

A DESCRIPTION OF THE CRITICAL POINT OF SIMPLE FLUIDS IN THE COLLECTIVE VARIABLES METHOD

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The investigations concerning the behaviour of the fluid near the critical point still remain actual. In the previous papers, by using the collective variables (CV) method, we have obtained the grand partition function in the form, suitable for investigation in the vicinity of the critical point.

The aim of the present paper is to describe the system both above and below T_c , to analyse a behaviour of the chemical potential μ below T_c and to obtain a horizontal plateau on the plot for μ corresponding to the liquid-gas phase transition.

1. Introduction

A homogeneous classical single-component system of N pairwise interacting particles in volume V at temperature T is considered in the vicinity of the critical point. Interaction between every two particles we will suppose to consist of two parts. The first one, denoted by Ψ describes impenetrability of the particles:

$$\Psi(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma \end{cases} ; \quad (1.1)$$

σ is a diameter of the particles. The second part, described by the function $\Phi(r)$ belonging to L_2 class, characterises attraction. It is negative at long distances r and possesses a potential well. For the Fourier transform one has: $\min \tilde{\Phi}(k) = \tilde{\Phi}(0)$ and $\tilde{\Phi}(0) < 0$. The shape of $\Phi(r)$ for small r in the region $r < \sigma$ is not completely defined. For the full potential $V(r) = \Phi(r) + \Psi(r)$ at $r < \sigma$ we have $V(r) = \infty$, because of the $\Psi(r)$'s behaviour. This uncertainty of $\Phi(r)$ at $r < \sigma$ one may employ to improve quantitatively the final results in further consideration of the theory.

For the starting form of the grand partition function in the CV method the following expression was obtained [1]:

$$\Xi = \Xi_0 \Xi_G \Xi_L , \quad (1.2)$$

where

$$\Xi = \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \int \exp[-\beta \Psi_N] d\Gamma_N$$

is the grand partition function of the reference system (RS), which we suppose to be known. Ξ_G is an additional part with respect to RS. It is connected with the contribution from the short wave density fluctuations, distributed according to Gaussian law. Values of the wave vectors $|\vec{k}|$ of these fluctuations are greater than certain quantity B , which obeys the following condition [7]:

$$M_2^{-1}(k) > \frac{N}{V} \beta \tilde{\Phi}(k) \quad (1.3)$$

for all $|\vec{k}| > B$, where $M_2(k)$ is the RS's binary structure factor:

$$M_2(k) \equiv M_2(k_1, k_2) = \delta_{\vec{k}_1 + \vec{k}_2} (1 - \delta_{\vec{k}_1}) \langle N \rangle + (\langle N^2 \rangle - \langle N \rangle^2) \delta_{\vec{k}_1} \delta_{\vec{k}_2} + \frac{1}{V} \langle N(N-1) \mu_2^N(k_1) \rangle \delta_{\vec{k}_1 + \vec{k}_2} \quad (1.4)$$

Here brackets $\langle \dots \rangle$ mean the grand canonical average over RS, $\delta_{\vec{k}}$ is the Kronecker symbol, $\mu_2^N(k)$ denotes the Fourier transform of the Bogolubov's pair correlation function of N particles:

$$\mu_2^N(k) = \int (F_2^N(r) - 1) e^{-i\vec{k}\vec{r}} d\vec{r}; \quad \frac{1}{V} \int F_2^N(r) d\vec{r} = 1 \quad (1.5)$$

As it was shown in [7]

$$\Xi_G = \int \exp \left\{ -\frac{1}{2} \sum_{|\vec{k}| > B} \alpha(k) \rho_{\vec{k}} \rho_{-\vec{k}} - \frac{(2\pi)^2}{2} \sum_{|\vec{k}| > B} M_2(k) \omega_{\vec{k}} \omega_{-\vec{k}} \right\} (1.6)$$

$$(1 + D_2 + \frac{1}{2} D_2^2 + \dots) \exp \left\{ i2\pi \sum_{|\vec{k}| > B} \omega_{\vec{k}} \rho_{\vec{k}} \right\} \prod_{|\vec{k}| > B} d\omega_{\vec{k}} d\rho_{\vec{k}},$$

where

$$D_2 = \sum_{m \geq 3} \frac{(-i2\pi)^m}{m!} \sum_{\vec{k}_1, \dots, \vec{k}_m, |\vec{k}_i| > B} M_m(k_1, \dots, k_m) \omega_{\vec{k}_1} \dots \omega_{\vec{k}_m}, \quad (1.7)$$

$$\alpha(k) = \frac{N}{V} \beta \tilde{\Phi}(k), \quad N \equiv \langle N \rangle.$$

The transformation

$$D_2 \rightarrow \hat{D}_2 = \sum_{m \geq 3} \frac{(-1)^m}{m!} \sum_{\vec{k}_1, \dots, \vec{k}_m, |\vec{k}_i| > B} M_m(k_1, \dots, k_m) \frac{\partial^m}{\partial \rho_{\vec{k}_1} \dots \partial \rho_{\vec{k}_m}} \quad (1.8)$$

leads to the following results

$$\Xi_G \approx \prod_{\vec{k}, |\vec{k}| > B} [1 + \tilde{M}_2(k) \alpha(k)]^{-\frac{1}{2}} - \theta \left\{ \frac{N(N-1)}{2V} \int (e^{g(r_{12})} - 1 - g(r_{12})) \right. \quad (1.9)$$

$$\left. - \frac{g^2(r_{12})}{2} \right) F_2(r_{12}) d\vec{r}_{12} + \frac{N(N-1)(N-2)}{3!V^2} \int [(e^{g(r_{12})} - 1 - g(r_{12})) \times$$

$$(e^{g(r_{23})} - 1 - g(r_{23}))(e^{g(r_{13})} - 1 - g(r_{13})) + 3g(r_{12})(e^{g(r_{23})} - 1 - g(r_{23})) \times (e^{g(r_{13})} - 1 - g(r_{13}))]F_3(r_{12}, r_{13})d\vec{r}_{12}d\vec{r}_{13} + \dots \} ,$$

where

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

$$\theta = \beta^{-1} = k_B T .$$

$\tilde{M}_2(k)$ is renormalized binary structure factor:

$$\tilde{M}_2(k) = M_2(k) + \frac{1}{4} \sum_{\vec{k}_1, |\vec{k}_1| > B} M_4(k, -k, k_1, -k_1) \langle \omega_{\vec{k}_1} \omega_{-\vec{k}_1} \rangle ,$$

$\langle \omega_{\vec{k}} \omega_{-\vec{k}} \rangle = g(k) = \frac{\alpha(k)}{1 + \alpha(k)M_2(k)}$ is the Fourier transform of the screened potential.

Thus, for $g(k)$ we get the equation

$$g(k) = \frac{\alpha(k)}{1 + \alpha(k)[M_2(k) + \frac{1}{4} \sum_{\vec{k}_1, |\vec{k}_1| > B} M_4(k, -k, k_1, -k_1)g(k_1)]} . \quad (1.10)$$

Within the first approximation one has

$$g(k) \approx \frac{g^0(k)}{1 + \frac{1}{4}g^0(k) \sum_{\vec{k}_1, |\vec{k}_1| > B} M_4(k, -k, k_1, -k_1)g^0(k_1)} , \quad (1.11)$$

where

$$g^0(k) = \frac{\alpha(k)}{1 + \alpha(k)M_2(k)} \quad (1.12)$$

is the zero approximation of $g(k)$.

One of the most important part of the preliminary investigation of the partition function's starting form is the examination of the cumulants $M_n(k_1, \dots, k_n)$ behaviour at small values of k [8]. In fig.1a the curves of $M_2(k)$ are plotted for some values of fraction density $\eta = \frac{\pi}{6} \frac{N}{V} \sigma^3$. The distance from the origin to the point B where $\tilde{\Phi}(k)$ curve crosses the k -axis is roughly inverse to the value of r^* which is an effective range of the attractive potential $\Phi(r)$ (see Fig.1b). As one can see from Fig.1, the interval $k \leq B$ corresponds to relatively weak dependence of $M_2(k)$ on k , where for $M_2(k)$, can be used, for example, the parabolic approximation or even a constant: $M_2(k) \approx M_2(0)$ for all $k \leq B$.

The same is true for higher cumulants M_3, M_4 . It allows us to replace functions $M_n(k_1, \dots, k_n)$ for all $k_i \leq B, i = 1, 2, \dots, n$, by the constant values as a zeroth approximation.

Thus, we can start with the explicit expression for Ξ_L in (1.2) which is the main part of the partition in the present investigation:

$$\Xi_L = \int (1 + D_5 + \frac{1}{2}D_5^2 + \dots)W_5(\rho, \omega)(d\omega)^{N_B}(d\rho)^{N_B} . \quad (1.13)$$

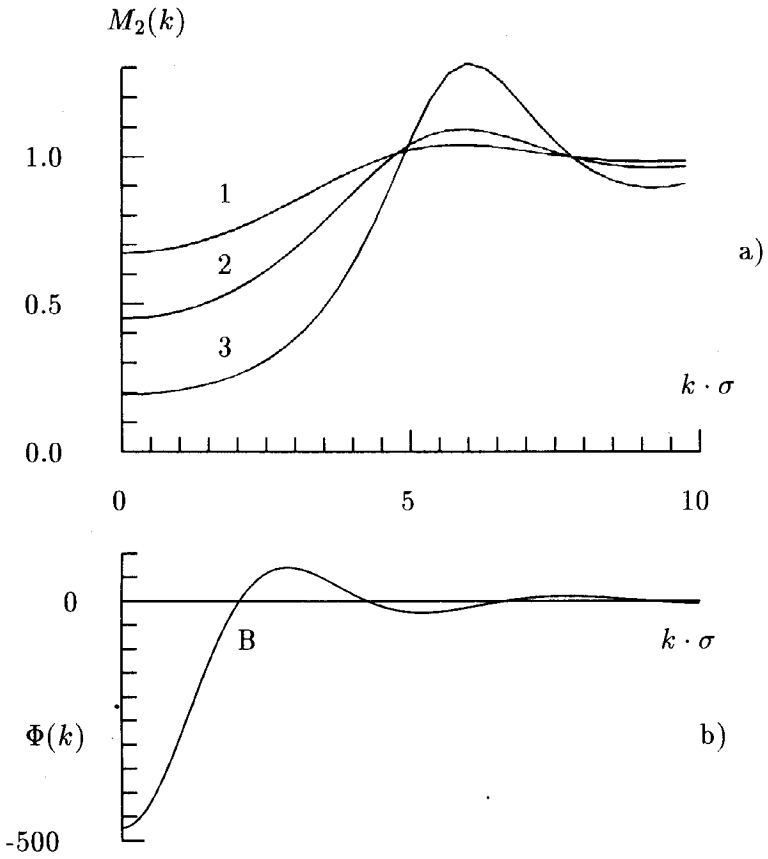


Figure 1. Plots of second cumulant $M_2(k)$ (a) and Fourier transform of the attraction part of the interaction potential $\tilde{\Phi}(k)$ (b). The point B separates the long- and short-wave density fluctuations. Curves 1, 2 and 3 corresponds to the values $\eta = 0.05, \eta = 0.1$ and $\eta = 0.2$, respectively.

Here

$$D_5 = \sum_{m>5} \frac{(-i2\pi)^m}{m!} \sum_{\vec{k}_1, \dots, \vec{k}_m, |\vec{k}_i| \leq B} \tilde{M}_m(0) \omega_{\vec{k}_1} \dots \omega_{\vec{k}_m} \quad (1.14)$$

W_5 is the basic density measure in vicinity of the critical point. As it was shown in [1]:

$$W_5(\rho, \omega) = \exp\left\{h\rho_0 - \frac{1}{2} \sum_{\vec{k}, |\vec{k}| \leq B} \alpha(k) \rho_{\vec{k}} \rho_{-\vec{k}} + i2\pi \sum_{\vec{k}, |\vec{k}| \leq B} \omega_{\vec{k}} \rho_{\vec{k}} + \sum_{n=1}^5 \frac{(-i2\pi)^n}{n!} \sum_{\vec{k}_1, \dots, \vec{k}_n, |\vec{k}_i| \leq B} M_n(0) \delta_{\vec{k}_1 + \dots + \vec{k}_n} \omega_{\vec{k}_1} \dots \omega_{\vec{k}_n}\right\} \quad (1.15)$$

$$h = \beta(\mu - \mu_0) + \frac{1}{2} \sum_{\vec{k}} \alpha(k) \quad .$$

Following the above arguments, we have neglected in (1.14) and (1.15) the dependence of $\tilde{M}_n(k_1, \dots, k_n)$ on k_i , as well as the renormalization terms of M_n due to integration over $d\omega_{\vec{k}}, d\rho_{\vec{k}}$ for $|\vec{k}| > B$, reducing $\tilde{M}_n(k_1, \dots, k_n)$ for $k_i \leq B$ to $M_n(0)$.

It is essential, that all odd cumulants M_1, M_3, M_5 in (1.15) possess factor i . The convergency of the integrals in (1.13) is guaranteed by the containing M_4 term. Thus, to describe the main events in the vicinity of the critical point it is sufficient to restrict the basic measure density by the fourfold one, putting $M_5 = 0$:

$$W_5(\rho, \omega) \rightarrow W_4(\rho, \omega) = \exp\left\{h\rho_0 - \frac{1}{2} \sum_{\vec{k}, |\vec{k}| \leq B} \alpha(k) \rho_{\vec{k}} \rho_{-\vec{k}} + i2\pi \sum_{\vec{k}, |\vec{k}| \leq B} \omega_{\vec{k}} \rho_{\vec{k}} + \sum_{n=1}^4 \frac{(-i2\pi)^n}{n!} \sum_{\vec{k}_1, \dots, \vec{k}_n, |\vec{k}_i| \leq B} M_n(0) \omega_{\vec{k}_1} \dots \omega_{\vec{k}_n} \delta_{\vec{k}_1 + \dots + \vec{k}_n}\right\} .$$

Then the shift

$$\omega_0 = \omega'_0 - \frac{i}{2\pi} \frac{M_3(0)}{M_4(0)} , \tag{1.16}$$

$$\rho_0 = \rho'_0 + \sqrt{N} \left(1 + \frac{M_2(0)M_3(0)}{|M_4(0)|} + \frac{M_3^3(0)}{3M_4^2(0)} \right) = \rho'_0 + \tilde{M}_1 ,$$

where

$$\tilde{M}_1 = \sqrt{N} \left(1 + \frac{M_2(0)M_3(0)}{|M_4(0)|} + \frac{M_3^3(0)}{3M_4^2(0)} \right)$$

transforms W_4 to the form containing terms \tilde{M}_1, \tilde{M}_2 and M_4 only. This expression for W_4 corresponds to the Ising model in the external field.

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

$$N_B = N \frac{(B\sigma)^3}{6\pi^2\eta} . \tag{1.17}$$

Therefore, one may consider the quantity B as the size of the first Brillain zone of this block lattice.

Setting for the Kronecker symbol

$$\delta_{\vec{k}} = \frac{1}{N_B} \sum_{\vec{r}_l} e^{i\vec{k}\vec{r}_l}$$

we obtain for W_4 :

$$W_4(\rho, \omega) = \exp\left\{\mu^* \rho_0 - \frac{1}{2} \sum_{\vec{k}, |\vec{k}| \leq B} \alpha(k) \rho_{\vec{k}} \rho_{-\vec{k}} + i2\pi \sum_{\vec{k}, |\vec{k}| \leq B} \omega_{\vec{k}} \rho_{\vec{k}} - \dots\right\}$$

$$\begin{aligned}
& i2\pi \tilde{M}_1 \sqrt{N} \omega_0 - \frac{(2\pi)^2}{2} \tilde{M}_2(0) \sum_{\vec{k}, |\vec{k}| \leq B} \omega_{\vec{k}} \omega_{-\vec{k}} \\
& \frac{(2\pi)^4}{4! N_B} |\bar{M}_4(0)| \sum_{\vec{k}_1, \dots, \vec{k}_4, |\vec{k}_i| \leq B} \delta_{\vec{k}_1 + \dots + \vec{k}_4} \omega_{\vec{k}_1} \dots \omega_{\vec{k}_4} \} \quad , \quad (1.18) \\
& \tilde{M}_2(0) = M_2(0) + \frac{M_3^2(0)}{2M_4(0)} \quad , \quad \bar{M}_4(0) = N_B M_4(0) \quad , \\
& \mu^* = \sqrt{N} h - a_1 \quad , \quad a_1 = \sqrt{N} \frac{M_3(0)}{|M_4(0)|} + \alpha(0) \tilde{M}_1 \quad .
\end{aligned}$$

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

$$\begin{aligned}
\Xi &= \Xi_0 \Xi_G^{(1)} Z(\tilde{M}_2, \bar{M}_4) \int \exp\left\{ \mu^* \rho_0 - \frac{1}{2} \sum_{\vec{k}, |\vec{k}| \leq B} d_2(k) \rho_{\vec{k}} \rho_{-\vec{k}} - \right. \\
& \left. \frac{a_4}{4! N_B} \sum_{\vec{k}_1, \dots, \vec{k}_4, |\vec{k}_i| \leq B} \delta_{\vec{k}_1 + \dots + \vec{k}_4} \rho_{\vec{k}_1} \dots \rho_{\vec{k}_4} + \dots \right\} (d\rho)^{N_B} \quad . \quad (1.19)
\end{aligned}$$

Here

$$\begin{aligned}
d_2(k) &= a_2 + \alpha(k) \quad , \quad a_2 = \sqrt{12} |\bar{M}_4(0)|^{-1/2} K(\zeta) \quad , \\
a_4 &= 6 |\bar{M}_4(0)|^{-1} L(\zeta), \quad \zeta = \frac{3\tilde{M}_2^2(0)}{4|\bar{M}_4(0)|}, \quad K(\zeta) = \sqrt{\zeta} \left[\frac{K_{\frac{3}{4}}(\zeta)}{K_{\frac{1}{4}}(\zeta)} - 1 \right], \\
L(\zeta) &= 6K^2(\zeta) + 4\sqrt{\zeta}K(\zeta) - 1 \quad , \\
Z(\tilde{M}_2, \bar{M}_4) &= \frac{\sqrt{12}}{2\pi} \left(\frac{\zeta}{|\bar{M}_4(0)|} \right)^{1/4} e^{\zeta} K(\zeta) \quad ,
\end{aligned}$$

$K_{\frac{1}{4}}(\zeta), K_{\frac{3}{4}}(\zeta)$ are Bessel functions of the imaginary argument,

$$\begin{aligned}
\Xi_G^{(1)} &= \Xi_G \exp\left\{ -N \left[\frac{M_3(0)}{|M_4(0)|} + \frac{M_2(0)M_3^2(0)}{2M_4^2(0)} + \frac{M_3^4(0)}{8|M_4(0)|^3} \right] + \right. \\
& \left. \frac{1}{2} \alpha(0) \tilde{M}_1^2 + \mu^* \tilde{M}_1 \right\} \quad .
\end{aligned}$$

Finishing the introduction let us now touch the question of separation of the RS potential $\Psi(r)$ from the complete potential $V(r) = \Psi(r) + \Phi(r)$. In the present paper we start with the Morse potential

$$\Phi_M(r) = \epsilon \left[e^{-2\frac{r-r_0}{\alpha}} - 2e^{-\frac{r-r_0}{\alpha}} \right]$$

with parameters α, ϵ and r_0 [10].

Its negative branch will be described by CV. Instead of its positive branch we shall use an adequate hard spheres system and choose the diameter of spheres providing coincidence of the binary correlation functions of the hard spheres and that of the system with the positive branch only.

So, one can perform a calculation of the hard sphere diameter σ in a way similar to that developed by Weeks, Chandler and Anderson in Ref. [2].

Equation of state will include a part corresponding to the hard sphere system pressure, for which we adopt the Carnahan-Starling equation [3]:

$$\frac{P_0 V}{N k_B T} = z_0 = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (1.20)$$

where z_0 is the compressibility factor of the reference system, $\eta = \frac{\pi}{6} \frac{N}{V} \sigma^3$, σ is a function of density and temperature. But in this paper we neglect the dependence of σ on η and T , and put for σ the value corresponding to the critical point: $\sigma = \sigma(\eta_c, T_c)$.

Equation (1.20) we can utilize for calculation of the chemical potential of the reference system μ_0 as a function of a density η . Thus, in our further investigation μ_0 is supposed to be known.

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

$$\Phi(r) = \begin{cases} 0, & r \leq r^* \\ \Phi_M(r), & r > r^* \end{cases} \quad (1.21)$$

Its Fourier transform is of the form

$$\begin{aligned} \tilde{\Phi}(k) = \int \Phi(r) e^{-i\vec{k}\vec{r}} d\vec{r} = \epsilon \alpha^3 \frac{4\pi}{k} e^{\frac{r_0 - r^*}{\alpha}} \left\{ \frac{e^{\frac{r_0 - r^*}{\alpha}}}{4 + k^2 \alpha^2} \left[\left(\frac{2r^*}{\alpha} + \right. \right. \right. \\ \left. \left. \frac{4 - k^2 \alpha^2}{4 + k^2 \alpha^2} \right) \sin kr^* + \left(kr^* + \frac{4kr^*}{4 + k^2 \alpha^2} \right) \cos kr^* \right] - \frac{2}{1 + k^2 \alpha^2} \left[\left(\frac{r^*}{\alpha} + \right. \right. \\ \left. \left. \frac{1 - k^2 \alpha^2}{1 + k^2 \alpha^2} \right) \sin kr^* + \left(kr^* + \frac{2k\alpha}{1 + k^2 \alpha^2} \right) \cos kr^* \right] \right\}. \quad (1.22) \end{aligned}$$

$\tilde{\Phi}(k)$ is plotted in Fig.1b. Point B of its first crossing with k - axis separates short and long wave density fluctuations. The condition (1.3) is satisfied at $|\vec{k}| > B$ and one can use the Gaussian measure density in integrals included in (1.6).

Summarising this section, note that the grand partition function defined in (1.2), (1.13) and (1.18) is now reduced to the functional integrals, specified on certain block lattice. The coefficients of the functional are known [8,6].

2. Equation of state at $T > T_c$

Consider a part of the grand partition function connected with the integrals over $\{\rho_{\vec{k}}\}$ for $|\vec{k}| \leq B$. The way of calculation of such integrals was developed in [4] for the case 3 - d Ising model.

The essence of the method consists in the subsequent integration over the layers of CV space, starting from $\rho_{\vec{k}}$, corresponding to the short-wave fluctuations. The aim is to obtain the distribution function of ρ_0 only. An average value of ρ_0 is connected with the order parameter. Variations of the coefficients of functionals as a result of integration over $\rho_{\vec{k}}$ in the n subsequent layers in CV phase space are described by recursion formulae, which are derived in Ref.[4]. The main peculiarity is the sign of ρ_0^2 term: it is positive at $T > T_c$ and negative at $T < T_c$.

Let us first consider the case $T > T_c$. In the interval $[0, B]$ there exist three characteristic regions [4]. The first one corresponds to the strongly correlated fluctuations $\rho_{\vec{k}}$, their density measure is non-Gaussian one. The procedure based on the renormalization group symmetry is valid there. The size of denoted by $[B_m, B]$ region is equal to

$$B - B_m = B(1 - |\tau|^\nu) \quad , \quad (2.1)$$

where $\tau = (T - T_c)/T_c$, ν is the correlation length critical exponents.

This is the critical regime (CR) region [1].

The second region $0 < k \leq B_m$ is related to the fluctuations distributed according to the Gaussian density measure. The expression for the dispersion of the density measure follows from the results of integration performed in CR. The correspondent partial free energy denoted by F_{LGR} is the free energy of limiting Gaussian regime (LGR).

The third region consists of one point $k = 0$. Value ρ_0 is the macroscopic one and corresponds to the fluctuations of the particle density in "external field" denoted by μ^* . Because of a presence of μ^* the first order phase transition occurs. We denote a contribution into the free energy due to third region by $E(\rho_0)$. $E(\rho_0)$ is some analog of Landau free energy. The essential difference consists in explicit and nonanalytic dependence on temperature τ .

Integration in (1.19) is performed along the following scheme.

The division of collective variables phase space into layers is carried out using some parameter $s > 1$. The variables $\rho_{\vec{k}}$ belong to the first layer, if the subscripts \vec{k} correspond to interval $B_1 < |\vec{k}| \leq B$, $B_1 = B/s$. In the second layer $B_2 < |\vec{k}| \leq B_1$, $B_2 = B_1/s = B/s^2$, and so on. For the layer number n one has $B_n < |\vec{k}| \leq B_{n-1}$, $B_{n-1} = B/s^{n-1}$, $B_n = B/s^n$.

As a result of integration over first layer of $\rho_{\vec{k}}$ the number of the variables under the integral changes from N_B to N_B/s^3 , and them to N_B/s^{3n} , as a result of the stepwise integration over n layers.

The coefficients of the functional will change: instead of initial $d_2(k) = a_2 + \alpha(k)$, a_4 one subsequently obtains $d_2^{(1)}(k) = a_2 + \alpha(k)$, $a_4^{(1)}$; $d_2^{(2)}(k) = a_2^{(2)} + \alpha(k)$, $a_4^{(2)}$; and so one.

To factorize the integrals we replace in each layer the coefficient $d_2^{(n)}(k)$ by the average value

$$d_2^n(k) \Rightarrow \bar{d}_2^n = a_2^n + \bar{\alpha}(B_{n+1} B_n) = a_2^n - \beta \frac{N}{V} \bar{\Phi}(B_{n+1} B_n) \quad ,$$

where $\bar{\Phi}(B_{n+1} B_n)$ is an average value of the Fourier transform of the attractive potential on the interval $(B_{n+1} B_n)$. A way of the averaging is not essential.

The value of the coefficients are related by recurrent equations. Applying the fixed point method, one obtains the renormalization group type solutions. As the initial values $d_2(k)$, a_4 , are known, these solutions are functions of temperature and density.

After integration in every subsequent layer a factor Q_n , which is a partition function of n -th layer, will emerge before the integral in (1.19). The partial sum Q_n are expressed in terms of Bessel functions depending on argument $z^{(n)} = \frac{3}{4} \bar{d}_2^{(n)2} / a_4^{(n)}$. Summing logarithms of Q_n over all $n = 1, 2, \dots, m$, where m is a number of the last layer, belonging to the critical regime, one

obtains F_{CR} - a free energy of the critical regime. Integration over variables $\rho_{\vec{k}}, 0 < |\vec{k}| \leq B_m$ is performed in the Gaussian moments approximation. So, the corresponding partial sum and a free energy of limiting Gaussian regime can be calculated.

The complete expression for the partition function now reads

$$\Xi_L(T, \eta, \mu) = \Xi_0 \Xi_G^{(1)} Z(\tilde{M}_2, \tilde{M}_4) \exp[-\beta(F_{CR} + F_{LGR}) + E(\rho_0)] \quad (2.2)$$

The value F_{CR} and F_{LGR} are common for the system belonging to the Ising class of symmetry. This is just the case we have here, when W_4 is used for description of Ξ_L (see (1.18) and (1.19)). Consequently, one can use available formulae for F_{CR} and F_{LGR} from [4].

$$F_{CR}(T, \eta) = -N_B k_B T \{ -m'_\tau s^{-3m_\tau} \ln s + (1 + s^{-3m'_\tau}) [1.043 - 0.828 \frac{r^* + q}{\sqrt{u^*}} - \frac{1}{4} \ln u^*] - 0.828(1 - E_1/s^3)^{m'_\tau} / (1 - E_1 s^{-3}) \} \frac{C_1}{\sqrt{u^*}} \quad (2.3)$$

where $m'_\tau = m + 1$, m is a number of the last layer in CV space belonging to the critical regime region, $B_m = B/s^m$, $E_1 > 1$ is the greater of two eigenvalues of the recurrent equations matrix [4], and

$$C_1 = \tau \tilde{C}_1, \quad \tilde{C}_1 = |\alpha(0)| [1 - \bar{r} + R^0 \sqrt{\bar{u}}] w^{-1} + |\alpha(0)|^{-1} a_4 R^0 (w \sqrt{\bar{u}})^{-1}, \quad (2.4)$$

$r^* = |\alpha(0)| \bar{r}$, $u^* = \alpha^2(0) \bar{u}$ - the fixed point coordinates,

$$R = R^0 |\alpha(0)|^{-1} = \frac{R_{12}^0}{R_{11} - E_2} |\alpha(0)|^{-1} \quad ,$$

here

E_2 is the smaller of two eigenvalues and $R_{12} = |\alpha| R_{12}^0$, R_{11} - are matrix elements of the matrix in RG method;

$$w = \frac{E_1 - E_2}{R_{11} - E_2} \quad , \quad q = |\alpha(0)| \bar{q} \quad .$$

The quantities $E_1, E_2, \bar{q}, R_{12}^0, \bar{r}, \bar{u}, \nu, R^0, w, \tilde{C}_1, R_{11}$ are universal function of s . Their values for $s = s^* = 3.58$ are the following: $E_1 = 8.235, E_2 = 0.377, \bar{q} = 0.612, R_{12}^0 = 3.837, \bar{r} = 0.6125, \bar{u} = 0.889, \nu = 0.605, R^0 = 0.562, w = 1.086, \tilde{C}_1 = 0.818, R_{11} = 7.613$ For $s = s^*$ the value of the argument $z^{(n)} = \frac{3}{4} (d_2^{(n)} (B_n B_{n+1}))^2 / a_4^{(n)}$ at fixed point is zero.

As a criterion which determines the size of critical regime interval, we use the following speculations.

During the integration over layers of CV phase space the following relations take place

$$a_2 < a_2^{(1)} < a_2^{(2)} < \dots < a_2^{(n)} < \dots \quad .$$

Therefore, the coefficient $d_2^{(n)}(0) = a_2^{(n)} - |\alpha(0)|$ is an increasing function of n . It's initial value is negative $d_2(0) < 0$. So, a boundary of CR region is

$B_m = Bs^{-m}$, where m is a number of the last phase space layer, for which $d_2^{(m)}(0) < 0$. After integration over all variables of this layer one obtains

$$d_2^{(m+1)}(0) \equiv d_2^{(m')}(0) = 0, \quad d_2^{(m')}(k) > 0, \quad 0 < k \leq B_{m'}$$

So, for all integrals over $\rho_{\vec{k}}$, $0 < |\vec{k}| \leq B_{m'}$, we can use the Gaussian approximation.

Finally, the result for F_{LGR} is:

$$F_{LGR} = \frac{1}{2} k_B T N_{m'} \sum_{\vec{k}, 0 < |\vec{k}| \leq B_{m'}} \ln \left[\frac{d_2^{(m')}(k) + A}{\pi} \right] =$$

$$\frac{1}{2} N_B k_B T s^{-3m'} \left\{ -2m' \ln s + \ln(|\alpha(0)| + A) - \frac{2}{3} + 2v - \right.$$

$$\left. \ln \pi - 2v^{3/2} \arctan v^{-1/2} \right\},$$

$$A = \frac{a_4^{(m')}}{4N_{m'}} \sum_{\vec{k}, |\vec{k}| \leq B_{m'}} \langle \rho_{\vec{k}} \rho_{-\vec{k}} \rangle \simeq \frac{|\alpha(0)|}{4} s^{-2m'} v,$$

v is defined from the self-consistence equation [1]:

$$v = \frac{3}{4} \bar{u}_{m'} (1 - v \arctan v^{-1/2})$$

From these results we obtain not only certain contributions to the free energy, but also the values of the critical exponents.

The last integral over ρ_0 is a peculiar one, because of the presence of some "external field" in the form of the chemical potential. Here we have to perform some special investigation, because this integral contains peculiarities related with the critical point.

$$\exp[E(\rho_0)] = \int \exp \left\{ \mu^* \rho_0 - A \rho_0^2 - \frac{a_4^{(m')}}{4! N_{m'}} \rho_0^4 \right\} d\rho_0 \approx$$

$$\sqrt{\frac{\pi}{A}} \exp \left(\frac{\mu^{*2}}{4A} \right) \left\{ 1 - \frac{a_4^{(m')}}{4! N_{m'}} \langle \rho_0^4 \rangle + \dots \right\} \quad (2.5)$$

For $\mu^* = 0$ the problem is reduced to the case of Ising model in zero field and corresponds to the second order phase transition. When $\mu^* \neq 0$ it is suitable to find the absolute maximum point of the integrand in (2.5). This point obeys the condition

$$\mu^* - 2A\rho_0 - \frac{a_4^{(m')}}{3! N_{m'}} \rho_0^3 = 0 \quad (2.6)$$

Here $A > 0$ and $a_4^{(m')} > 0$. The discriminant

$$Q = \left(\frac{\vartheta}{3} \right)^3 + \left(\frac{\varpi}{2} \right)^2, \quad (2.7)$$

$$\vartheta = \frac{12AN_{m'_\tau}}{a_4^{(m'_\tau)}} \quad , \quad \varpi = -\frac{6N_{m'_\tau}\mu^*}{a_4^{(m'_\tau)}} \quad (2.8)$$

is always positive. Equation (2.6) has one real and two complex roots. The real one is

$$\rho_1 = \left(-\frac{\varpi}{2} + \sqrt{Q}\right)^{1/3} + \left(-\frac{\varpi}{2} - \sqrt{Q}\right)^{1/3} \quad . \quad (2.9)$$

On the $\mu^* = 0$ or $\varpi = 0$ surface the root equals zero. Near to the surface $\mu^* = \varpi = 0$ it is close to value (see (2.5)):

$$\rho_1 \approx \frac{\mu^*}{2A} \quad . \quad (2.10)$$

For $E(\rho_1)$ one finds:

$$E(\rho_1) = \mu^* \rho_1 - A\rho_1^2 - \frac{a_4^{(m'_\tau)}}{4!N_{m'_\tau}} \rho_1^4 \simeq \frac{\mu^{*2}}{4A} \quad . \quad (2.11)$$

Thus, we obtain an explicit expression for the grand partition function at temperature $T > T_c$

$$\Xi = \Xi_0 \Xi_G \exp\left\{-N\left[\frac{M_3(0)}{|M_4(0)|} + \frac{M_2(0)M_3^2(0)}{2M_4^2(0)} + \frac{M_3^4(0)}{8|M_4(0)|^3}\right] - \mu^* \tilde{M}_1 - \frac{1}{2} |\alpha(0)| \tilde{M}_1^2 - \beta(F_{CR} + F_{LGR}) + E(\rho_1)\right\} \quad (2.12)$$

Now let us calculate the chemical potential μ^* and after its substitution into (2.2) obtain the equation of state. We have:

$$\frac{\partial \ln \Xi}{\partial \mu} = \tilde{N} \equiv N \quad .$$

Taking into account (2.11) and (2.12), this leads to

$$\sqrt{N}(\tilde{M}_1 + \rho_1) = N \quad , \quad (2.13)$$

or

$$\rho_1 = \Delta \quad ,$$

$$\Delta = \sqrt{N} - \tilde{M}_1 = -\sqrt{N}\left[\frac{M_2(0)M_3(0)}{|M_4(0)|} + \frac{M_3^3(0)}{3M_4^2(0)}\right] \quad . \quad (2.14)$$

(for $M_n(0)$ see Table 1).

Here Δ depends only on density due to approximation which we have adopted at the very beginning of the consideration. Substituting in (2.14) expression (2.10) for ρ_1 , one obtains

$$\mu^* = 2A\Delta \quad , \quad h = \frac{1}{\sqrt{N}}(a_1 + 2A\Delta) \quad . \quad (2.15)$$

Table 1. The dependence on density of the cumulants $M_n(k_1, \dots, k_n)$ at zero values of arguments k_i .

η	$M_2(0)$	$M_3(0)$	$M_4(0)$	$M_5(0)$
0.05	0.673	0.275	-0.0781	-0.181×10^{-5}
0.1	0.456	0.0461	-0.0866	0.02038
0.15	0.309	-0.01597	-0.0283	0.0274
0.2	0.208	-0.0249	-0.0396	0.00964
0.25	0.141	-0.0198	0.00216	0.00181

Because of $Q > 0$, the chemical potential is a continuous function of Δ in the whole region $T > T_c$. For the equation of state we have:

$$\frac{P - P_0}{k_B T} = \ln \Xi_G - \beta(F_{CR} + F_{LGR}) - \frac{1}{2} N |\alpha(0)| + \wp \Delta^2 + \frac{\Re}{N} \Delta^4 + 2AN\Delta, \quad (2.16)$$

where

$$\wp = \frac{1}{2} [\alpha(0) - M_2^{-1}(0) - 2A], \quad \Re = \frac{9M_4(0)}{8M_2^4(0)} - \frac{N}{4!N_{m'_r}} a_4^{(m'_r)},$$

P_0 a pressure of the reference system, defined by (1.20). Here the total pressure P is monotoneous function of density.

3. The critical point

At the critical point the critical regime, according to its definition [4,7], takes place for all variables $\rho_{\vec{k}}$. Therefore, the critical temperature may be determined from the solution of the recurrent equations, which are the renormalization group type equations. Using the obtained in Ref.[4] we adduce the formula

$$T_c = \frac{N \tilde{\Phi}(0)}{V k_B} \frac{2[1 - \bar{r} + R_{12}^0 (R_{11} - E_2)^{-1} \sqrt{\bar{u}}]}{a_2 + [a_2^2 + \frac{4a_4 R_{12}^0}{(R_{11} - E_2) \sqrt{\bar{u}}} (1 - \bar{r} + \frac{R_{12}^0 \sqrt{\bar{u}}}{R_{11} - E_2})]^{1/2}}. \quad (3.1)$$

The involved coefficients a_2 and a_4 generally are some functions of density, thus, $T_c = T_c(\eta)$. Nevertheless, as it follows from the concrete calculations, this dependence is quite weak in a wide vicinity of the critical point, so the function $T_c(\eta)$ determines almost a plane, parallel to (μ, η) plane. To find the critical point coordinates, one needs two more equations. The second plane is determined by the condition $\mu^* = 0$. According to (1.18) we have:

$$\mu^* = \sqrt{N} h - a_1 = 0, \quad (3.2)$$

or

$$\beta(\mu - \mu_0) + \frac{1}{2} \sum_{\vec{k}} \alpha(k) = \frac{M_3(0)}{|M_4(0)|} + \alpha(0)(1 - \Delta). \quad (3.3)$$

The third equation follows from the results (2.10) and (2.14):

$$\mu^* = \rho_1 \quad ,$$

which means that

$$\Delta = 0 \quad . \quad (3.4)$$

In accordance with (1.19), (2.5), the second order phase transition takes place at $\tau = 0$ on the surface determined by (2.19). The intersection of (2.17), (2.19) and (2.20) surfaces determines the critical point coordinates. If one neglects the renormalization of cumulants connected with integrating over $\rho_{\vec{k}}, |\vec{k}| > B$, then the conditions (2.20) define a surface, parallel to (T, η) plane. We shall have the crossing of two curves (see Fig. 2). The point of intersection is the critical point of the system.

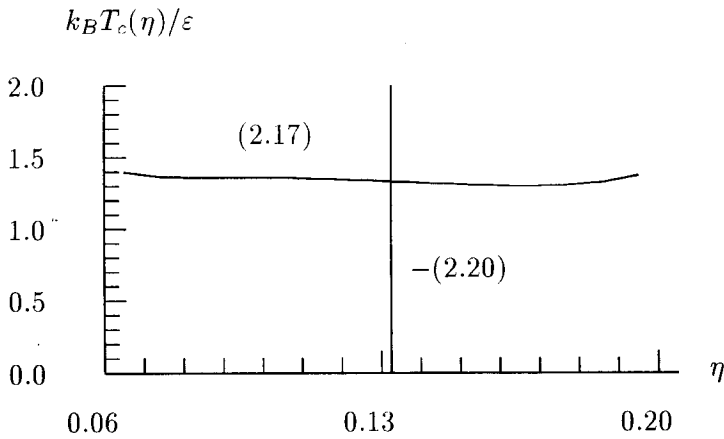


Figure 2. The critical point (T_c, η_c) is the point of intersection of curves (2.17) and (2.20).

4. Investigation of the system below the critical point

We regard a small interval of temperatures very close to T_c ($|\tau| \leq 0.01$).

As well as in $T > T_c$ case, one should start from the integration over $\rho_{\vec{k}}$ by the layers of CV phase space for $B_{\mu\tau} < |\vec{k}| \leq B$, where $B_{\mu\tau}$ is a boundary of the critical regime region. The same recurrent equations for the coefficients $d_2^{(n)}(0), a_4^{(n)}$ as in $T > T_c$ case are valid here[4]. A minimum of $d_2^{(n)}(k)$ curve is situated always at $k = 0$.

However, in $T > T_c$ case after integration over $\rho_{\vec{k}}$'s, $B_{\mu\tau} < |\vec{k}| \leq B$, the whole curve $d_2^{(\mu\tau)}(k)$ will be located below the k -axis. The boundary point $B_{\mu\tau}$ of the critical regime is defined by the following condition:

$$d_2^{(\mu\tau)}(B_{\mu\tau}) = 0 \quad , \quad d_2^{(\mu\tau)}(k) < 0 \quad , \quad (4.1)$$

for all $0 < |\vec{k}| \leq B_{\mu\tau}$; here $B_{\mu\tau} = Bs^{-\mu\tau}$ and

$$\mu_\tau = -\frac{\ln |\tau|}{\ln E_1} + \frac{\ln |r^* - \alpha(0)|}{\ln E_1} \tilde{C}_1^{-1}, \quad (4.2)$$

μ_τ is a number of the last layer of CV phase space, related with the critical regime.

This means, that in every cell of a block lattice with spacing $C_{\mu\tau} = \pi/B_{\mu\tau}$ a non zero value of the order parameter exists. During the process of the further integration over $\rho_{\vec{k}}$ for \vec{k} belonging to region $0 < |\vec{k}| \leq B_{\mu\tau}$ a shifted Gaussian measure density for fluctuations can be used. The calculations are performed applying the rules developed in [4,5]. Having integrated over all variables $\rho_{\vec{k}}$ excepting ρ_0 , one finds:

$$\Xi_L(\tau, \mu, \eta) = \exp\{-\beta(F_{CR} + F_{IGR})\} \int_{-\infty}^{\infty} \exp[E(\rho'_0)] \sqrt{N} d\rho'_0. \quad (4.3)$$

Here

$$-\beta F_{CR} = N_B[-\mu_\tau A^{3\nu} |\tau|^{3\nu} \ln s + (1 - A^{3\nu} |\tau|^{3\nu})\varphi_1 + |\tau| (1 - A^{3\nu-1} |\tau|^{3\nu-1})\varphi_2], \quad (4.4)$$

$$-\beta F_{IGR} = N_B A^{3\nu} |\tau|^{3\nu} (\varphi_3 + \mu_\tau \ln s), \quad (4.5)$$

$$\varphi_1 = 1.043 - 0.828 \frac{r^* + q}{\sqrt{u^*}} - \frac{1}{4} \ln u^*, \quad \varphi_2 = 0.828 \frac{\tilde{C}_1}{\sqrt{u^*}} (1 - E_1 s^3)^{-1},$$

$$\varphi_3 = -\frac{1}{2} \ln \left[\frac{3 |\alpha(0)|}{\pi} \right] + \frac{3}{4} \Upsilon \left(\frac{1}{\sqrt{2}} \right) - \frac{1}{32} \Upsilon^2 \left(\frac{1}{\sqrt{2}} \right) \bar{u} + 0.0345 \bar{u},$$

$$A = \frac{\tilde{C}_1}{r^* + |\alpha(0)|}, \quad \Upsilon(x) = 3 \frac{x - \arctan x}{x^3}.$$

It was shown in [9], that the main contribution comes from last integral over the macroscopic variables $\rho_0 = \rho'_0 \sqrt{N}$. Let us write $E(\rho'_0)$ in the form:

$$E(\rho_0) = N(\mu^* \rho_0 + B \rho_0^2 - G \rho_0^4), \quad (4.6)$$

(we omit prime near ρ_0).

where

$$B = \frac{1}{2} |d_2^{(\mu\tau)}(0)| - \frac{a_4^{(\mu\tau)}}{8 |d_2^{(\mu\tau)}(0)|} \Upsilon(x) = B_0 |\tau|^{2\nu},$$

$$G = \frac{a_4^{(\mu\tau)} N}{4! N_{\mu\tau}} = G_0 |\tau|^\nu, \quad (4.7)$$

$$B_0 = \frac{1}{2} |r_{\mu\tau}| \left(1 - \frac{u_{\mu\tau}}{4 |r_{\mu\tau}|^2} \Upsilon(x) \right) \left[\frac{\tilde{C}_1}{|r^* - \alpha(0)|} \right]^{2\nu},$$

$$G_0 = \frac{N u_{\mu\tau}}{4! N_B} \left[\frac{\tilde{C}_1}{|\tau^* - \alpha(0)|} \right]^\nu, \quad x = \frac{\pi}{C_{\mu\tau}} \sqrt{\frac{|\alpha(0)|}{|\alpha(\mu\tau)(0)|}},$$

$r_{\mu\tau}$ and $u_{\mu\tau}$ are coefficients of the block Hamiltonian for block lattice with spacing $C_{\mu\tau}$. The function $-k_B T E(\rho_0)$ is some analogue of the Landau energy. Essential difference consists in that, first, we know the explicit dependence of μ^* , B , G on the temperature τ , density η and chemical potential μ , and, second, the dependence of B and G on τ is nonanalytic, namely, $B \sim \tau^{2\nu}$, $G \sim \tau^\nu$. At $\tau \rightarrow 0$ both quantities B and G tend to zero, but the ratio B^2/G remains constant and the integral over ρ_0 exists.

Integral

$$I = \int \exp[E(\rho_0)] \sqrt{N} d\rho_0, \tag{4.8}$$

can be calculated by the steepest descent method. We need to solve the equation

$$\begin{aligned} \rho_0^3 + v\rho_0 + w &= 0, \tag{4.9} \\ v &= -\frac{B}{2G}, \quad w = -\frac{\mu^*}{4G}, \end{aligned}$$

and to find a point of the absolute maximum of $E(\rho_0)$. The discriminant

$$Q = \left(-\frac{w}{2}\right)^2 + \left(\frac{v}{3}\right)^3 \tag{4.10}$$

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

Surface $Q = 0$ separates two thermodynamic regions of (τ, η, μ) space: the external one, which is the region of single phase states, here $Q > 0$, and the inner region, where $Q < 0$ -it is the phase transition region. Surface $Q = 0$ represents a coexistence boundary.

In accordance with (2.13), for both regions there exists the same dependence between the point of maximum of $E(\rho_0)$, which is proportional to the order parameter, and the function $\Delta(\eta)$, namely, $\rho = \Delta$. Therefore, we call Δ the order parameter. It describes the density jump at the phase transition. Our main aim is to find the dependence between μ^* and Δ .

We start with describing of the coexistence boundary. When $Q = 0$, there are three real roots of cubic equation (4.9), two of which are equal. We have to take the single root

$$\rho_0 = \tilde{\rho}_1 = \left(\frac{\mu^*}{G}\right)^{1/3}, \tag{4.11}$$

which provides an absolute maximum of $E(\rho_0)$. From the equations $\rho = 0$ and $Q = 0$ we get equation for two boundary surfaces.

$$\mu^* = G\Delta^3, \tag{4.12}$$

$$\mu^* = \pm m |\tau|^{5/2\nu}. \tag{4.13}$$

Isotherm plane $|\tau| = |\tau_0|$ intersects both surfaces and forms a rectangle.

Its two sides have the coordinates

$$\begin{cases} \mu^* = -m |\tau_0|^{5/2\nu}; \\ \mu^* = +m |\tau_0|^{5/2\nu}. \end{cases} \tag{4.14}$$

Our principal task is to plot the isotherm $\mu = \mu(\tau_0, \Delta)$. We start from negative values μ^* and $Q > 0$.

For two external sides we get the same form for single real root $\tilde{\rho}_1$, which gives us the relation between μ^* and Δ in external region

$$\mu^* = 4G \frac{\Delta^3}{1 + \frac{1}{4} |\beta|^{1/3} - \frac{1}{12} |\beta| + \dots} \quad , \quad (4.15)$$

here $\beta = (\frac{v}{3})^3 / (\frac{w}{2})^2$.

For $\mu^* < 0$ we have $\Delta < 0$ and for $\mu^* > 0$ one has $\Delta > 0$, too. When $\beta \rightarrow 1$, $\mu^* \rightarrow G\Delta^3$, which coincidence with (4.15).

Now let us regard the inner region, $Q < 0$. Here we have three real roots, ρ_1, ρ_2, ρ_3 :

$$\begin{aligned} \rho_1 &= 2\sqrt{\frac{|v|}{3}} \cos \frac{\varphi}{3} \quad , \\ \rho_2 &= 2\sqrt{\frac{|v|}{3}} \cos \frac{\varphi + 2\pi}{3} \quad , \\ \rho_3 &= 2\sqrt{\frac{|v|}{3}} \cos \frac{\varphi + 4\pi}{3} \quad , \end{aligned} \quad (4.16)$$

where

$$\varphi = \arccos t \quad , \quad t = -\frac{w}{2(-\frac{v}{3})^{3/2}} = \frac{\mu^*}{8G(-\frac{v}{3})^{3/2}} \quad . \quad (4.17)$$

Near the coexistence boundary their argument t is close to 1. Therefore, we put $\cos \varphi = -1 + \delta$ for $\mu^* < 0$ and $\cos \varphi = 1 - \delta$ for $\mu^* > 0$.

Then we see, that ρ_2 root approaches root $\tilde{\rho}_1$ when δ and Q tend to zero, $\mu^* < 0$, and the root ρ_1 approaches root ρ_2 in the right side (see Fig. 3), when μ^* is positive.

So, we have found, that for negative values of μ^* we must take root ρ_2 . For positive μ^* the root ρ_1 is the proper one. So, the extension of curve μ^* from the point $\mu^* = G\Delta^3$ is:

$$\begin{aligned} \mu^* &= \mu^*(\rho_2(\Delta)) = 2B\Delta - 4G\Delta^3, \quad \mu_1 \leq \mu^* < 0 \\ \mu^* &= \mu^*(\rho_1(\Delta)) = 2B\Delta - 4G\Delta^3, \quad 0 < \mu^* \leq \mu_2 \\ \mu^* &= 0, \quad -\sqrt{|v|} \leq \Delta \leq \sqrt{|v|} \quad . \end{aligned} \quad (4.18)$$

We have to take into account in (4.16) only root ρ_2 for $\mu^* < 0$ and only root ρ_1 for $\mu^* > 0$, because only for these roots we have absolute maximum of $E(\rho_0)$, as it is shown in Fig. 4.

When μ^* tends to zero, we come to the point $\sqrt{|v|}$ from the right side and to the point $-\sqrt{|v|}$ from the left one. At point $\mu^* = 0$ there is a density jump of the magnitude $2\sqrt{|v|}$.

Now let us evaluate the value

$$\Delta = -\sqrt{N} \frac{M_3(0)}{|M_4(0)|} (M_2(0) + \frac{M_3^2(0)}{3|M_4(0)|}) \quad .$$

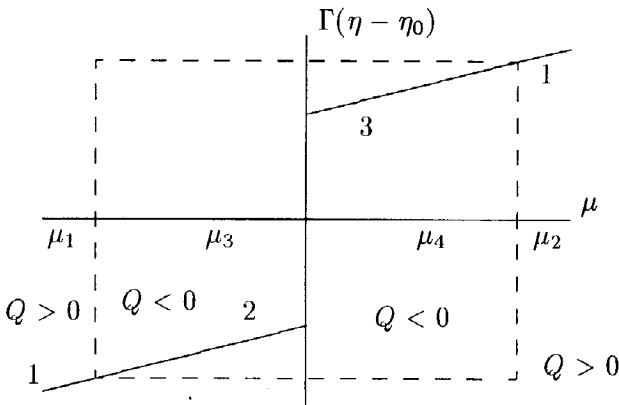


Figure 3. Schematic plot of the chemical potential jump. $Q < 0$ and $Q > 0$ corresponds to the region inside and outside rectangle, respectively.

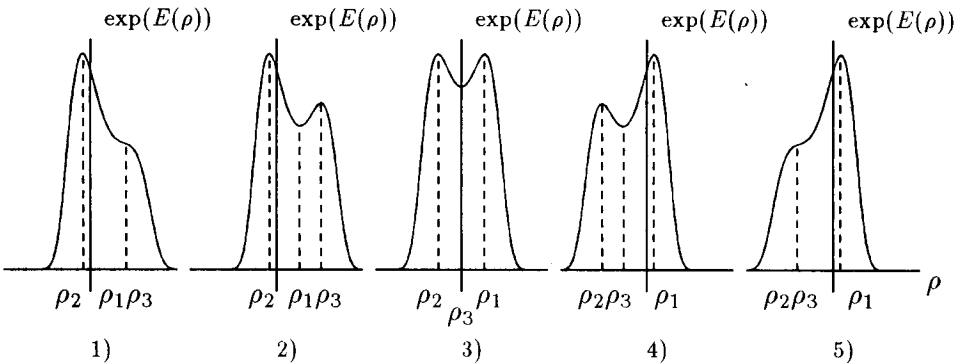


Figure 4. The position of the points of extremum of $\exp[E(\rho_0)]$ in dependence on the value of μ^* (see Fig. 3) 1). $\mu^* = \mu_1$ 2). $\mu^* = \mu_3$ 3). $\mu^* = 0$ 4). $\mu^* = \mu_4 = -\mu_3$ 5). $\mu^* = \mu_2 = -\mu_1$

Not very far from the critical point we can write

$$\Delta = \Delta_c + \left(\frac{\partial \Delta}{\partial \eta}\right)_{\Delta_c} (\eta - \eta_c) = \Gamma(\eta - \eta_c) \quad (4.19)$$

Value $\Delta = 0$ corresponds to $M_3 = 0$. In Table 1 the dependence of M_n on density is given. We see, that M_3 is the decreasing function of η .

$$\Gamma = -\left(\frac{\partial M_3(0)}{\partial \eta}\right)_{|M_3=0} \frac{M_2(0)}{M_4(0)_{|M_3=0}} > 0 \quad (4.20)$$

Thus, the isotherm for μ^* one may consider as function of $\eta - \eta_c$.

For the equation of state the following expression is valid for small Δ , when we can neglect the terms proportional to Δ^3 , holding only linear on Δ term:

$$\frac{P - P_0 - P_1}{Nk_B T} \simeq \frac{1}{2} |\alpha(0)| + \mu^* \quad (4.21)$$

where P_0 is defined in (1.20),

$$\frac{P_1 V}{N k_B T} = \ln Z_G - \beta(F_{CR} + F_{IGR}) \quad , \quad (4.22)$$

and on the plot of P we shall have the jump similar to that the plot of μ^* possesses.

In such a way the principal questions of the description of the liquid-gas phase transition may be solved.

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ОПИС КРИТИЧНОЇ ТОЧКИ ПРОСТИХ РІДИН В МЕТОДІ КОЛЕКТИВНИХ ЗМІННИХ

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Дослідження поведінки рідин поблизу критичної точки рідина-газ все ще залишаються актуальними. В попередніх роботах, використовуючи метод колективних змінних з виділеною системою відліку, нами отримано, виходячи з перших принципів, вираз для великої статистичної суми, придатний для досліджень в околі критичної точки.

Мета даної роботи – опис системи як вище, так і нижче T_c та аналіз поведінки хімічного потенціалу нижче T_c .