density and chemical potential. The latter is equivalent to the insertion in the Ising model of a constant external field.

4. EQUATION OF STATE AT $T > T_c$

Let us examine first the case $T > T_c$; the value of T_c is determined below. As was noted in the previous section, we distinguish in the CV space three fluctuational regions, which give different contributions to the partition function. The last at $T > T_c$ can be written in form

$$\begin{aligned} \bar{\Xi} = & \Xi_0 \Xi_G Z(\bar{\mathfrak{M}}_2, \bar{\mathfrak{M}}_4) \\ & \times \exp \left\{ -N \left[\frac{\mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|} + \frac{\mathfrak{M}_2(0) \mathfrak{M}_3^2(0)}{2\mathfrak{M}_4^2(0)} + \frac{\mathfrak{M}_3^4(0)}{8 |\mathfrak{M}_4(0)|^3} \right] \right\} \\ & \times \exp \left\{ \mu^* \bar{\mathfrak{M}}_1 - \frac{1}{2} |\alpha(0)| \bar{\mathfrak{M}}_1^2 - \beta(F_{\text{CR}} + F_{\text{LGR}}) + E_0 \right\} \quad (25) \end{aligned}$$

where F_{CR} is the free energy of the critical regime and corresponds to $B_{n_c} < k \leq B$; F_{LGR} is the free energy of the limiting Gaussian regime, $0 < k \leq B_{n_c}$; and E_0 is a contribution connected with ρ_0 , which we separate because this variable is a macroscopic one.

Let us return to formula (13). Integration over all ρ_k in the critical regime interval, $B_{n_c} < |\mathbf{k}| \leq B$, can be performed by the same method as in the Ising model case, and therefore for F_{CR} we will use a result from ref. 8,

$$\begin{aligned} F_{\text{CR}} = & -N_B k_B T \left\{ -n_\tau s^{-3n_\tau} + (1 - s^{-3n_\tau}) \left[1.043 - 0.828(r^* + q)(u^*)^{-1/2} \right. \right. \\ & \left. \left. - \frac{1}{4} \ln u^* \right] - 0.828 \frac{C_1}{(u^*)^{1/2}} \left(1 - \frac{E_1}{s^3} \right)^{n_\tau} \left(1 - \frac{E_1}{s^3} \right)^{-1} + \ln s \right\} \quad (26) \end{aligned}$$

The remaining integral over $\rho_{\mathbf{k}}$, $0 < |\mathbf{k}| \leq B_{n_\tau}$, is of the form

$$\int \exp \left\{ \mu^* \rho_0 - \frac{1}{2} \sum_{\mathbf{k}, |\mathbf{k}| \leq B_{n'_\tau}} d_2^{(n'_\tau)}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{a_4^{(n'_\tau)}}{4! N_{n'_\tau}} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ |\mathbf{k}_i| \leq B_{n'_\tau}}} \rho_{\mathbf{k}_1} \cdots \rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4} \right\} (d\rho)^{N_{n'_\tau}} \quad (27)$$

where $n'_\tau = n_\tau + 1$.

The density measure in (27) has a nonanalytic dependence on temperature. This nonanalyticity is a result of the integration in the interval $B_{n_\tau} \leq k \leq B$.

Because $d_2^{(n'_\tau)}(0) = 0$, the interval $0 < k \leq B_{n_\tau}$ will be considered separately. Here

$$d_2^{(n'_\tau)}(k) > 0$$

and the integrals over $\rho_{\mathbf{k}}$, $|\mathbf{k}| \neq 0$, in (27) can be calculated using the Gaussian density measure:

$$\exp \left\{ -\frac{1}{2} \sum_{\substack{\mathbf{k} \\ 0 < |\mathbf{k}| \leq B_{n'_\tau}}} [d_2^{(n'_\tau)}(k) + A] \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right\}$$

where

$$A = \frac{a_4^{n'_\tau}}{4N_{(n'_\tau)}} \sum_{\substack{\mathbf{k} \\ 0 < |\mathbf{k}| \leq B_{n'_\tau}}} \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle$$

is defined in a self-consistent way:

$$\frac{\partial \ln \Xi_L}{\partial A} = -\frac{1}{2} \sum_{\substack{\mathbf{k} \\ 0 < |\mathbf{k}| \leq B_{n'_\tau}}} \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle \quad (28)$$

Let us represent A in the form

$$A = \frac{1}{4} |\alpha(0)| s^{-2n_\tau} \mathcal{R}$$

Then from (28) we obtain the following self-consistency equation:

$$\mathcal{R} = \frac{3}{4} \bar{u}_{n'_\tau} [1 - (\mathcal{R})^{1/2} \arctg(\mathcal{R})^{-1/2}]$$

In (27) we integrate over all ρ_k except ρ_0 and find the corresponding contribution to the free energy:

$$F_{\text{LGR}} = N_B k_B T s_{-3n'_t} \left\{ \ln |\alpha(0)| + A' - n'_t \ln s - \frac{1}{3} + \mathcal{R} + \mathcal{R}^{3/2} \operatorname{arctg}(\mathcal{R})^{-1/2} - \frac{1}{2} \ln \pi \right\} \quad (29)$$

Here $A' = A s^{2n'_t}$.

For the remaining integral over ρ_0 one has

$$\begin{aligned} \exp(E_0) &= \int \exp \left\{ \mu^* \rho_0 - A \rho_0^2 - \frac{a_4^{(n'_t)}}{4! N_{n'_t}} \rho_0^4 \right\} d\rho_0 \\ &\approx \left(\frac{\pi}{A} \right)^{1/2} \exp \left(\frac{\mu^{*2}}{4A} \right) \left(1 - \frac{a_4^{(n'_t)}}{4! N_{n'_t}} \langle \rho_0^4 \rangle + \dots \right) \end{aligned} \quad (30)$$

This result can also be obtained in another way. Let us determine the point of the absolute maximum of the expression in the exponent of the integral (30). This point satisfies the condition

$$\mu^* - 2A\rho_0 - \frac{a_4^{(n'_t)}}{4! N_{n'_t}} \rho_0^3 = 0 \quad (31)$$

The solution of this equation is an important characteristic of the system.

Here $A > 0$ and $a_4^{(n'_t)} > 0$. Hence, the discriminant of Eq. (31)

$$\begin{aligned} Q &= (V/3)^3 + (W/2)^2 \\ v &= 12AN_{n'_t}/a_4^{(n'_t)}; \quad w = -6\mu^*N_{n'_t}/a_4^{(n'_t)} \end{aligned}$$

is always positive. Equation (31) has one real and two imaginary roots. The real one is

$$\rho_0^{(1)} = (-W/2 + Q^{1/2})^{1/3} + (-W/2 - Q^{1/2})^{1/3} \quad (32)$$

At the surface $\mu^* = 0$ ($W = 0$) the root (32) is equal to zero. In the neighborhood of the surface $\mu^* = w = 0$ it is close to the value

$$\rho_0^{(1)} \approx \frac{\mu^*}{2A} \quad (33)$$

For E_0 we obtain

$$E_0 = E_0(\rho_0^{(1)}) = \mu^* \rho_0^{(1)} - A(\rho_0^{(1)})^2 - \frac{a_4^{(n'_t)}}{4! N_{n'_t}} (\rho_0^{(1)})^4 \approx \frac{\mu^{*2}}{4A} \quad (34)$$

and again find the result (30).

Therefore we obtain an explicit expression for the grand partition function at $T > T_c$ [see (25), (26), (29), (34)].

Let us now calculate the chemical potential and, after substitution of the result into (25), obtain the equation of state. We proceed from the equation

$$\frac{\partial \ln \Xi}{\partial \mu} = \langle N \rangle = N \tag{35}$$

From (25) we obtain

$$N^{1/2}(\tilde{\mathfrak{M}}_1 + \rho_0^{(1)}) = N \tag{36}$$

or

$$\rho_0^{(1)} = \Delta \tag{37}$$

where

$$\Delta = N^{1/2} - \tilde{\mathfrak{M}}_1 = N^{1/2} \frac{\mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|} \left(\mathfrak{M}_2(0) + \frac{\mathfrak{M}_3^2(0)}{3 |\mathfrak{M}_4(0)|} \right) \tag{38}$$

Δ is an important quantity in the region of the critical behavior of the system. In the present approach it depends only on density, because we use a system of hard spheres as a reference system, and neglect all modes $\rho_{\mathbf{k}}$, $|\mathbf{k}| > B$. After substitution of the root $\rho = \rho_0^{(1)}$ into (33), we obtain

$$\mu^* \approx 2A\Delta \tag{39}$$

Because $Q > 0$, the chemical potential μ^* is a continuous function of Δ in the whole region $T > T_c$.

For the equation of state at $T > T_c$ we obtain

$$\begin{aligned} \frac{P - P_0}{k_B T} = & \ln \Xi_G + \ln Z(\tilde{\mathfrak{M}}_2, \tilde{\mathfrak{M}}_4) - N \frac{\mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|} \left[1 + \frac{\mathfrak{M}_2(0) \mathfrak{M}_3(0)}{2 |\mathfrak{M}_4(0)|} \right. \\ & \left. + \frac{\mathfrak{M}_3^3(0)}{8 \mathfrak{M}_4^2(0)} \right] - \frac{1}{2} N |\alpha(0)| - \beta(F_{CR} + F_{LGR}) + N^{1/2} [|\alpha(0)| + 2\Delta] \Delta \\ & - \mathfrak{P} \Delta^2 - \mathfrak{R} \Delta^4 \end{aligned} \tag{40}$$

where

$$\mathfrak{P} = \frac{1}{2} (|\alpha(0)| + 2A); \quad \mathfrak{R} = \frac{a_4^{(n_c)}}{4! N_{n_c}}$$

P_0 is the pressure of the RS defined by Eq. (2).

The terms F_{CR} and F_{LGR} determine the critical exponents and will be considered below. The isotherms of pressure calculated with (40) are plotted in Fig. 5.

5. THE CRITICAL POINT

Let us return to the equation (23) for the critical temperature. The coefficients a_2 , a_4 on the right-hand side are certain functions of density. However, as was proved by numerical calculations, the right-hand side of (23) in a wide range of concentrations is weakly dependent on density, and determines a surface almost parallel to the (μ, η) plane in (μ, η, T) space (see Fig. 3). To find the critical point coordinates, one needs two more equations. The first one is the equation (23) for the critical temperature. The second equation is determined by the condition $\mu^* = 0$. Indeed, with $\mu^* = 0$ the problem is reduced to the case of the Ising model in zero field and describes the second-order phase transition. Therefore, the conditions $\mu^* = 0$ and $C_1 = 0$ from (22) determine the critical point coordinates. The condition $\mu^* = 0$ leads to the relation

$$\mu^* \equiv N^{1/2}h - \bar{a}_1 = 0 \quad (41)$$

or

$$\beta(\mu - \mu_0) + \frac{1}{2N} \sum_{\mathbf{k}} \alpha(k) = \frac{\mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|} + |\alpha(0)| (1 - \Delta N^{-1/2}) \quad (42)$$

To find the critical density, one needs to calculate the chemical potential. This was done in the previous section, where for μ^* we obtained

$$\mu^* \approx 2A\Delta$$

It follows that at the critical point the following condition holds from the above relation and previous considerations

$$\Delta = 0 \quad (43)$$

The intersection of curves determined by (23) and (43) determines the critical point coordinates (see Fig. 3).

As follows from (38), the condition $\Delta = 0$ coincides with the condition $\mathfrak{M}_3(0) = 0$. As the expressions for the cumulants $\mathfrak{M}_n(0)$ are known, and we have neglected their renormalization due to integration over the short-wave fluctuations $\rho_{\mathbf{k}}$ ($|\mathbf{k}| > B$), the left-hand side of (38) depends only on density, and for the critical density the calculation yields

$$\eta_c = 0.130443$$

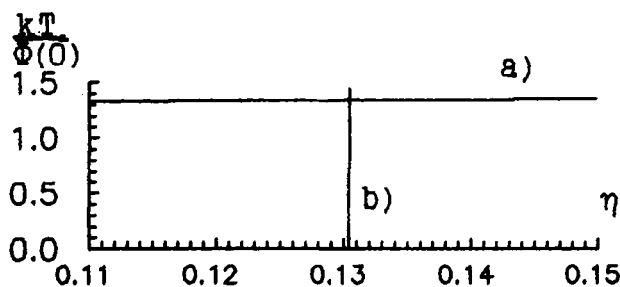


Fig. 3. Determination of coordinates of the critical point. Curves (a) and (b) correspond to Eqs. (23) and (43), respectively.

Note that the same value for the critical density was obtained in ref. 31 with the help of a revised van der Waals equation for hard spheres.

A comparison of the hard-sphere diameter calculated from the expression

$$\eta_{CP} = \frac{\pi}{6} \rho_{CP} \sigma_{CP}^3$$

where the experimental value of density at the critical point (at $\eta_{CP} = 0.13044$) was substituted instead of ρ_{CP} , with the effective diameter of a molecule σ_{sf} determined from the structure factor, namely, using the position of its first peak, was performed in ref. 32. The author points out that for the examined molecular liquids the relation

$$\sigma_{CP} \approx \sigma_{sf}$$

holds.

So we have a value of the critical density that is true for all fluids for which the structure and intersection at small distances can be described by means of hard spheres.

Next, let us calculate the critical temperature of the system, employing the expression (23).

Taking for Ar the same choice of the potential that used in calculating the renormalization of cumulants by formula (6) of Section 1, we find from (23) for the critical temperature

$$k_B T_c / \epsilon \approx 1.31$$

Summarizing, let us note that the definition of the critical point naturally emerges here from physical considerations. In particular, the expression (23) for the critical temperature reflects the presence of a

renormalization-group type symmetry at the critical point for a system of effective blocks, which coincides in essence with the definition of critical temperature in Wilson's theory.

At the (T_c, η_c) point the chemical potential μ^* is equal to zero, and all terms of odd powers in $\rho_{\mathbf{k}}$ in the exponent of the integrand in Ξ_L are absent. They do not arise in the process of layer-by-layer integration as well. Therefore, at the critical point we have a phase transition of the second order.

If one takes into account the contribution of the short-wave density fluctuations $\rho_{\mathbf{k}}$, $|\mathbf{k}| > B$, the set of equations (23), (43) becomes more complicated, and the coordinates of the critical point will change, but we do not suppose that this change will be significant.

6. THE FREE ENERGY AND EQUATION OF STATE AT $T < T_c$

In the present paper we consider a narrow interval of temperatures very close to T_c . In the same way as in the $T > T_c$ case, we start from an integration over variables $\rho_{\mathbf{k}}$ belonging to the layer of PS with $B_{n_\tau} < |\mathbf{k}| \leq B$, where B_{n_τ} defines the boundary of the critical regime region. The same recursion relations for $a_2^{(n)}$, $a_4^{(n)}$ as in the $T > T_c$ case are valid.

As $T \neq T_c$, the current point of the trajectory (r_n, u_n) will be close to the fixed point (r^*, u^*) in the course of the finite number of layer-by-layer integrations. The curve $d_2^{(n)}(k)$ shifts during the process of integration, but its upper end $d_2^{(n)}(B_n)$ at the right boundary of the interval $[0, B_n]$, $B_n = Bs^{-n}$, moves downward faster than the lower one $d_2^{(n)}(0)$ at the left boundary moves upward (see Fig. 6). That is why after a certain number of steps of integration $n = n(\tau) \equiv n_\tau$ we have

$$\begin{cases} d_2^{(n_\tau)}(B_{n_\tau}) = 0 \\ d_2^{(n_\tau)}(k) < 0, \quad 0 \leq k \leq B_{n_\tau} \end{cases}$$

This is the definition of the point n_τ .

We call the interval $(B_{n_\tau}, B]$ the critical regime interval at $T < T_c$.

Using (22), we obtain for n_τ

$$n_\tau = -\frac{\ln |\tau|}{\ln E_1} + \frac{\ln \{ [|r^* + |\alpha(0)||] / \tilde{C}_1 \}}{\ln E_1} \quad (44)$$

Integration over $\rho_{\mathbf{k}}$, $B_{n_\tau} < |\mathbf{k}| \leq B$, yields the contribution $\exp(-\beta F_{\text{CR}})$ to the thermodynamic potential. As in the case of the Ising model, the integration over $\rho_{\mathbf{k}}$, $0 \leq |\mathbf{k}| \leq B_{n_\tau}$, is performed with the Gaussian density measure, with the prior shift

$$\rho_{\mathbf{k}} = \tilde{\rho}_{\mathbf{k}} + (N_B)^{1/2} \delta_{\mathbf{k}} \sigma$$

by σ ensuring the convergence of Gaussian integrals with respect to $\rho_{\mathbf{k}}$. The result of the integration is written below as $\exp(-\beta F_{\text{IGR}})$. Therefore, after integration over all $\rho_{\mathbf{k}}$ except ρ_0 we have for \mathcal{E}_L

$$\mathcal{E}_L(\eta, \mu, T) = Z(\bar{\mathfrak{M}}_2, \bar{\mathfrak{M}}_4) \exp[-\beta(F_{\text{CR}} + F_{\text{IGR}})] \int_{-\infty}^{\infty} \exp[E(\rho_0)] d\rho \quad (45)$$

It is suitable to use in the calculations the expressions for F_{CR} and F_{IGR} from ref. 7:

$$F_{\text{CR}} + F_{\text{IGR}} = N_B k_B T [(1 - \mathcal{A}^{3\nu} |\tau|^{3\nu}) \tilde{\varphi}_1 + (|\tau| - \mathcal{A}^{3\nu-1} |\tau|^{3\nu}) \tilde{\varphi}_2 + \mathcal{A}^{3\nu} |\tau|^{3\nu} (\tilde{\varphi}_3 + \tilde{\varphi}_4)] \quad (46)$$

Here \mathcal{A} , $\tilde{\varphi}_1$, $\tilde{\varphi}_2$, $\tilde{\varphi}_3$, φ_4 are known functions⁽⁷⁾ which are weakly dependent on density in the vicinity of the critical point.

The main contribution to the partition function at $T < T_c$ is connected with the last integral over the macroscopic variable $\rho_0 = \rho'_0 N^{1/2}$. Having integrated over all $\rho_{\mathbf{k}}$, $|\mathbf{k}| \neq 0$, for the exponent in (45) we obtain⁽⁷⁾

$$E(\rho_0) \equiv E(\rho'_0 N^{1/2}) = N(\mu^* N^{-1/2} \rho_0 + \mathcal{B} \rho_0^2 - \mathcal{G} \rho_0^4) \quad (47)$$

(we omit the prime on ρ_0), where

$$\begin{aligned} \mathcal{B} &= \mathcal{B}_0 |\tau|^{2\nu}; & \mathcal{B}_0 &= \frac{1}{2} |r_{n_r}| \left[1 - \frac{1}{4} \frac{u_{n_r}}{|r_{n_r}|^2} \mathcal{L}_1(X) \right] \left(\frac{\tilde{C}_1}{|r^* + |\alpha(0)||} \right)^{2\nu} \\ r_{n_r} &= r^* + C_1 E_1^{n_r} - C_2 R E_2^{n_r}; & u_{n_r} &= u^* + C_1 R' E_1^{n_r} + C_2 E_2^{n_r} \\ \mathcal{L}_1(X) &= 3 \frac{X - \text{arctg } x}{x^2}; & x &= B \left(\frac{\tilde{q}}{2 |r_{n_r}| s^{-2n_r}} \right)^{1/2}; & \tilde{q} &= 2 \frac{\pi^2}{B^2} |\alpha(0)| \\ \mathcal{G} &= \mathcal{G}_0 |\tau|^\nu; & \mathcal{G}_0 &= \left(\frac{\tilde{C}_1}{|r^* + |\alpha(0)||} \right)^\nu \frac{u_{n_r}}{4!}; & \nu &= \frac{\ln s}{\ln E_1} \end{aligned} \quad (48)$$

The function $-k_B T E(\rho_0)$ is an analog of the Landau free energy. An essential difference consists in that, first, we know the explicit expressions for μ^* , \mathcal{B} , \mathcal{G} , and, second, the dependence of \mathcal{B} and \mathcal{G} on τ is nonanalytic, namely, $\mathcal{B} \sim |\tau|^{2\nu}$, $\mathcal{G} \sim |\tau|^\nu$. At $\tau \rightarrow 0$ both \mathcal{B} and \mathcal{G} tend to zero, but \mathcal{B} does so faster, so that the integral over ρ_0 exists.

The integral

$$E_0 = \int \exp\{E(\rho_0)\} d\rho_0 \quad (49)$$

will be calculated by the steepest descent method. The equation for the extremum

$$\rho_0^3 + \mathcal{V} \rho_0 + \mathcal{W} = 0 \quad (50)$$

should be solved, where

$$\mathcal{V} = -\frac{\mathcal{B}}{2\mathcal{G}}, \quad \mathcal{W} = -\frac{\mu^*}{4\mathcal{G}N^{1/2}}$$

Then the point of the absolute maximum of $E(\rho_0)$ is to be found. The discriminant

$$Q = (-\mathcal{W}/2)^2 + (\mathcal{V}/3)^3 \quad (51)$$

may be positive, equal to zero, or negative. One has to examine all three cases.

Note that the nonanalytical dependence of \mathcal{B} and \mathcal{G} on temperature is a result of integration over the interval of the critical regime.

The surface $Q=0$ separates two thermodynamic regions in (μ, η, T) space: an external one, which is the region of single-phase states, where $Q>0$, and an inner region ($Q<0$), which is the phase transition region. The surface $Q=0$ represents the coexistence boundary.

Let us now write the equation for the chemical potential μ . Suppose that the point $\rho_0 = \rho_0^{(1)}$ is a point of the absolute maximum for $E(\rho_0)$. Then $E'(\rho_0 = \rho_0^{(1)}) = 0$ and $E''(\rho_0 = \rho_0^{(1)}) < 0$. Using the bridgewall method, we obtain

$$\Xi_L(\mu, \eta, T) = Z(\mathfrak{M}_2, \mathfrak{M}_4) \exp[-\beta(F_{\text{CR}} + F_{\text{IGR}}) + E(\rho_0^{(1)})] \left(\frac{2\pi}{|E''(\rho_0^{(1)})|} \right)^{1/2}$$

Because N is a large number, from $\partial \ln \Xi / \partial \mu = N$ we again obtain

$$\rho_0^{(1)} = \Delta / N^{1/2} \quad (52)$$

The quantity $\rho_0^{(1)}$ is proportional to the order parameter. Therefore, we will call Δ the order parameter, too.

Our aim is to find the relation between μ^* and Δ . Let us first describe the coexistence boundary. When $Q=0$, Eq. (50) has three real roots. Two of them coincide

$$\rho_0^{(2)} = \rho_0^{(3)} = -\frac{1}{2} \left(\frac{\mu^*}{\mathcal{G}N^{1/2}} \right)^{1/3} \quad (53)$$

The only root providing the absolute maximum of $E(\rho_0)$ is

$$\rho_0^{(1)} = \left(\frac{\mu^*}{\mathcal{G}N^{1/2}} \right)^{1/3} \quad (54)$$

Indeed,

$$E''(\rho_0^{(1)}) = -6N\mathcal{B} < 0$$

$$E''(\rho_0^{(2)}) = E''(\rho_0^{(3)}) = 0$$

$$E'''(\rho_0^{(2)}) = 4N(6\mathcal{B}\mathcal{G})^{1/2}$$

From (52) and (54), we obtain for $Q = 0$ (at the coexistence boundary)

$$\mu^* = \mathcal{G}\Delta^3 \quad (55)$$

Along the curve determined by the condition

$$Q = (-\mathcal{W}/2)^2 + (\mathcal{V}/3)^3 = 0$$

the following relation is valid:

$$\mu^* = \pm m |\tau|^{(5/2)\nu} \quad (56)$$

Here

$$m = \frac{4}{3(6)^{1/2}} \left(\frac{\mathcal{B}_0^3}{\mathcal{G}_0} \right)^{1/2}$$

Let us consider the case $Q > 0$. Equation (50) has one real root

$$\rho_0^{(1)} = (-\mathcal{W}/2 + Q^{1/2})^{1/3} + (-\mathcal{W}/2 - Q^{1/2})^{1/3} \quad (57)$$

and two complex roots.

A positive sign of the discriminant is provided by the condition $(-\mathcal{W}/2)^2 > -(\mathcal{V}/3)^3$. Then we can write for Q

$$Q^{1/2} = |\mathcal{W}/2| (1 + b/2 + \dots)$$

where $b = (\mathcal{V}/3)^3/(\mathcal{W}/2)^2$; $|b| < 1$.

The only real root $\rho_0^{(1)}$, (57), is equal to

$$\rho_0^{(1)} \approx \left(\frac{\mu^*}{4\mathcal{G}N^{1/2}} \right)^{1/3} \left\{ 1 + \left(\frac{|b|}{4} \right)^{1/3} - \frac{|b|}{12} + \dots \right\}$$

Together with Eq. (52) this yields an isotherm for the chemical potential μ^* in the $Q > 0$ region:

$$\left(\frac{\mu^*}{4\mathcal{G}N^{1/2}}\right)^{1/3} \left\{ 1 + \left(\frac{|b|}{4}\right)^{1/3} - \frac{|b|}{12} + \dots \right\} = \Delta \quad (58)$$

The signs of μ^* and Δ coincide.

Equation (58) transforms into (55) at $|b| \rightarrow 1$ (which corresponds to $Q \rightarrow 0$).

Let us now consider the internal region $Q < 0$. In this case Eq. (50) has three real roots $\rho_0^{(1)}$, $\rho_0^{(2)}$, $\rho_0^{(3)}$:

$$\begin{aligned} \rho_0^{(1)} &= 2 \left(\frac{|\mathcal{V}'|}{3}\right)^{1/2} \cos \frac{\varphi}{3} \\ \rho_0^{(2)} &= 2 \left(\frac{|\mathcal{V}'|}{3}\right)^{1/2} \cos \frac{\varphi + 2\pi}{3} \\ \rho_0^{(3)} &= 2 \left(\frac{|\mathcal{V}'|}{3}\right)^{1/2} \cos \frac{\varphi + 4\pi}{3} \end{aligned} \quad (59)$$

where $\varphi = \arccos t$, $t = \mu^* / [8\mathcal{G}(-\mathcal{V}'/3)^{3/2}]$.

Near the coexistence boundary ($Q=0$) the value $|\cos t|$ is close to unity. Setting $\cos t = -1 + \delta$ for $\mu^* < 0$ and $\cos t = 1 - \delta$ for $\mu^* > 0$, one can show that for negative μ^* it is necessary to take the root $\rho_0^{(2)}$ and for positive μ^* the root $\rho_0^{(1)}$.⁽¹⁹⁾

Only these roots should be taken into account, as they provide absolute maxima of $E(\rho_0)$. The other ones should be dropped.

Let us now evaluate the parameter Δ ,

$$\Delta = -N^{1/2} \frac{\mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|} \left[\mathfrak{M}_2(0) + \frac{\mathfrak{M}_3^2(0)}{3 |\mathfrak{M}_4(0)|} \right]$$

One can write near the critical point

$$\Delta = \Delta_c + \left. \frac{\partial \Delta}{\partial \eta} \right|_{\eta = \eta_c} (\eta - \eta_c) = \Gamma(\eta - \eta_c) \quad (60)$$

The value $\eta = \eta_c$ corresponds to $\Delta = \Delta_c = 0$ and $\mathfrak{M}_3(0) = 0$. The dependence of $\mathfrak{M}_3(0)$ on density is given in Table II. $\mathfrak{M}_3(0)$ is a decreasing function of η . Then

$$\Gamma = - \left. \frac{\partial \mathfrak{M}_3(0)}{\partial \eta} \right|_{\mathfrak{M}_3(0)=0} \left| \frac{\mathfrak{M}_2(0)}{\mathfrak{M}_4(0)} \right|_{\mathfrak{M}_3(0)=0} > 0$$

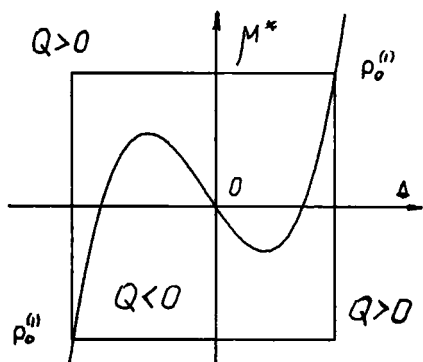


Fig. 4. Schematic dependence of the chemical potential μ^* on Δ .

Thus, the isotherm of μ^* can be expressed as a function of $\eta - \eta_c$ or Δ . The dependence of μ^* on Δ is plotted schematically in Fig. 4.

For the equation of state we have (see Fig. 5)

$$\frac{P - P_0}{k_B T} = \ln \Xi_G^{(1)} + \ln Z(\tilde{\mathfrak{M}}_2, \tilde{\mathfrak{M}}_4) - \beta(F_{CR} + F_{IGR}) + \ln E_0 \quad (61)$$

Here $\exp(E_0) = \int \exp[E(\rho_0)] d\rho_0$ is calculated by the bridgewall method, taking into account the above analysis of the absolute extremum of the function $E(\rho_0)$.

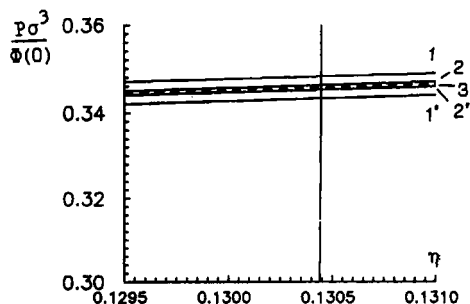


Fig. 5. Equation of state in the vicinity of the critical point. (1, 2) $\tau = 0.005, 0.001$; (1', 2') $\tau = 0.005, -0.001$; (3) $\tau = 0$ (the critical isotherm). The vertical line marks the critical density $\eta = 0.13044$.

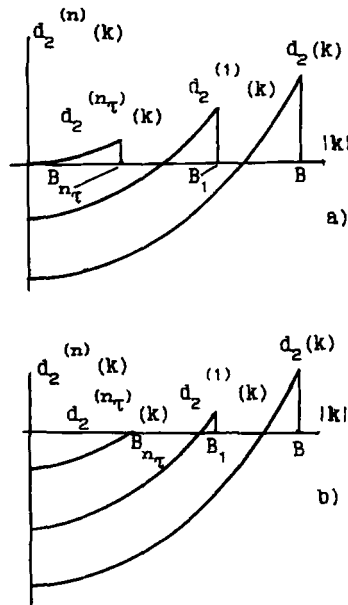


Fig. 6. Evolution of the coefficient $d_2^{(n)}(k)$ in the course of layer-by-layer integration. (a) $T > T_c$. (b) $T < T_c$. [See Eq. (18); Section 6 (p. 430); and Appendix C.]

In the present paper we have considered the foundations of the liquid-gas phase transition theory. For a more complete description of processes in the vicinity of the critical point it is necessary to perform calculations of thermodynamic functions. These will be performed elsewhere.

In addition, all calculations in this paper were in the quartic basic density measure. That is why at the critical point, where $\Delta = 0$, the critical exponents are the same as for the Ising model. The law of rectilinear diameters $\rho_c = \frac{1}{2}(\rho_L + \rho_G)$ will also hold. To describe the effects connected with asymmetry of the boundary, one should compute the partition function using the sixfold density measure. However, the general approach to the computation will be the same as that in the present paper.

APPENDIX A. CONTRIBUTION OF THE SHORT-WAVE FLUCTUATIONS IN THE GRAND PARTITION FUNCTION

Consider the integration over the “short-wave” variables $\omega_{\mathbf{k}}, \rho_{\mathbf{k}}, |\mathbf{k}| > B$. We have to calculate

$$\begin{aligned} \Xi_G = & \int \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}, |\mathbf{k}| > B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{(2\pi)^2}{2!} \sum_{\mathbf{k}, |\mathbf{k}| > B} \mathfrak{M}_2(k) \omega_{\mathbf{k}} \omega_{-\mathbf{k}} \right\} \\ & \times \left(1 + D_2 + \frac{1}{2} D_2^2 + \dots \right) \exp \left(i2\pi \sum_{\mathbf{k}, |\mathbf{k}| > B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right) \prod_{\mathbf{k}, |\mathbf{k}| > B} d\omega_{\mathbf{k}} d\rho_{\mathbf{k}} \end{aligned} \quad (\text{A1})$$

where

$$D_2 = \sum_{m \geq 3} \frac{(-i2\pi)^m}{m!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_m} \mathfrak{M}_m(k_1, \dots, k_m) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_m} \quad (\text{A2})$$

The transformation

$$\begin{aligned} D_2 \rightarrow \hat{D}_2 = & \sum_{m \geq 3} \sum_{m_1=1}^m \frac{(-1)^{m_1} (-i2\pi)^{m-m_1}}{m!} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_{m_1}, |\mathbf{k}_i| > B \\ \mathbf{k}_{m_1+1}, \dots, \mathbf{k}_m, |\mathbf{k}_i| \leq B}} \mathfrak{M}_m(k_1, \dots, k_m) \\ & \times \frac{\partial^m}{\partial \rho_{\mathbf{k}_1} \dots \partial \rho_{\mathbf{k}_m}} \omega_{\mathbf{k}_{m_1+1}} \dots \omega_{\mathbf{k}_m} \end{aligned} \quad (\text{A3})$$

and integration over $\omega_{\mathbf{k}}, \rho_{\mathbf{k}}$ in (A1) gives for Ξ_G (with the accuracy up to the fourth virial coefficient)

$$\begin{aligned} \Xi_G \simeq & \prod_{\mathbf{k}, |\mathbf{k}| > B} [1 + \alpha(k) \mathfrak{M}_2(k)]^{-1/2} \exp \left\{ \frac{N(N-1)}{2V} \int [e^{g(r_{12})} - 1 - g(r_{12}) \right. \\ & \left. - \frac{g^2(r_{12})}{2}] F_2(r_{12}) d\mathbf{r}_{12} + \frac{N(N-1)(N-2)}{3! V^2} \int \{ [e^{g(r_{12})} - 1 - g(r_{12})] \right. \\ & \times [e^{g(r_{23})} - 1 - g(r_{23})] [e^{g(r_{31})} - 1 - g(r_{31})] + 3g(r_{12}) \\ & \times [e^{g(r_{23})} - 1 - g(r_{23})] [e^{g(r_{31})} - 1 - g(r_{31})] \} F_3(r_{12}, r_{13}) d\mathbf{r}_{12} d\mathbf{r}_{13} \\ & \left. + \frac{N(N-1)(N-2)(N-3)}{4! V^3} \int \{ 2g(r_{12}) g(r_{34}) [e^{g(r_{41})} - 1 - g(r_{41})] \right. \\ & \times [e^{g(r_{23})} - 1 - g(r_{23})] + 4g(r_{12}) [e^{g(r_{23})} - 1 - g(r_{23})] \\ & \times [e^{g(r_{34})} - 1 - g(r_{34})] [e^{g(r_{41})} - 1 - g(r_{41})] + [e^{g(r_{12})} - 1 - g(r_{12})] \\ & \times [e^{g(r_{23})} - 1 - g(r_{23})] [e^{g(r_{34})} - 1 - g(r_{34})] [e^{g(r_{41})} - 1 - g(r_{41})] \} \\ & \left. \times F_4(r_{12}, r_{13}, r_{14}) \times d\mathbf{r}_{12} d\mathbf{r}_{13} d\mathbf{r}_{14} + \dots \right\} \end{aligned} \quad (\text{A4})$$

Hence $g(r)$ is the screened potential

$$g(r_{ij}) \equiv g(|\mathbf{r}_i - \mathbf{r}_j|) = \frac{1}{V} \sum_{\mathbf{k}, |\mathbf{k}| > B} g(k) e^{-i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)};$$

$$g(k) = \frac{\alpha(k)}{1 + \alpha(k) \mathfrak{M}_2(k)}$$

In the whole interval $|\mathbf{k}| > B$ the following condition holds:

$$1 + \alpha(k) \mathfrak{M}_2(k) > 0$$

The cumulant $\mathfrak{M}_2(k)$ is the RS structure factor:

$$\mathfrak{M}_2(k) = 1 + \frac{N}{V} \int [F_2(r) - 1] e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r}$$

$F_2(r)$ is the RS pair distribution function.

Expression (A4) can be calculated with the appropriate approximation for the distribution functions (for example, with the known Kirkwood approximation).

APPENDIX B. THE REFERENCE SYSTEM STRUCTURE FUNCTIONS WITH REDUCED DEPENDENCE ON WAVE VECTOR

In this appendix we calculate the coefficients $\mathfrak{M}_n(k_1, \dots, k_n)$ of the grand partition function (4).

The cumulants $\mathfrak{M}_n(k_1, \dots, k_n)$ have been expressed in terms of the RS correlation functions; for example,

$$\begin{aligned} \mathfrak{M}_2(k_1, k_2) &= \delta(\mathbf{k}_1 + \mathbf{k}_2) [1 + \mu_2(k_1)] \\ \mathfrak{M}_3(k_1, k_2, k_3) &= \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) [1 + 3\mu_2(k_1) + \mu_3(k_2, k_3)] \\ \mathfrak{M}_4(k_1, k_2, k_3, k_4) &= \delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4) [1 + 4\mu_2(k_1) + 3\mu_2(k_1 + k_2) \\ &\quad + 6\mu_3(k_2, k_3 + k_4) + \mu_4(k_2, k_3, k_4)] \end{aligned}$$

where $\mu_n(k_2, \dots, k_n)$ is the Fourier transform of the n -particle RS correlation function:

$$\begin{aligned} \mu_2(k) &= \frac{N}{V} \int [F_2(r) - 1] e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r} \\ \mu_3(k_2, k_3) &= \frac{N^2}{V^2} \int e^{-i\mathbf{k}_2\mathbf{r}_{12} - i\mathbf{k}_3\mathbf{r}_{13}} \\ &\quad \times [F_3(r_{12}, r_{13}) - 3F_2(r_{12}) + 2] d\mathbf{r}_{12} d\mathbf{r}_{13} \end{aligned}$$

$$\begin{aligned} \mu_4(k_2, k_3, k_4) &= \frac{N^3}{V^3} \int e^{-ik_2 r_{12} - ik_3 r_{13} - ik_4 r_{14}} \\ &\times [F_4(r_{12}, r_{13}, r_{14}) - 4F_3(r_{12}, r_{13}) \\ &- 3F_2(r_{12}) F_2(r_{13}) + 12F_2(r_{12}) - 6] dr_{12} dr_{13} dr_{14} \end{aligned}$$

where

$$\frac{F_s(r_{12}, \dots, r_{1s})}{V^{s-1}} = \frac{\int \exp(-\beta\psi) dr_{1,s+1} \dots dr_{1N}}{\int \exp(-\beta\psi) (d\mathbf{r})^N}$$

is the s -particle RS distribution function.

To calculate the cumulants $\mathfrak{M}_n(k_1, \dots, k_n)$ in the case when some arguments are equal to zero, we use a sequence of equations for the correlation functions:

$$\frac{\partial}{\partial z} \left[\frac{u(1, 2, \dots, s)}{z^s} \right] = \int \frac{u(1, 2, \dots, s+1)}{z^{s+1}} d(s+1) \tag{B1}$$

where z is the fugacity; $u(1, 2, \dots, s) = \rho^s \mu_s(1, 2, \dots, s)$, with $\rho = N/V$; and $\mu_s(1, 2, \dots, s)$ are correlation functions, connected to their long-wave values $\mu_s(0)$ by the relation

$$\mu_s(0) = \rho^{s-1} \int \mu(1, 2, \dots, s) d2 d3 \dots ds$$

Together with (B1), it is necessary to use the thermodynamic relations

$$\left(\frac{\partial \ln \rho}{\partial \ln z} \right)_T = k_B T \left(\frac{\partial \rho}{\partial p} \right)_T = \rho k_B T \chi_T = \mathfrak{M}_2(0)$$

Applying Fourier transformation to both sides of (B1), we obtain a sequence of equations for the Fourier transforms of correlation functions:

$$\begin{aligned} \frac{\partial}{\partial z} \frac{\rho^s}{z^s} \mu_s(k_1, k_2, \dots, k_{s-1}, k_s = -k_1 - k_2 - \dots - k_{s-1}) \\ = \frac{\rho^{s+1}}{z^{s+1}} \mu_{s+1}(k_1, k_2, \dots, k_{s-1}, -k_1 - k_2 - \dots - k_{s-1}, 0) \end{aligned} \tag{B2}$$

Setting $s=1$ in (B2), we obtain the well-known relation for the structure factor and compressibility:

$$\mathfrak{M}_2(0) = 1 + \rho \mu_2(0) = k_B T \left(\frac{\partial \rho}{\partial p} \right)_T$$

In the general case, we obtain for the Fourier transform of the n -particle correlation function from (B2)

$$\begin{aligned} & \mu_n(k_1, k_2, \dots, k_{n-2}, -k_1 - k_2 - \dots - k_{n-2}, 0) \\ &= \mu_{n-1}(k_1, k_2, \dots, k_{n-2}, -k_1 - k_2 - \dots - k_{n-2}) [\mathfrak{M}_2(0) - n + 1] \\ & \quad + \eta \mathfrak{M}_2(0) \frac{\partial}{\partial \eta} \mu_{n-1}(k_1, k_2, \dots, k_{n-2}, -k_1 - k_2 - \dots - k_{n-2}) \end{aligned}$$

In this way, we obtain for $\mathfrak{M}_3(k, -k, 0)$ and $\mathfrak{M}_4(k, -k, 0, 0)$

$$\begin{aligned} N^{-1/2} \mathfrak{M}_3(k, -k, 0) &= \mathfrak{M}_2(0) \left[\mathfrak{M}_2(k, -k) + \eta \frac{\partial \mathfrak{M}_2(k, -k)}{\partial \eta} \right] \\ N \mathfrak{M}_4(k, -k, 0, 0) &= \mathfrak{M}_2(0) \left[\mathfrak{M}_2(k, -k) \mathfrak{M}_2(0) + 3\eta \mathfrak{M}_2(0) \frac{\partial \mathfrak{M}_2(k, -k)}{\partial \eta} \right. \\ & \quad + \eta \mathfrak{M}_2(-k, k) \frac{\partial \mathfrak{M}_2(0)}{\partial \eta} + \eta^2 \frac{\partial \mathfrak{M}_2(0)}{\partial \eta} \frac{\partial \mathfrak{M}_2(k, -k)}{\partial \eta} \\ & \quad \left. + \eta^2 \mathfrak{M}_2(0) \frac{\partial^2 \mathfrak{M}_2(k, -k)}{\partial^2 \eta} \right] \end{aligned}$$

An analogous result for $\mathfrak{M}_3(k, -k, 0)$ was obtained in ref. 33. Therefore, to calculate $\mathfrak{M}_3(k, -k, 0)$ and $\mathfrak{M}_4(k, -k, 0, 0)$ one needs to have only the hard-sphere structure factor $\mathfrak{M}_2(k)$.

The cumulants $\mathfrak{M}_n(k_1, \dots, k_n)$ for $k_i \rightarrow 0$ also can be expressed in terms of the fluctuations of the number of particles:

$$\begin{aligned} \mathfrak{M}_2(0) &= \langle (N - \langle N \rangle)^2 \rangle / \langle N \rangle; \quad \mathfrak{M}_3(0, 0, 0) = \langle (N - \langle N \rangle)^3 \rangle / \langle N \rangle \\ \mathfrak{M}_4(0, 0, 0, 0) &= [\langle (N - \langle N \rangle)^4 \rangle - 3 \langle (N - \langle N \rangle)^2 \rangle^2] / \langle N \rangle \end{aligned}$$

One can find the last values from the thermodynamics, using the relation between the long-range limit of the structure factor and the compressibility.

APPENDIX C. AN EXPLICIT FORM OF THE RECURSION RELATIONS (18)

Analysis of the relations (18) allows us to describe the critical behavior of the system, that is, to calculate critical exponents and obtain explicit

expressions for thermodynamic functions. It is suitable to write down the recursion relations (18) in the explicit form

$$\begin{cases} d_2^{(n+1)}(k) = \frac{N}{V} \beta [\Phi(B_n, B_{n+1}) - \Phi(k)] + \left(\frac{3}{P_4^{(n)}}\right)^{1/2} U(\zeta^{(n)}) \\ a_4^{(n+1)} = \frac{9}{P_4^{(n)}} \left[U^2(\zeta^{(n)}) + \frac{2}{3} \zeta^{(n)} U(\zeta^{(n)}) - \frac{2}{3} \right] \end{cases} \quad (C1)$$

where

$$\zeta^{(n)} = \left(\frac{3}{P_4^{(n)}}\right)^{1/2} P_2^{(n)}, \quad U(\zeta^{(n)}) = \frac{U(1, \zeta^{(n)})}{U(0, \zeta^{(n)})}$$

with

$$U(l, \zeta^{(n)}) = \frac{2}{\Gamma(l+1/2)} e^{-\zeta^{(n)2/4}} \int_0^\infty x^{2l} e^{-\zeta^{(n)}x^2 - x^4/2} dx$$

the parabolic cylinder function, and

$$P_2^{(n)} = \left(\frac{3}{a_4^{(n)}}\right)^{1/2} U(z^{(n)});$$

$$P_4^{(n)} = \frac{9}{a_4^{(n)}} \left[U^2(z^{(n)}) + \frac{2}{3} z^{(n)} U(z^{(n)}) - \frac{2}{3} \right]$$

$$z^{(n)} = \left(\frac{3}{a_4^{(n)}}\right)^{1/2} d_2^{(n)}(B_n B_{n+1});$$

$$U(z^{(n)}) = \frac{U(1, z^{(n)})}{U(0, z^{(n)})}$$

$$d_2^{(n)}(B_n, B_{n+1}) = a_2^{(n)} + \frac{N}{V} \beta \Phi(B_n, B_{n+1})$$

$$U(l, z^{(n)}) = \frac{2}{\Gamma(l+1/2)} e^{-z^{(n)2/4}} \int_0^\infty x^{2l} e^{-z^{(n)}x^2 - x^4/2} dx$$

The feature of Eqs. (C1) is that one performs the transition from $d_2^{(n)}$, $a_4^{(n)}$ to $d_2^{(n+1)}$, $a_4^{(n+1)}$ in two steps, using values $P_2^{(n)}$, $P_4^{(n)}$ which characterize the density of the distribution by the effective field $\phi_{\mathbf{k}}$.

APPENDIX D. ELEMENTS OF THE LINEARIZED RENORMALIZATION GROUP TRANSFORMATION MATRIX

The main difference as compared with refs. 15, 16, and 29 consists in that we have explicit expressions for the matrix elements,⁽⁷⁾

$$\begin{aligned}
 R_{11} &= \left(\frac{\partial r_{n+1}}{\partial r_n} \right)^* = s^2 \left[N(z^{(*)}) + (z^{(*)})^{1/2} \frac{\partial N(z^{*})}{\partial (z^{*})^{1/2}} \right] \\
 R_{12} &= \left(\frac{\partial r_{n+1}}{\partial r_n} \right)^* = - \frac{s^2 z^*}{(3u^*)^{1/2}} \frac{\partial N(z^*)}{\partial (z^*)^{1/2}} = \frac{R_{12}^0}{(u^*)^{1/2}} \\
 R_{21} &= \left(\frac{\partial u_{n+1}}{\partial r_n} \right)^* = s \frac{(3u^*)^{1/2}}{2} \frac{\partial N(z^*)}{\partial (z^*)^{1/2}} = (u^*)^{1/2} R_{21}^0 \\
 R_{22} &= \left(\frac{\partial u_{n+1}}{\partial u_n} \right)^* = s \left[E(z^{(*)}) - \left(\frac{z^*}{2} \right)^{1/2} \frac{\partial E(z^*)}{\partial (z^*)^{1/2}} \right]
 \end{aligned}$$

where r^* , u^* are the fixed-point coordinates:

$$\begin{aligned}
 r^* &= -|\alpha_c(0)| \bar{r}; & \bar{r} &= \frac{s^2 [N(z^*) - 1]}{s^2 N(z^*) - 1} \bar{q} \\
 u^* &= |\alpha_c(0)| \bar{u}; & \bar{u} &= \frac{3(1-s^{-2})^2}{4z^* [N(z^*) - s^{-2}]} \bar{q}^2 \\
 \alpha_c(0) &= \frac{N}{V k_B T_c} \bar{\Phi}(0); & N(z^*) &= \left(\frac{\zeta^*}{z^*} \right)^{1/2} \frac{U(\zeta^*)}{U(z^*)} \\
 E(z^*) &= \frac{U^2(\zeta^*) + \frac{2}{3} \zeta^* U(\zeta^*) - \frac{2}{3}}{U^2(z^*) + \frac{2}{3} z^* U(z^*) - \frac{2}{3}}
 \end{aligned}$$

ζ^* and z^* are the fixed-point values of the parameters $\zeta^{(n)}$ and $z^{(n)}$.

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