Ігор Рафаїлович Юхновський

Фазовий перехід рідина-газ в критичній точці і нижче

Роботу отримано 27 грудня 2011 р.

Затверджено до друку Вченою радою ІФКС НАН України

Рекомендовано до друку відділом статистичної теорії
конденсованих систем

Виготовлено при ІФКС НАН України

Національна академія наук України

ІНСТИТУТ
ФІЗИКИ
КОНДЕНСОВАНИХ
СИСТЕМ

ICMP–11–15E

I.R.Yukhnovskii

LIQUID-GAS PHASE TRANSITION AT AND BELOW THE CRITICAL POINT

ЛЬВІВ

УДК: 536.7, 538.9

PACS: 64.70.F-, 64.60.F-, 05.70.Jk

Фазовий перехід рідина-газ в критичній точці і нижче

І.Р.Юхновський

Анотація. Дана робота є продовженням циклу робіт [16–23], де ми описали поведінку простої системи взаємодіючих частинок в області температур вище критичної точки, включаючи критичну температуру, $T \geq T_c$. Описано поведінку системи в критичній точці (T_c, η_c) і в області нижче критичної точки. Розрахунки ведуться з перших принципів. Вираз для великої статистичної суми приведений до функціонального інтегралу на множині колективних змінних і записаний у ізінгоподібній формі. Виведено рівняння стану. Нижче T_c , коли в системі відбувається фазовий перехід першого роду типу "рідина-газ", відбувається скачок системи з газового стану, який має дуже велику ймовірність, в рідкий стан, теж з дуже високою ймовірністю. Під час такого процесу поглинається або виділяється прихована теплота переходу. Також виведено умови фазової рівноваги.

Liquid-gas phase transition at and below the critical point

I.R.Yukhnovskii

Abstract. This article is a continuation of previous works [16–23], where we have described the behavior of a simple system of interacting particles in the region of temperatures at and about the critical point, $T \geq T_c$. A description of the behavior of the system is given at the critical point (T_c, η_c) and in the region below the critical point. The calculation is carried out from the first principles. The expression for the grand canonical partition function is brought to the functional integrals defined on the set of collective variables. The Ising-like form is singled out. The equation of state is derived. Below T_c, when a gas-liquid system undergoes a phase transition of the first order, i.e., boiling, a "jump" occurs from the "extreme" high probability gas state to the "extreme" high probability liquid state, releasing or absorbing the latent heat of the transition. The phase equilibria conditions are also derived.

Подається в Condens. Matter Phys.
Submitted to Condens. Matter Phys.

Introduction

In this work we complete the first stage of the study of a system at the gas-liquid critical point by means of the collective variables method.

The research in this direction started already in the early 1980s by work [1]. By that time the collective variables method had already been developed in the approach proposed by D. M. Zubarev [2,5], as well as in the Hubbard transformation approach [3,4]. Application of this method has been successful with respect to a number of physical problems in the theory of condensed particle systems interacting via long-range as well as short-range potentials, an effective approximate solution of the three-dimensional Ising model was achieved and applied to describe phase transitions of the second order in a variety of systems [7–9]. A whole bunch of brilliant papers and monographs on the phase transition theory has emerged [10–13].

The transformation from the real space of Cartesian coordinates to the set of collective variables defined in the space of wave vectors $\mathbf{k}$ gave an obvious advantage in the description of systems of the interacting particles that attract one another at large separations. It is this attraction, which is usually given by a long-range "tail" of a Van der Waals attraction type, that is the source of liquid-gas phase transitions. In the k-space such attraction is described by the behaviour of the Fourier transform of the interaction potential at small k's, and, more importantly, in the close vicinity of $k = 0$. This is one gain from passing from the Cartesian space to the wave vector $\mathbf{k}$ space. Another gain comes from the set of collective variables. This set contains one variable (in the gas-liquid system case, it is $\rho_{\mathbf{k}}$ for $k = 0$) which is directly linked to the order parameter that characterizes the phase transition.

Therefore, the system of collective variables (CV) $\rho_{\mathbf{k}}$ or their Fourier-conjugates $\omega_{\mathbf{k}}$ can be thought of as the most suitable one for the description of the gas-liquid phase transition.

The results of the CV method application to a variety of Ising-like systems, obtained with the precision up to quartic and even sextic measure density, are given with a large bibliography in monograph [14], executed with accuracy thanks to the great devotion to their work of M. Kozlovski and I. Pyliuk.

The work on the liquid-gas critical point has been performed in close collaboration with my colleagues I. M. Idzyk and V. O. Kolomiets. Starting expressions for the partition function, given here in Eqs. (17) and (18), and for the quartic measure density, given in Eq. (20), were obtained [15–21]. Similar expressions were obtained in the works of Hubbard, Hubbard and Scofield [24], and in the work of Vouse and Sac [25]. In the latter, the contribution from the transformation Jacobian was counted as addition of some entropic term. These starting expressions were so complex that there seemed to be no chance of solving the problem. Thanks to the extraordinary persistence of I. Idzyk [16,17], the values of the cumulants $\mathfrak{M}_n(\mathbf{k}_1 \ldots \mathbf{k}_n)$ in the vicinity of $\mathbf{k}_i = 0$ were found. It was shown that for all $\mathfrak{M}_n(\mathbf{k}_1 \ldots \mathbf{k}_n)$ at small k near to the points $k_i = 0$, $i = 1, \ldots, n$, there exist plateaus. Wide enough for the values of the Fourier transform of the attractive potential for the regions $k < B$ where $\tilde{\Phi}(k) < 0$ and $\tilde{\Phi}(B) = 0$ to lie entirely within the span of those plateaus of $\mathfrak{M}_n(\mathbf{k}_1 \ldots \mathbf{k}_n)$. Moreover, it has turned out that the values $\mathfrak{M}_n(0 \ldots 0)$ can be expressed through the compressibility of the reference system and its derivatives. The nature itself granted us a possibility to bring the problem of the liquid-gas phase transition to a solvable form.

In the works [18–20] expressions for the equation of state for $T \geq T_c$ were obtained. A formula for the critical temperature of a liquid-gas system was found. The calculations were carried out in the critical region of temperatures close to T_c. The region $T \leq T_c$ has not received a proper treatment in [19–22]. With this work, after a twenty-year interruption, we renew the endeavor to reveal the processes that take place at $T \leq T_c$ in the critical region. The critical region means a region where a renormalization-group symmetry characterizes the relations between the coefficients of the block Hamiltonians.

Before the present work started, a number of authors had produced a huge amount of immensely interesting works. For example, a systematic review of these works can be found in [26].

The statistical-field methods still work finely, as they always did. Their basics are presented in a coherent logical development in the elegant monograph by J. Parisi [27].

An immense scope of work devoted to the investigation of the nature of gas-liquid phase transitions, with asymmetric exponents of the equilibrium curves within the “complete scaling” method, is presented in the works by M. Fisher and his colleagues [28,29].

The significance of “complete scaling” is shown in the works by Wang and Anisimov team [30].

The elegant equation of Van der Waals and his brilliant Nobel Prize lecture from the 12th of December 1910 [31] still retain their undoubted value and is discussed in present work. As one may conclude from the works by M. Fisher, J. Wang, and M. Anisimov regarding the phase equilibrium problems, thermodynamics acquires a new embodiment. Meanwhile, the methods and results of statistical physics, which, in particular, are being developed by us in the present work, and which to a great extent depend on the choice of initial potentials, are derived from first principles and characterize the microscopic processes.

An important intermediary link is provided by the methods and results of computer modeling of the processes. In particular, the review paper by J. de Pablo, K. Yan, and F. Escovedo [32] covers the modern techniques of phase equilibrium simulation in complex fluids. The case of phase equilibrium between gas and liquid states, studied by the mentioned authors, is really quite important in our work. By means of simulations with the simple histogram method, a transition–“jump” between two maxima: liquid and gas states, is studied. The reference system is used. A similar situation obtained in the present work is shown in Fig. 7 for the equation of state $P = p(\tau, \eta)$.

The present paper is concluded with a plot of the equation of state for a simple system of interacting particles at temperatures in the critical region below T_c, $T \leq T_c$. We would like to highlight here the important stages.

In the introduction, the starting form of the partition function in the grand canonical distribution is given in terms of collective variables $\rho_{\mathbf{k}}$ and their Fourier-conjugates $\omega_{\mathbf{k}}$. The long-range attraction of a Van der Waals type is described by the set $\rho_{\mathbf{k}}$, whereas the short-range repulsion of an elastic spheres type is described by the set $\omega_{\mathbf{k}}$. We start with a quartic measure density, instead of a Gaussian one. The curves for the cumulants of the transformation Jacobian are presented in [21]. Their form allows us to reduce the problem to the Ising model in an external field. The role of the latter is played by the generalized chemical potential μ^*.

The displacement transformation, applied to the macroscopic variables ρ_0 and ω_0 in order to achieve a proper Ising-like term, has a profound meaning.

We suppose here that the main events, connected with the phase transition in the vicinity of the critical point, occur in the region $k_i \leqslant B$. Solutions in the region $k > B$ may be obtained in the virial expansion form using the Gaussian density measure.

Therefore, we do not explicitly consider the wave-vector region $k > B$.

Integration in the partition function at $T \leq T_c$ is done in three regimes. In the renormalization group regime for the wave vectors $B_{m_\tau} \leq k \leq B$, the Wilson linear approximation [31–34] in the expansion of the recursive equations around the fixed point and the Kadanoff's hypothesis of scale invariance [37] are used. Further, for $0 < k \leqslant B_{m_\tau}$, the integration is carried out in the Inverse Gaussian regime (IGR), just like it is done in the Ising model at $T \leq T_c$ [9]. Let us note that without the integration in the IGR, one would not be able to obtain the correct behaviour of the system entropy [9], even in the limit $T \to T_c$, $T = T_c$.

And finally, we come to the integration over the variable ρ_0. The corresponding "Hamiltonian" would be somewhat an analogue of the Landau problem [38]. However, herein everything is done in a coherent manner and the "Hamiltonian" coefficients, which are, in fact, the characteristics of a thermodynamic quantity P, V, are known. Their non-analytic dependence on the temperature is known as well.

The most significant part of the work concerns the part of the partition function, presented in Eqs. (40) and (55), which is connected to the generalized chemical potential μ^* and the integral over ρ_0. It also much differs from the Landau type form due to the presence of a factor $\exp[\mu^* N(1-\Delta)]$ before the integral. The integration over ρ_0 is done by the steepest descend method. In a way, we are "traveling" along the ridge of the integrand's maxima.

The study of the maxima reveals the behaviour of the generalized chemical potential μ^*. Fig.5 shows the curves for μ^* that evidence the existence of a region $\mu^* = 0$ within which the system experiences a discontinuity of the density. The generalized chemical potential μ^* and the equation of state $P = p(\mu, \tau, \eta)$ as well as $P = p(\tau, \eta)$ are scrupulously studied. It is here that the order parameter value Δ appears when going from $P = p(\mu, \tau, \eta)$ to $P = p(\tau, \eta)$. The quantity Δ is a function of the cumulants $\mathfrak{M}_2(0)$, $\mathfrak{M}_3(0)$, and $\mathfrak{M}_4(0)$, which characterize the reference system. Hereafter, the variable ρ_0 is replaced with Δ. This way, the reference system characterized by the potential $\psi(r_{ij})$ of an elastic spheres system (see (4)) "intrudes" into the function $E(\rho_0)$ obtained from the integration corresponding to the long-range attractive potential $\phi(r_{ij})$.

Considering different theories of particle systems in equilibrium, in our pursuit we followed the idea offered to us by M. M.Bogolyubov [37], that a correct description of long-range and short-range interactions should rather be done in different phase spaces. And their combined consideration should be performed by means of functional differentiation. In the present work, this idea has been proved right. The short-range interactions were included in the picture of the phase transition by using the relation $\frac{\partial \ln \Xi}{\partial \mu^*} = N$ (see Eqs. (56) and (59)).

The main result of the work is the plot of the isotherm $(P - P_0)V$ given in Fig. 7. Here, the "jump" of the density at the transition from the gas state to the liquid state is presented and a formula for the latent heat of the transition is given.

It was shown that the events describing the instability region on the Van der Vaals isoterm are of vanishing small probability.

In an attempt to highlight the main results connected with the generalized chemical potential μ^* and integrals over ρ_0, not all the terms appearing during the transformations of ω_0 and ρ_0 were properly analyzed. They all can be expressed through the functions $\xi(\eta) = \frac{\mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|}$. The comparison of the results obtained herein with the data of other authors, in particular, with those of the groups of M. Fisher and M. Anisimov [28–30], will be the subject of a separate study.

1. The grand partition function in collective variables representation

We consider an equilibrium system of interacting equivalent particles. All its thermodynamical properties are described by the grand partition function Ξ:

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} z^N Z_N, \tag{1}$$

where N is the number of particles, z is the system activity,

$$z^N = \left[\sqrt{2\pi m k_B T}^3 \hbar^{-3}\right]^N \exp(\beta\mu N), \tag{2}$$

m is the mass of a particle, k_B is the Boltzmann constant, T is the temperature, $\hbar$ is the Planck constant, $\beta = (k_B T)^{-1}$, μ is chemical potential of the system, Z_N is the configurational integral of N particles:

$$Z_N = \int \exp(-\beta\Psi_N) d\Gamma_N, \tag{3}$$

$d\Gamma_N$ is the volume element in a phase space of coordinates of particles, Ψ_N is the potential interaction energy. It is equal to a sum of interactions of two kinds:

$$\Psi_N = \frac{1}{2} \sum_{\substack{i \leq j, j \leq N \\ i \neq j}} \psi(r_{ij}) + \Phi(r_{ij}), \tag{4}$$

where

$$\psi(r_{ij}) = \left\{ \begin{array}{ll} \infty & r_{ij} \leq \sigma \\ 0 & r_{ij} > \sigma \end{array} \right. \tag{5}$$

is the potential interaction energy of two equivalent hard spheres with a diameter σ,

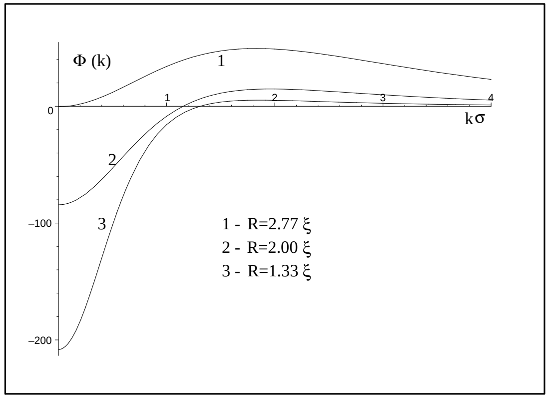


Figure 1. Curves of $\tilde{\Phi}(k)$ for different values R/ξ: 1. $R/\xi = \ln 16 = 2.77$; 2. $R/\xi = 2$; 3. $R/\xi = 1.33$.

$\Phi(r_{ij})$ is the potential interaction energy of van der Waals type. The necessary condition for the choice of the function $\Phi(r)$ is the existence of its Fourier-image. As the simplest form of $\Phi(r_{ij})$ we use the Morse potential:

$$\Phi(r) = \varepsilon \left[\exp\left(-2\frac{r-R}{\xi} \right) - 2\exp\left(-\frac{r-R}{\xi} \right) \right], \tag{6}$$

where ε characterizes the potential well depth, R is the abscissa of the potential well, ξ is the interaction radius.

The Fourier-image for $\Phi(r)$ follows:

$$\tilde{\Phi}(k) = 16\pi\varepsilon\xi^3 f \left[f \times (k^2\xi^2+4)^{-2} - (k^2\xi^2+1)^{-2} \right], \tag{7}$$

where $f = \exp(R/\xi)$. For $k = 0$, with

$$\tilde{\Phi}(0) = -\varepsilon\pi\xi^3 f(16-f) < 0 \tag{8}$$

we have $R/\xi < \ln 16 \cong 2.77$.

Figure 1 shows curves of $\tilde{\Phi}(k)$ for different values of R/ξ.

Other functions might also be used as $\Phi(r)$. The necessary feature for $\tilde{\Phi}(k)$ is the condition

$$\min \tilde{\Phi}(k) = \tilde{\Phi}(0) < 0. \tag{9}$$

Phase transition occurs due to an attraction of the particles at large distances. This is the main requirement for the very existence of condensed matter.

The phenomena occurring on long scales are of long-wave character. They are described in k-space by a region of low values of wave vectors k. Thus, we split the space $\{\bar{k}\}$ into two subspaces. Let B correspond to the value $\tilde{\Phi}(B) = 0$, and $\tilde{\Phi}(k) < 0$ for all $k < B$.

We consider that the main phenomena related to a phase transition occur in the region $k < B$.

We pass on to an extended phase space which consists of space of Cartesian coordinates of particles $\{r\}$ and of space of density oscillations, collective variables $\{\rho_k\}$. Overfilling of the phase space is eliminated by introducing the “identity condition” in the form of a Jacobian.

2. Reference expressions for the partition function.

a) *Collective variables.*

We introduce a system of notations:

$$\sum_{\substack{i\le j,j\le N\\ i\ne j}} \phi(r_{ij}) = \frac{N}{V}\sum_{\mathbf{k}} \tilde{\phi}(k)\big(\hat{\rho}_N(\mathbf{k})\hat{\rho}_N(-\mathbf{k})\big), \tag{10}$$

where

$$\begin{aligned}
\hat{\rho}_N(\mathbf{k}) &= \frac{1}{\sqrt{N}}\sum_{i=1}^{N} \exp -i\mathbf{k}\mathbf{r_i},\\
\hat{\rho}_N(\mathbf{k}) &= \rho_N^c(\mathbf{k}) - i\rho_N^s(\mathbf{k}),\\
\rho_N^c(\mathbf{k}) &= \frac{1}{\sqrt{N}}\sum_{i=1}^{N} \cos(\mathbf{k}\mathbf{r_i}),\\
\rho_N^s(\mathbf{k}) &= \frac{1}{\sqrt{N}}\sum_{i=1}^{N} \sin(\mathbf{k}\mathbf{r_i}),\\
\hat{\rho}_N(0) &= \sqrt{N},
\end{aligned}$$

we also consider that

$$\frac{1}{V}\sum_{\mathbf{k}} \tilde{\phi}(k)e^{i\mathbf{k}\mathbf{r}}|_{r\to 0} = \phi(0) = 0.$$

We define the collective variables system $\rho_{\mathbf{k}}^c$, $\rho_{\mathbf{k}}^s$, $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}^c - i\rho_{\mathbf{k}}^s$; ρ_0 by the following relations

$$\begin{aligned}
&\hat{\rho}_N^c(\mathbf{k}) \int \rho_{\mathbf{k}}^c J_N\big(\rho - \hat{\rho}_N(\mathbf{k})\big)(d\rho),\\
&\hat{\rho}_N^s(\mathbf{k}) \int \rho_{\mathbf{k}}^s J_N\big(\rho - \hat{\rho}_N(\mathbf{k})\big)(d\rho), \qquad (11)\\
&\sqrt{N} = \int \rho_0 J_N(\rho - \rho_N)(d\rho).
\end{aligned}$$

Here,

$$\rho^c_{\mathbf{k}} = \rho^c_{-\mathbf{k}}, \ \ \rho^s_{\mathbf{k}} = -\rho^s_{-\mathbf{k}},$$

$$J_N(\rho - \hat{\rho}_N) = \delta(\rho_0 - \sqrt{N}) \sideset{}{'}\sum_{\mathbf{k}} \delta\big(\rho^c_{\mathbf{k}} - \hat{\rho}^c_N(\mathbf{k})\big)\delta\big(\rho^s_{\mathbf{k}} - \hat{\rho}^s_N(\mathbf{k})\big),$$

$$(d\rho) = d\rho_0 \sideset{}{'}\prod_{\mathbf{k}} d\rho^c_{\mathbf{k}} d\rho^s_{\mathbf{k}}.$$

Prime means restriction of $\mathbf{k}$ only to the values from the upper subspace.

b) Our *reference system* is a system of hard spheres with diameter σ, and interaction potential, defined by equation (5), with chemical potential μ_0 and partition function Ξ_0,

$$\Xi_0 = \sum_{N=0}^{\infty} \frac{1}{N!} z_0^N \int \exp(-\beta\psi_N(r)) d\Gamma_N, \tag{12}$$

where $\psi_N(r) = \frac{1}{2}\sum_{ij}\psi(r_{ij})$, $z_0^N = \sqrt{2m\pi k_B T}^{\,3N}/\hbar^{3N} = \exp\beta\mu_0 N$, $d\Gamma_N = d\mathbf{r}_1 d\mathbf{r}_2 ... d\mathbf{r}_N$.

c) *Expression for the partition function in an extended phase space.*

According to the definitions (1), (11) and (12):

$$\begin{aligned} \Xi = \Xi_0 \sum_{N=0}^{\alpha} \frac{z_0^N}{N!} \int\int \frac{\exp(-\beta\psi_N)}{\Xi_0} J_N(\rho - \hat{\rho}_N) \times \\ \times \exp\big[h\sqrt{N}\rho_0 - \frac{1}{2}\sum_{\mathbf{k}} \alpha(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\big](d\rho)d\Gamma_N, \end{aligned} \tag{13}$$

where

$$h = \beta(\mu - \mu_0); \ \alpha(k) = \frac{N}{V}\beta\tilde{\phi}(k); \ \phi(r) = \frac{1}{V}\sum_{\mathbf{k}} \tilde{\phi}(k) e^{-i\mathbf{kr}}.$$

We introduce the Jacobian function

$$J(\rho) = \sum_{N=0}^{\alpha} \frac{z_0^N}{N!} \int \frac{1}{\Xi_0} \exp(-\beta\psi_N) J_N(\rho - \hat{\rho}_N) d\Gamma_N. \tag{14}$$

After its substitution into (13) we obtain:

$$\Xi = \Xi_0 \int \exp\left[\sqrt{N}h\rho_0 - \frac{1}{2}\sum_{\mathbf{k}}\big(\alpha(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\big)\right] J(\rho)(d\rho). \tag{15}$$

3. *Jacobian*

Instead of Dirac delta-functions of expression $J_N(\rho - \hat{\rho}_N)$ given by (11) we use in equation (14) their integral representation

$$\delta\big(\rho^c_{\mathbf{k}} - \hat{\rho}^c_N(\mathbf{k})\big) = \int_{-\infty}^{\infty} \exp\big[i2\pi\big(\rho^c_{\mathbf{k}} - \hat{\rho}^c_N(\mathbf{k})\big)\omega^c_{\mathbf{k}}\big] d\omega^c_{\mathbf{k}}.$$

Then,

$$J(\rho) = \int \exp\Big(i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}}\rho_{\mathbf{k}}\Big) \tilde{J}(\omega)(d\omega), \tag{16}$$

where $\rho_{\mathbf{k}} = \rho^c_{\mathbf{k}} - i\rho^s_{\mathbf{k}}$, $\omega_{\mathbf{k}} = \frac{1}{2}(\omega^c_{\mathbf{k}} + i\omega^s_{\mathbf{k}})$, $(d\omega) = d\omega_0 \sideset{}{'}\prod_{\mathbf{k}} d\omega^c_{\mathbf{k}} d\omega^s_{\mathbf{k}}$, $\tilde{J}(\omega)$ is the Fourier transform of $J(\rho)$,

$$\tilde{J}(\omega) = \sum_{N=0}^{\infty} \frac{z_0^N}{N!} \Xi_0^{-1} \int \exp(-\beta\psi_N) \exp\big(-i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}}\hat{\rho}_N(\mathbf{k})\big) d\Gamma_N.$$

After integration and summation we get $\tilde{J}(\omega)$ in an exponential form:

$$\begin{aligned} \tilde{J}(\omega) = \exp\left\{-i2\pi\mathfrak{M}_1\omega_0 - \frac{(2\pi)^2}{2}\sum_{\mathbf{k}} \mathfrak{M}_2(k)\omega_{\mathbf{k}}\omega_{-\mathbf{k}}\right\} \times \\ \times \exp\left\{\sum_{m\geq 3} \frac{(-i2\pi)^m}{m!} \sum_{\mathbf{k}_1,\ldots,\mathbf{k}_m} \mathfrak{M}_m(\mathbf{k}_1,\ldots,\mathbf{k}_m)\omega_{\mathbf{k}_1}\ldots\omega_{\mathbf{k}_m}\right\} \end{aligned} \tag{17}$$

Here $\mathfrak{M}_1, \mathfrak{M}_2, \ldots, \mathfrak{M}_m$ are cumulants of the reference system.

We substitute the expression for $J(\omega)$ into (16). Then we substitute the obtained result into (15) and get

$$\begin{aligned} \Xi \ = \ \Xi_0 \int \exp\left[\sqrt{N}h\rho_0 - \frac{1}{2}\sum_{\mathbf{k}} \alpha(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\right] \\ \times \exp(i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}}\rho_{\mathbf{k}})\tilde{J}(\omega)(d\rho)(d\omega). \end{aligned} \tag{18}$$

All expressions entering (18), h, $\alpha(k)$ and cumulants $\mathfrak{M}_n$ are the functions of density and temperature. This is the starting formula for the study of the grand partition function. Due to its complexity, it seemed that there was no chance of solving the problem. Still...

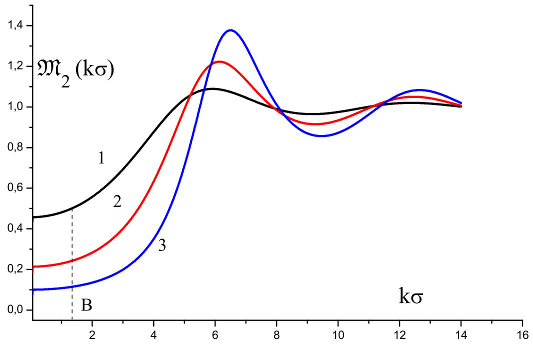


Figure 2. Curves of cumulant $\mathfrak{M}_2(k)$ for different densities: 1: $\eta = 0,1$, 2: $\eta = 0,2$, 3: $\eta = 0,3$. The dashed line indicates the value of B for which $\tilde{\phi}(B) = 0$, $\eta = \frac{N}{V}\frac{\pi}{6}\sigma^3$.

2. Integration of the grand partition function

2.1. Separation of an integration region in k space

Let us compare the form of the curves of $\tilde{\Phi}(k)$ with that of $\mathfrak{M}_2(k)$. As it follows from Fig. 1 and as it was agreed upon, $\tilde{\Phi}(k)$ at $k = 0$ is a negative and finite quantity, $\tilde{\Phi}(k)$ is going to zero with an increasing k and at $k \to \infty$.

Curves of $\mathfrak{M}_2(k)$ are given in Fig. 2.

We suppose that the main attraction effects created by potential $\Phi(r)$ are concentrated in the expression for $\tilde{\Phi}(k)$ in the narrow region of k between the values 0 and B. For these values of k, the curves for cumulant $\mathfrak{M}_2(k)$ and for all cumulants $\mathfrak{M}_n(k)$ have wide plateaus that begin for $\mathbf{k}_1, \ldots, \mathbf{k}_n = 0$ [21]. Thus, for all cumulants $\mathfrak{M}_n(\mathbf{k}_1 \ldots \mathbf{k}_n)$ in the region $\mathbf{k}_i < B$ we are able to choose their values for $\mathbf{k}_i = 0$. This means that

$$\mathfrak{M}_n(\mathbf{k}_1, \ldots, \mathbf{k}_n) = \mathfrak{M}_n(0, \ldots, 0) \quad \text{for} \quad \mathbf{k}_i < B.$$

These quantities are macroscopic. Their values are equal to the corresponding fluctuations in the number of particles of the reference system.

We have an equation

$$\mathfrak{M}_n(0 \ldots 0) = \frac{\partial^n \ln \Xi_0}{\partial(\beta\mu_0)^n} = \frac{\partial^{n-1}\langle N\rangle_0}{\partial(\beta\mu_0)^{n-1}}.$$

Therefore,

$$\mathfrak{M}_1(0) = \sqrt{\langle N\rangle_0};\;\; \mathfrak{M}_2(0) = \frac{1}{N}\langle\Big(N - \langle N\rangle\Big)^2\rangle_0;$$
$$\mathfrak{M}_3(0) = \langle\Big(N - \langle N\rangle\Big)^3\rangle_0 \frac{1}{\sqrt{N}^3};$$
$$\mathfrak{M}_4(0) = \frac{\langle\Big(N - \langle N\rangle\Big)^4\rangle_0 - 3\langle\Big(N - \langle N\rangle\Big)^2\rangle_0^2}{N^2},$$

etc.

The cumulants $\mathfrak{M}_n(0 \ldots 0)$ are functions of the chemical potential μ_0 and of the density in general. One can perform the elimination of the dependence on μ_0 either in the standard way extracting the value of μ_0 from the equation $\frac{\partial \ln \Xi_0}{\partial \mu_0} = N$, or using for fluctuation $\langle(N - \langle N\rangle)^n\rangle$ their values for canonical ensemble.

$$\left(\frac{\partial\langle N\rangle}{\partial\mu_0}\right)_{TV} = \frac{N}{V}\kappa, \text{ where } \kappa = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{TN}$$

is the compressibility in the reference system.

Then,

$$\mathfrak{M}_2(0) = Nk_BT\frac{1}{v}\kappa,$$
$$\mathfrak{M}_3(0) = N(k_BT)^2\left[2\left(\frac{1}{v}\kappa\right)^2 - \frac{\kappa}{v}\frac{\partial\kappa}{\partial v}\right),$$
$$\mathfrak{M}_4(0) = N(k_BT)^3\frac{\kappa}{v}\left[6\left(\frac{\kappa}{v}\right)^2 - 6\left(\frac{\kappa}{v}\frac{\partial\kappa}{\partial v}\right) + \left(\frac{\partial\kappa}{\partial v}\right)^2 + \kappa\frac{\partial^2\kappa}{\partial v^2}\right],$$

where $v = \frac{V}{N}$, $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{TN}$ is compressibility in the reference system. Here we should refer to an equivalency of the results for compressibility and its derivatives obtained for canonic and grand canonical ensembles.

Concerning the dependence of the cumulants $\mathfrak{M}_n(k_1, \ldots, k_n)$, as it was shown in [13,20] the following expansion is valid

$$\mathfrak{M}_n(k_1, \ldots, k_n) = \mathfrak{M}_n(0, \ldots, 0) + C_n^2\mathfrak{M}_{n-2}(0 \ldots 0)\mu_2(k)k^2 + \ldots,$$

where $\mu_2(k)$ is the pair correlation function of the reference system.

The above described situation for the cumulant values for $k_i < B$ and for $k = 0$ has become a real key to the solution of a problem of the liquid-gas critical point as well as to the description of the phenomena related to a liquid-gas phase transition, that is to the boiling processes occurring at temperatures below $T = T_c$. We owe this to an insistent work by I. Idzyk, who was the first to construct the graphs for the cumulants $\mathfrak{M}_n(k_1 \dots k_n)$ [1] [16,17].

Concerning an integration of the mixed terms with factors of the type

$$\sum_{\substack{\mathbf{k}_1,\dots,\mathbf{k}_i<B \\ \mathbf{k}_{i+1},\dots,\mathbf{k}_m>B}} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_i} \omega_{\mathbf{k}_{i+1}} \dots \omega_{\mathbf{k}_m},$$

the integration over $\omega_{\mathbf{k}}$ with $\mathbf{k} > B$ leads to the renormalization of cumulants $\mathfrak{M}_i(\mathbf{k}_1 \dots \mathbf{k}_i)$ with $\mathbf{k}_1, \dots, \mathbf{k}_i < B$. However, as it was shown in [21], their effect on the change of cumulants values $\mathfrak{M}_i$ is very weak. In particular, at the integration of the expression $\exp \frac{(2\pi i)^4}{2} \sum\limits_{\substack{k_1>B \\ k<B}} \mathfrak{M}_4(\mathbf{k}_1, -\mathbf{k}_1, \mathbf{k}, -\mathbf{k}) \omega_{\mathbf{k}_1} \omega_{-\mathbf{k}_1} \omega_{\mathbf{k}} \omega_{-\mathbf{k}}$ the correction to $\sum\limits_{k<B} \mathfrak{M}_2(0,0) \omega_{\mathbf{k}} \omega_{-\mathbf{k}}$ is less than one percent of value $\mathfrak{M}_2(0,0)$.

As a result, we have the following reference expression for Ξ:

$$\Xi = \Xi_0 \Xi_G \Xi_L, \tag{19}$$

where Ξ_0 is the partition function of the reference system,
Ξ_G is the result of integration over $\rho_{\mathbf{k}}$ and over $\omega_{\mathbf{k}}$ for the values $\mathbf{k} > B$. It has a form of group expansions. In particular, the second virial coefficient has the following form:

$$\frac{N(N-1)}{2V} \int \left(\exp - \Big(\beta(\psi(r) + g(r) \Big) - 1 - g(r) - \frac{g(r^2)}{2!} \right) d\mathbf{r},$$

where $g(r)$ is the screened potential, $g(r) = \frac{1}{V} \sum\limits_{k>B} \frac{\alpha(k)}{1+\mathfrak{M}_2(k)\alpha(k)} e^{i\mathbf{kr}}$ (or possibly another more compact form). In expression (19) integration over ρ_k and ω_k in the region $B \le k < \infty$ might be performed with the Gaussian basic measure density. In this way, we obtain the free energy and the equation of state in a form of the virial expansion with convergent integrals. This part of calculations was performed in the papers [6,16]. However, we should return to it again in order to relate the virial series with the description of the phenomena below the critical point.

Integrals over ρ_k and ω_k in the region $k < B$ are taken with quartic basic measure density. [2]

Ξ_L is the partition function in the region $k < B$.

$$\Xi_L = \int w_4(\rho\omega)(d\rho)^{N_B}(d\omega)^{N_B}, \tag{20}$$

$$w_4(\omega\rho) = \exp\left\{ h\rho_0 - \frac{1}{2} \sum_{k<B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + i2\pi \sum_{k<B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \right.$$

$$\left. + \sum_{n=1}^{4} \frac{(-i2\pi)^n}{n!} N^{1-n/2} \mathfrak{M}_n \sum_{\substack{k_1 \dots k_n \\ k_i<B}} \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n} \delta_{\mathbf{k}_1+\dots+\mathbf{k}_n} \right\}. \tag{21}$$

We want to exclude the cubic term from the expression in the exponent function (21) keeping the form $i2\pi \sum\limits_{k<B} \omega_{\mathbf{k}} \rho_{\mathbf{k}}$ for the inverse Fourier-transform from ω-space to ρ-space in the integral (20). This can be performed by two substitutions

$$\omega_0 = \omega_0' + \frac{\sqrt{N}\mathfrak{M}_3}{(2\pi i)\mathfrak{M}_4} \quad \text{and} \quad \rho_0 = \rho_0' + \tilde{\mathfrak{M}}_1, \tag{22}$$

where

$$\tilde{\mathfrak{M}}_1 = \sqrt{N}\Big(1 + \mathfrak{M}_2\xi + \frac{1}{3}\mathfrak{M}_3\xi^2\Big),$$

$$\xi = \frac{\mathfrak{M}_3}{|\mathfrak{M}_4|}.$$

From now on, we omit the argument (0) in the notations of cumulants and write down $\mathfrak{M}_2(0) \equiv \mathfrak{M}_2$, $\mathfrak{M}_3(0) \equiv \mathfrak{M}_3$, $\mathfrak{M}_4(0) \equiv \mathfrak{M}_4$ etc. After some tedious transformations we get Ξ_L in the following form

$$\Xi_L = \boldsymbol{\Upsilon} \int \exp\left\{ \sqrt{N}\mu^*(\rho_0 + \tilde{\mathfrak{M}}_1) - \frac{1}{2} \sum_{k<B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \right.$$

$$+ i2\pi \sum_{k<B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} - \frac{1}{2}(2\pi)^2 \sum_{k<B} \tilde{\mathfrak{M}}_2 \omega_{\mathbf{k}} \omega_{-\mathbf{k}} -$$

$$\left. - \frac{(2\pi)^4}{4!} \frac{1}{N_B} \sum_{k<B} |\tilde{\mathfrak{M}}_4| \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_4} \delta_{\mathbf{k}_1+\dots+\mathbf{k}_4} \right\} (d\omega)^{N_B} (d\rho)^{N_B}, \tag{23}$$

where

$$\boldsymbol{\Upsilon} = \exp\left\{ N(\xi + \frac{1}{2}\mathfrak{M}_2\xi^2 + \frac{1}{3!}\mathfrak{M}_3\xi^3 + \frac{1}{4!}\mathfrak{M}_4\xi^4) + \frac{1}{2}|\alpha(0)|\tilde{\mathfrak{M}}_1^2 \right\},$$

---

[1] "Nature always gives a chance to people" as I have said concerning this point during my first reports on this topic in the 80-ies of the last century.

[2] To be correct, with quartic measure density for integration over ω_k, if $\mathfrak{M}_4(0 \dots 0) < 0$ and with sextic measure density, if $\mathfrak{M}_4(0) > 0$ and $(i)^6 M_6 < 0$.

$$\mu^* = h - \xi + |\alpha(0)|\frac{\tilde{\mathfrak{M}}_1}{\sqrt{N}},$$
$$\tilde{\mathfrak{M}}_2 = \mathfrak{M}_2 + \frac{1}{2}\frac{\mathfrak{M}_3^2}{|\mathfrak{M}_4|}, \ \ \tilde{\mathfrak{M}}_4 = \frac{N_B}{N}\mathfrak{M}_4,$$
$$\tilde{\mathfrak{M}}_1 = \sqrt{N}[1-\Delta], \ \ \xi = \frac{\mathfrak{M}_3}{|\mathfrak{M}_4|}, \ \ \Delta = -\Big(\mathfrak{M}_2\xi + \frac{1}{3}\mathfrak{M}_3\xi^2\Big).$$

We have obtained the first fundamental result. We bring the expression for Ξ_L into the form which is analogous to the form of the partition function of three-dimensional Ising model in a field of generalized chemical potential μ^*. This means that we have built a mathematical framework for the study of a phase transition.

We treat the quantity B as a border of the Brillouin zone for a simple cubic lattice with the spacing $c = \frac{\pi}{B}$. The number of lattice sites in a volume V is equal to $N_B = \frac{V}{c^3} = V\left(\frac{B}{\pi}\right)^3$, $V = \frac{\pi}{6}\sigma^3\frac{N}{\eta}$. It means that for each physical system undergoing phase transition one can correspondingly put the crystal lattice on which this transition is described.

In particular, in the case of interaction $\phi(r)$, described by Morse potential:

$$\tilde{\phi}(B) = 0, \ \ B = \xi^{-1}\left[\Big(4 - f^{1/2}\Big)\Big(f^{1/2}-1\Big)^{-1}\right]^{1/2},$$
$$N_B = \frac{V}{(\xi\pi)^3}\left[\frac{4-f^{1/2}}{f^{1/2}-1}\right]^{3/2}, \ \ f = \exp(R/\xi) > 1. \qquad (24)$$

Two essential points should be emphasized in our formulations:
1) The existence of plateaus for cumulant values $\mathfrak{M}_n(k_1 \dots k_n)$ in the region of negative values of Fourier-image of attraction potential;
2) The possibility to introduce the crystal lattice in order to study the problem of a liquid-gas critical point and to reduce this problem to the Ising model in an external field.

Integration in expression (23) is taken over $\omega_{\mathbf{k}}$. Since the coefficients $\mathfrak{M}_n$ do not depend on k, passing from $\omega_{\mathbf{k}}$ to $\tilde{\omega}_{\mathbf{l}}$

$$\tilde{\omega}_{\mathbf{k}} = \sum_{l=1}^{N_B}\tilde{\omega}_{\mathbf{l}}e^{-i\mathbf{kl}}$$

and replacing

$$\delta_{\mathbf{k}_1+\dots+\mathbf{k}_4} = \frac{1}{N_B}\sum_l e^{i(\mathbf{k}_1+\dots+\mathbf{k}_4)l}$$

we factorize the integrals over $\tilde{\omega}_{\mathbf{l}}$ in (23) and get a reference expression for integration over $\rho_{\mathbf{k}}$ [9]

$$\Xi_L = Z(\tilde{\mathfrak{M}}_2\tilde{\mathfrak{M}}_4)\boldsymbol{\Upsilon}\Xi_L^{(1)}, \qquad (25)$$

where

$$\Xi_L^{(1)} = \int \exp\Bigg\{\sqrt{N}\mu^*(\rho_0 + \tilde{\mathfrak{M}}_1) - \frac{1}{2}\sum_{k<B}d_2(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}} -$$
$$-\frac{a_4}{4!N_B}\sum \rho_{\mathbf{k}_1}\dots\rho_{\mathbf{k}_4}\delta_{\mathbf{k}_1+\dots+\mathbf{k}_4}\Bigg\}(d\rho)^{N_B},$$
$$d_2(k) = a_2 + \alpha(k), \ \ a_2(k) = \sqrt{12}|\tilde{\mathfrak{M}}_4|^{-1/2}K(\zeta), \ \ a_4 = 6|\tilde{\mathfrak{M}}_4|^{-1}L(\zeta),$$
$$K(\zeta) = \zeta^{1/2}\Big[K_{3/4}^3/K_{1/4}(\zeta) - 1\Big] > 0,$$
$$L(\zeta) = 6K^2(\zeta) + 4\zeta^{1/2}K(\zeta) - 1 > 0,$$
$$Z(\tilde{\mathfrak{M}}_2, \tilde{\mathfrak{M}}_4) = \frac{1}{2\pi}\left(\frac{144\zeta}{|\tilde{\mathfrak{M}}_4|}\right)e^{\zeta}K(\zeta), \ \ \zeta = \frac{3}{4}\frac{\tilde{\mathfrak{M}}_2^2}{|\tilde{\mathfrak{M}}_4|} \gg 1. \qquad (26)$$

$K_{1/4}$ and $K_{3/4}$ are Bessel functions of an imaginary argument. It is important to have $d_2(B) > 0$ and $d_2(0) < 0$. We are working in the narrow temperature region containing the critical point $T = T_0$, see fig. 3.

Table 1. Numerical values of the coefficients a_2 and a_4 at different values of the density η. [19]

η	a_2	a_4
0.08	0.9257	0.2756
0.10	0.9532	0.1570
0.12	0.9704	0.0796
0.14	0.9807	0.0384
0.16	0.9824	0.0183
0.18	0.9723	0.0087
0.20	0.9446	0.0038

The integral (25) describes the phenomena in the critical point $T = T_c$, as well as in the critical region $T > T_c$ and $T < T_c$.

After an integration over $\rho_{\mathbf{k}}$, apart from integration over ρ_0, the form of the integral (26) completely coincides with the corresponding expression for the Ising model. For the purpose of its integration, we use Kadanoff's idea concerning the scale invariance of the phenomena on block lattices as well as Wisons's idea concerning the use of a linear approximation for the expansions around the fixed point in recurrent relations [33-37].

Integration is performed in the real three-dimensional space without any *a priori* statements about the temperature dependence of appearing coefficients.

The integration region $0 < k \leq B$ is divided into layers (BB_1), that is $B_1 < k \leq B$, $(B_1B_2), \ldots, (B_{n-1}B_n)$, where $B_n = \frac{B}{s^n}$, s is a division constant. The first integration over $\rho_{\mathbf{k}}$ is performed in the layer (BB_1), and then integration in the layer (B_1B_2) is performed, etc. The originality of the integration procedure consists in the following.

Let us denote by η_k the variables $\rho_{\mathbf{k}}$ with index k in the interval $B_1 < k \leq B$ (over these variables the integration is performed). That is, the integration in (26) is written as follows:

$$\int \ldots (d\rho)^{N_B} = \int \ldots (d\rho)^{N_{B_1}} (d\eta)^{N_B - N_{B_1}}.$$

Further, in order to factorize the integrands for integration over $(N_B - N_{B_1})$ variables η_k (we keep unchanged N_{B_1} variables $\rho_{\mathbf{k}}$), we need to use the integral form for the Kronecker delta $\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_4}$. This can be achieved by the following trick [9]

$$\int \ldots (d\eta)^{N-N_{B_1}} = \int \cdots \prod_{0<k\leq B_1} \delta(\eta_{\mathbf{k}} - \rho_{\mathbf{k}})(d\eta)^{N_B}.$$

This is the main point. After integration over $\rho_{\mathbf{k}}$ that belongs to the first layer $B_1 < k \leq B$ it was found that the new expression for the partition function with N_{B_1} variables $\rho_{\mathbf{k}}$ is characterized by a measure density which is similar to the original one, with new coefficients $d_2^{(1)}(k)$ and $a_4^{(1)}$ instead of the initial $d_2(k)$ and a_4 and a new number N_{B_1} of variables $\rho_{\mathbf{k}}$, $N_{B_1} = N_B/s^3$. Applying the same integration procedure, in the next layer $\rho_{\mathbf{k}}$ with $B_2 < k \leq B_1$, where $B_2 = \frac{B_1}{s^3} = \frac{B}{(s^3)^2}$, we receive a new measure density with the coefficients $d^{(2)}$ and $a_4^{(2)}$ and so on. As a result of each integration, there appear new partial partition functions that characterize the partial thermodynamic potentials connected with the energy of density fluctuation in the corresponding intervals of wave vectors k: $B_1 < k \leq B$, $B_2 < k \leq B_1$ and so on.

The sequence of coefficients d_2, a_4; $d_2^{(1)}$, $a_4^{(1)}$; $\ldots d_2^{(n)}$, $a_4^{(n)}$ reveals

amazing symmetry properties:

$$d^{(n)}(B_nB_{n+1}) = \frac{r_n + q}{s^{2n}}; \;\; a_4^{(n)} = \frac{u_n}{s^{4n}},$$

with: $\lim\limits_{n\to\infty} r_n = r^*$, $\lim\limits_{n\to\infty} u_n = u^*$ – fixed points coordinates; q – coefficient of averaging of the potential, $q \simeq \frac{3}{5}\alpha(0)$. Thus, the expressions

$$\frac{d^{(n)}}{r_n + q} = s^{-2n}; \;\; \frac{a_n}{u_n} = s^{-4n}$$

are the elements of a cyclic semi-group. This theorem quantitatively expresses the brilliant statement by Kadanoff, that the system of block lattices, each embedded in the volume V, is characterized by scale invariance.

We have named such a behavior of coefficients $d^{(n)}$ in $a_4^{(n)}$ as a critical regime [9]. At temperatures above and below T_c, the critical regime occurs at some finite number of steps in the intervals $0 < k \leq B$ on the layer (BB_1), (B_1B_2), …, $(B_{n-1}B_n)$. The curve built on the values of the coefficients $d^{(n)}$ at $T > T_c$ and at $T < T_c$ is presented in Fig. 3.

At $T > T_c$, after a number of integration steps n_τ the coefficients $d^{(n_\tau)}(k)$ become positive at all values k, $0 < k \leq B_{n_\tau}$. The integral $\int \ldots (d\rho)^{N_{n_\tau}}$, where $N_{n_\tau} = \frac{N}{s^{3n_\tau}}$ can be calculated with the Gaussian density measure:

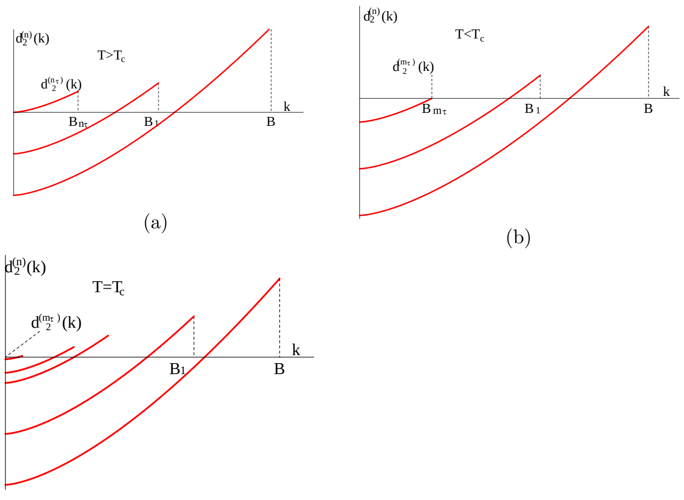
$$\exp\left[\mu^*\sqrt{N}(\rho_0 + \tilde{\mathfrak{M}}_1) - \frac{1}{2}\sum_{k<B_{n_\tau}} d^{(n_\tau)}(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\right].$$

Coefficient $d^{(n_\tau)}(k)$ can be renormalized by terms $a_4^{(n_\tau)}$, but this is a question of precision of the results. Formally, at $T > T_c$ and at $k < B_{n_\tau}$ the Gaussian density measure is a basic one.

At $T < T_c$, as can be seen from Fig. 3, after the step m_τ in integration over the shells of phase space, the curve $d^{(m_\tau)}(k)$ becomes negative at every k, $0 \leq k \leq B_{m_\tau}$. The region of critical regime terminates at the point B_{m_τ}. As a result, an interval of indexes k at the integration over $\rho_{\mathbf{k}}$ in the partition function $\Xi_L^{(1)}$ in (26) is divided into three parts: $B \geq k \geq B_{m_\tau}$, $B_{m_\tau} \geq k > 0$ and $k = 0$ correspondingly.

$$\Xi_L^{(1)} = \Xi_{\mathrm{cr}}^{(1)}\, \Xi_{\mathrm{igr}}^{(1)}, \tag{27}$$

here $\Xi_{\mathrm{cr}}^{(1)}$ is a result of integration in critical regime, $B_{m_\tau} \leq k \leq B$, $\Xi_{\mathrm{igr}}^{(1)}$ is a result of integration in the inverse Gauss regime (IGR) and includes the integration over the variable ρ_0, $0 \leqslant k < B_{m_\tau}$.



(a)

(b)

(c)

Figure 3. Coefficients $d^{(n)}(k)$ at temperatures: (a) $T > T_c$, (b) $T < T_c$, (c) $T = T_c$.

We have two quite important numbers n_τ, m_τ and the points $B_{n_\tau} = B/S^{n_\tau}$ for $T > T_c$ and $B_{m_\tau} = B/S^{m_\tau}$ for $T < T_c$, these points are shown in fig. 3.

They separate two regions of wave vectors **k**, namely the critical one, where the renormalization group symmetry exists ($B_{m_\tau} \leqslant k \leqslant B$ for $T < T_c$, and $B_{n_\tau} \leqslant k \leqslant B$ for $T > T_c$) and the limit-Gaussian ($T > T_c$) or inverse-limit-Gaussian ($T < T_c$) regions.

In the interval ($B_{m_\tau} \leq k \leq B$), the integration is performed on the basis of the quartic density measure, applying the method developed for the Ising model. For the partition function in the critical regime we receive:

$$\Xi^{(1)}_{\text{cr}} = \exp\left(-\frac{1}{kT}F_{\text{cr}}\right), \tag{28}$$

where

$$F_{\text{cr}} = -NkT\left\{-m_\tau \mathfrak{a}^{3\nu}|\tau|^{3\nu}\ln s + \right.$$
$$\left. + \left(1 - \mathfrak{a}^{3\nu}|\tau|^{3\nu}\right)\varphi_1 + |\tau|\left(1 - \mathfrak{a}^{3\nu-1}|\tau|^{3\nu-1}\right)\varphi_2\right\}.$$

Here s is the parameter of separation of the phase space into layers,

$B_{m_\tau} = B/s^{m_\tau}$

$$\mathfrak{a} = \tilde{c}_1\left(r^* + \beta\tilde{\Phi}(0)\right)^{-1},$$
$$\varphi_1 = 1,043 - 0,828\frac{r^* + q}{\sqrt{u^*}} - 0,250\ln u^*,$$
$$\varphi_2 = 0,828\frac{\tilde{c}_1}{\sqrt{u^*}}(1 - s^{-3}E_1)^{-1}, \quad q = 3/5\beta\tilde{\Phi}(0);$$

at $s = s^* = 3,5862$, $\tilde{c}_1 = 0,818\beta\tilde{\Phi}(0) + 0,011[\beta_c\tilde{\Phi}(0)]^{-1}$, $E_1 = 8,235$. The inverse Gaussian regime is observed after integration over $\rho_{\mathbf{k}}$ in the critical region. The initial integral $\Xi^{(1)}_{\text{igr}}$ reads:

$$\Xi^{(1)}_{\text{igr}} = \int \exp\Big[\sqrt{N}\mu^*\left(\rho_0 + \tilde{\mathfrak{M}}_1\right) - \frac{1}{2}\sum_{0\leqslant k\leqslant B_{m_\tau}} d^{(m_\tau)}(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}} -$$
$$- \frac{1}{4!}\frac{1}{N_{m_\tau}}\sum_{\substack{\mathbf{k}_1\ldots\mathbf{k}_4\\ 0\leqslant\mathbf{k}_i\leqslant B_{m_\tau}}} a_4^{(m_\tau)\rho_{\mathbf{k}_1}\ldots\rho_{\mathbf{k}_4}\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_4}}\Big](d\rho)^{N_{m_\tau}}. \tag{29}$$

Coefficients $d^{(m_\tau)}(k)$ and $a_4^{(m_\tau)}$ appear as a result of integration in the critical regime (renormalization group regime)

$$d^{(m_\tau)}(k) = \left(r^* + C_1E_1^{m_\tau} - C_2E_2^{m_\tau}R\right)s^{-2m_\tau} + \tilde{q}k^2,$$
$$a_4^{(m_\tau)} = \left(u^* + C_1E_1^{m_\tau}R' + C_2E_2^{m_\tau}\right)s^{-4m_\tau}$$

$d^{(m_\tau)}(B_{m_\tau}) = 0$; $B_{m_\tau} = \frac{B}{s^{m_\tau}}$; $N_{m_\tau} = \frac{N}{s^{3m_\tau}}$; $\tilde{q} = 2b^2\alpha(0)$; $\alpha(0) < 0$; E_1 and E_2 are eigenvalues of the matrix of the linear approximation of recurrent equations. $R = \frac{R_{12}}{R_{11}-E_2}$; $R' = \frac{E_1-R_{11}}{R_{12}}$, R_{ij} are the matrix elements of the matrix of linear approximation, $C_1 = \tau\tilde{c}_1$, where $\tilde{c}_1 \simeq \alpha(0)$, $c_2 \sim 0,02$. The exact values of τ^*, C_1, C_2, E_1 and E_2, R in R' are given in [9,14]. Here $d^{(m_\tau)}(k) < 0$ for all $k < B_{m_\tau}$. Nevertheless, the integral (29) is convergent due to the fact that $a_4^{(m_\tau)}$ is always positive for all $k < B_{m_\tau}$. Taking this into account, we shift ρ_k by

$$\rho_{\mathbf{k}} = \rho'_{\mathbf{k}^*} + \sigma\sqrt{N}\delta_k, \tag{30}$$

here σ is found from the condition of maximum:

$$E_{\text{igr.}}(\sigma) = \frac{1}{2}|d^{(m_\tau)}(0)|\sigma^2 - \frac{1}{4!}a_4^{(m_\tau)}s^{3m_\tau}\sigma^4 \quad \text{and} \quad \sigma = \sqrt{\frac{3!|d^{m_\tau}(0)|}{a_4^{(m_\tau)}s^{3m_\tau}}}.$$

As a result of such shifting, the coefficient $d^{(m_\tau)}(k)$ in (29), which is negative, is substituted by a positive one:

$$\bar{d}(k) = 2|d^{m_\tau}(0)| + \tilde{q}k^2 > 0.$$

According to this, at accurate calculations (29) [9] we can use the Gaussian density measure. The integration in (29) is performed over all $\rho_{\mathbf{k}}$ with the exception of ρ_0.

As it follows from (30), the cubic term appears in the integral over the variable ρ_0 in (29). To get rid of it, one more shift of ρ_0 is performed, which appears to be the inverse shift to (30)

$$\rho_0' = \rho_0'' - \sigma\sqrt{N}. \tag{31}$$

As a result, an expression for $\Xi^{(1)}_{\text{igr}}$ is rewritten as:

$$\Xi^{(1)}_{\text{igr}} = \exp\Big(-\beta F_{m_\tau}\Big) \int \exp\Big(\sqrt{N}\mu^*(\rho_0 + \tilde{\mathfrak{M}}_1) + B\rho_0^2 - \frac{1}{N}G\rho_0^4\Big)d\rho_0, \tag{32}$$

here F_{m_τ} is the result of integration in the inverse Gaussian regime that starts from the expression (29), which in turn is a relult of integration in the critical regime. F_{m_τ} includes the results of displacement transformations (30) and (31) and of an integration over $\rho_{\mathbf{k}}$ with $0 < k \le B_{m_\tau}$. The integration is performed with the Gaussian density measure. It is the same as in the Ising model at $T \le T_c$ and is described in detail in [9,14,19].

As a result, for F_{m_τ} we have:

$$F_{m_\tau} = -NkTA^{3\nu}|r|^{3\nu}(\tilde{\varphi}_3 + m_\tau \ln s), \tag{33}$$

where

$$\begin{aligned}
\tilde{\varphi}_3 &= \frac{3}{4}\mathcal{L}_1(1/\sqrt{2}) - \frac{1}{32}\bar{u}[\mathcal{L}_1(1/\sqrt{2})]^2 + 0,07\bar{u}/2 + \frac{1}{3}[1 - \mathcal{L}_1(1/\sqrt{2})] - \\
&\quad - \frac{1}{2}\ln 3\alpha(0)/\pi, \\
A &= \frac{\tilde{c}_1}{r^* + \alpha(0)}, \quad \bar{u} = u^*/(\alpha(0))^2 \approx 0,9, \\
\tilde{\mathcal{L}}_1(x) &= 3\frac{x - \operatorname{arctg} x}{x^3}, \quad \tilde{\mathcal{L}}_1(x) = 1 + 0(x^2), \\
x &= \frac{\pi}{c_{m_\tau}}\sqrt{\frac{\tilde{q}}{2|d^{(m_\tau)}(0)|}}, \quad c_{m_\tau} = cs^{m_\tau}.
\end{aligned}$$

The results of integration in the critical regime and in the inverse Gaussian regime depend on the parameter s, the parameter of dividing the phase space into layers.[3] The optimal value of s after integration is $s = s^* = 3,5862$, and the parameter $\sqrt{z^*} = (3/4)^{1/2}(r^* + q)/\sqrt{u^*}$ equals zero. For $s = s^*$ the fixed point coordinates are known:

$$r^* = \bar{r}\alpha(0), \;\; \bar{r} = 0,6122; \;\; u^* = \bar{u}[\alpha(0)]^2; \;\; \bar{u} = 0,8894.$$

The coefficients B and G in an exponent in the integrand in (32) are important:

$$\begin{aligned}
B &= \frac{1}{2}|d^{(m_\tau)}(0)| - \frac{a_4^{(m_\tau)}}{8|d^{(m_\tau)}(0)|}\mathcal{L}_1(x) = |\tau|^{2\nu}B_0, \\
B_0 &= \frac{1}{2}|r_{(m_\tau)}|\left(1 - \frac{u_{m_\tau}}{4|r_{(m_\tau)}|^2}\tilde{\mathcal{L}}_1(x)\right)\left(\frac{\tilde{c}_1}{|r^* + \alpha(0)|}\right)^{2\nu}
\end{aligned} \tag{34}$$

and

$$\begin{aligned}
G &= \frac{u_{m_\tau}}{4}s^{-m_\tau} = |\tau|^{\nu}G_0, \\
G_0 &= \left(\frac{\tilde{c}_1}{|r^* + \alpha(0)|}\right)^{\nu}\frac{u_{m_\tau}}{4!}, \quad \nu = 0,605.
\end{aligned}$$

Whereas in the Ising model the cumulants $\mathfrak{M}_1$, $\mathfrak{M}_2$, $\mathfrak{M}_4$, $\mathfrak{M}_6$, … and $a_2, a_4, \ldots$ are constants, in the present problem they are functions of density η.

In (32) we received a starting expression to study the phenomena bellow T_c.

Let us emphasize the importance of considering both the critical and the inverse Gaussian regime. The starting distribution in (29) for integration in the inverse Gaussian regime appears as a result of integration in the critical regime. The starting expression (32) for integration on ρ_0 is obtained in the next stage, i.e., after integration in the inverse Gaussian regime (IGR), taking into account the shift transformation (30). As it follows from (34), coefficient B is a sum of two terms. The first $\frac{1}{2}|d^{(m_\tau)}(0)|$ is determined in the critical regime and is connected with the renormalization group transformations, whereas the second term $\frac{a_4^{(m_\tau)}}{8|d^{(m_\tau)}(0)|}\mathcal{L}_1(x)$ is a contribution after integration in the inverse Gaussian regime.

Here we need to make a short retreat. From equations for the critical regime, one receives an equation for determination of critical temperature. Judging from the behavior of the curves $d^{(n)}(k)$, presented in

---

[3] Let us remind that integration is performed in the narrow temperature region $T = T_c$, $\tau < 0,01$.

Fig. 3(c), the critical temperature is defined as T_{cr}, at which the critical regime exists in the whole region $k \leqslant B$. By definition, for the critical temperature:

$$\lim_{n\to\infty} d^{(n)}(B_n)_{T=T_c} \geq 0, \qquad \lim_{n\to\infty} d^{(n)}(0)_{T=T_c} \leq 0 \ \ \mathit{and} \ \ \lim_{n\to\infty} B_n = 0. \tag{35}$$

In the linear approximation of renormalization group, this is equivalent to

$$\begin{gathered}\frac{\tau^* + C_1(T_c)E_1^n - C_2(T_c)R(T_c)E_2^n}{s^{2n}} + \frac{\alpha(0)}{s^{2n}} \geq 0,\\ \frac{\tau^* + C_1(T_c)E_1^n - C_2(T_c)R(T_c)E_2^n}{s^{2n}} \leq 0\end{gathered} \tag{36}$$

as $n \to \infty$.

This is possible only when $C_1(T_c) = 0$, since the eigenvalue E_1 satisfies: $E_1 > 1$.

As a result, in [9] we receive an expression for the critical temperature of three-dimensional Ising model:

$$T_c(\eta) = \frac{|\bar{\alpha}(0)|}{k_B} f(\eta), \qquad \bar{\alpha}(0) = \frac{N}{V}\tilde{\phi}(0).$$

The first term in the right hand side determines T_c in the mean field approximation, $f(\eta)$ is an additional factor, which appears from (36) as a result of the solutions of the recurrent relations. The above relation holds for the Ising model. In the liquid-gas critical point problem, there is an essential difference: $T_c(\eta)$ is a function of density. To obtain the coordinates of the critical point, one needs two more equations. As it follows from (32), the first one is:

$$\mu^* = 0, \tag{37}$$

here $\mu^* = h - \xi + |\alpha(0)|\tilde{\mathfrak{M}}_1/\sqrt{N}$. This reduces our problem to the Ising model. To satisfy this condition, we need to determine the generalized chemical potential μ^* from the relation $\frac{\partial \ln \Xi}{\partial \mu^*} = N$. It was studied in [17,18] under consideration of phenomena at $T \geq T_c$ and resulted in the following

$$\mu^* = 2A\tilde{\rho}_0^{(1)}, \ \ \tilde{\rho}_0^{(1)} = \Delta,$$

here $A = \frac{1}{4}\frac{a_4(n_\tau)}{N_{n_\tau}} \sum\limits_{k<B_{n_\tau}} \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle$, $\Delta = -(\mathfrak{M}_2\xi + \frac{1}{3}\mathfrak{M}_3\xi^2)$, $\xi = \frac{\mathfrak{M}_3}{|\mathfrak{M}_4|}$,

$\tilde{\rho}_0^{(1)}$ is the extremum point of $E(\rho_0)$ at $T \geq T_c$; n_τ denotes the number of the last shell in momentum space k, where the renormalization group

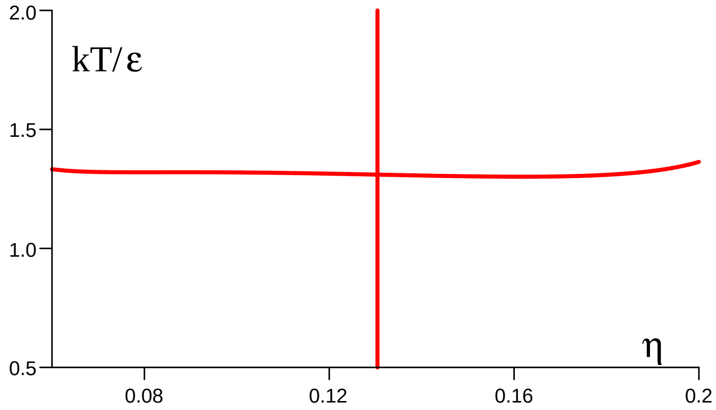


Figure 4. Coordinates of the liquid-gas critical point on the plane $\mu^* = 0$.

symmetry holds [Fig. 3 (a)]. As it follows from the formula (59) Δ is the systems order parameter below $T < T_c$. It has to be equal zero at $T = T_c$.

So for the liquid-gas critical point we have three following conditions:

$$\begin{aligned}&C_1 = 0, \ \ \text{from (36)}\\ &\mu^* = 0 \ \ \text{and}\\ &\Delta = 0.\end{aligned}$$

In such a way, the coordinates of the critical point are determined by the crossing point of three surfaces [19]:

$$\begin{aligned} T_c(\eta) &= \frac{|\bar{\alpha}(0)|}{k_B} \frac{2\left[1-\bar{r}+R_{12}^0(\bar{u})^{1/2}/(R_{11}-E_2)\right]}{a_2+\left\{a_2^2+\left[4a_4R_{12}^0/\bar{u}^{1/2}(R_{11}-E_2)\right]\left[1-\bar{r}+R_{12}^0\bar{u}^{1/2}/(R_{11}-E_2)\right]\right\}},\\ \mu^* &= \beta(\mu-\mu_0) - \xi + |\alpha(0)|\tilde{\mathfrak{M}}_1/\sqrt{N} = 0, \\ \Delta &= -\left(\mathfrak{M}_2\frac{\mathfrak{M}_3}{\mathfrak{M}_4} - \frac{1}{3}\mathfrak{M}_3\left(\frac{\mathfrak{M}_3}{\mathfrak{M}_4}\right)^2\right) = 0.\end{aligned} \tag{38}$$

In Fig. 4, the crossing point of the curves gives the coordinate of a critical point. This plot was obtained by V. Kolomiyets and I. Idzyk in [15,16,19]. For the case of argon, an equation (38) produces the coordinates:

$$\frac{k_B T_c}{\varepsilon} = 1,31, \ \ \eta_c = 0,130443,$$

which perfectly coincides with the experiment $\left(\eta_c^{(\mathrm{exp.})} = 0,13044\right)$. Let us note, that relation $\Delta = 0$ is equivalent to $\mathfrak{M}_3 = 0$.

At the critical point, all the terms with odd powers of ω and ρ are canceled in (26) and under the condition $\mu* = 0$ the expression is reduced to the Ising model. Thus the phase transition or the critical point T_c is of the second order.

In the red region of density oscillation modes $0 < k \leq B$, we have the following situation. In the critical regime $B_{m_\tau} \leq k \leq B$, the system is not thermodynamically stable, the signs of compressibility and of the heat capacity are non-physical $\left(\frac{\partial P}{\partial V}\right)_T > 0$ and $C_V < 0$. Only taking additionally into account the results of integration in the limiting Gaussian regime (at $T \geq T_c$) and in the inverse Gaussian regime (at $T \leqslant T_c$), the total value of free energy is obtained, which satisfies all conditions of physical stability. This means that thermodynamics at critical point T_c is a limit of sums of contributions from the critical $B_{m_\tau} \leq k \leq B$ and from the inverse (limiting) Gaussian regimes $0 < k \leq B_{m_\tau}$ [4]. The studies at $T \geq T_c$ can be found in [19–21]. In the present paper, we study the region $T \leq T_c$. Thus, we have finished the above retreat and we continue our considerations.

We assume that in (32) the complete integration in space ρ_k is performed in the partition function Ξ, with the exception of integration over the variable ρ_0.

The generalised chemical potential μ^*.

Our task here is to study the integral over ρ_0 in expression (32). After substitution $\rho_0 = \sqrt{N}\rho_0'$, omitting the terms proportional to $\ln N$, we have:

$$\int \exp N\left\{\mu^*\rho_0 + B\rho_0^2 - G\rho_0^4\right\} d\rho_0. \tag{39}$$

This integral is a function of the generalized chemical potential μ^*, density η and temperature τ. We denote

$$E(\rho_0) = \mu^*\rho_0 + B\rho_0^2 - G\rho_0^4. \tag{40}$$

Here

$$\mu^* = \beta(\mu - \mu_0) - \xi + |\alpha(0)|\tilde{\mathfrak{M}}_1.$$

B and G are given by (34), and they turn out to be positive. Coefficient at ρ^2 in (39) is positive and the integrand increases at small ρ_0, whereas at $\rho_0 \to \infty$ the function $\exp\{NE_0(\rho_0)\}$ tends to zero due to the term $G\rho_0^4$.

---

[4] During integration in the inverse Gaussian regime, the limiting point $k = 0$ is included.

As a result, the function can have one or several very high maxima. Due to this fact, the integral (39) can be found using the method of the steepest descent. To do this, first we find the maximum of $E(\rho_0)$:

$$\frac{\partial E}{\partial \rho_0} = 0; \quad \frac{\partial^2 E}{\partial \rho_0^2} < 0 \quad \mathit{or}$$
$$\mu^* + 2B\rho_0 - 4G\rho_0^3 = 0, \;\; 2B - 2G\rho_0^2|_{\rho_0 = \rho_{0\,max}} < 0, \tag{41}$$

or in a standard form:

$$\rho_0^3 + V\rho_0 + W = 0, \tag{42}$$

here $V = \frac{-B}{2G}$, $W = -\frac{1}{4}\frac{\mu^*}{G}$, with the condition $3\rho_0^2 + V > 0$, which corresponds to (41). Equation (42) has three solutions that may be found by Cardano formula:

$$\rho_0 = \sqrt[3]{-\frac{W}{2} + \sqrt{Q}} + \sqrt[3]{-\frac{W}{2} - \sqrt{Q}}, \tag{43}$$

here Q is a discriminant of the equation:

$$Q = \frac{W^2}{4} + \frac{V^3}{27}. \tag{44}$$

The first term in the discriminant is always positive, the second one is always negative. Thus, three possibilities may be observed: $Q > 0$, $Q < 0$ and $Q = 0$. Depending on the sign of Q, we have one real ($Q > 0$) or three real solutions($Q < 0$).[5] The case $Q = 0$ is a limiting case that separates the solutions.

a) Let us start with $Q > 0$. Equation (42) has one real and two complex solutions. $Q > 0$ means that $\frac{W^2}{4} > \left|\frac{V^3}{27}\right|$ and $\left|\frac{W}{2}\right| > \sqrt{Q}$. Thus,

$$\rho_0^{(1)} = \sqrt[3]{-\frac{W}{2}}\left\{\left[1 - \frac{2\sqrt{Q}}{W}\right]^{1/3} + \left[1 + \frac{2\sqrt{Q}}{W}\right]^{1/3}\right\},$$
$$\sqrt{Q} = \pm\frac{|W|}{2}\Big(1 + \frac{1}{2}\gamma - \frac{1}{8}\gamma^2 + \ldots\Big),$$
$$\gamma = \left(\frac{V}{3}\right)^3 \Big/ \left(\frac{W}{2}\right)^2.$$

Expanding in powers of γ, we receive:

$$\rho_0^{(1)} = \left(\frac{\mu^*}{4G}\right)^{1/3}\left[1 + \left(\frac{|\gamma|}{4}\right)^{1/3} - \frac{1}{12}|\gamma| + \frac{\sqrt[3]{2}}{24}|\gamma|^{4/3} - 0(\gamma^2)\right]. \tag{45}$$

---

[5] At $T > T_c$ the discriminant Q is always positive, $Q > 0$.

Hence

$$\mu^* = 4G\left[1+\left(\frac{|\gamma|}{4}\right)^{1/3} - \frac{1}{12}|\gamma| + \dots\right]^{-3} (\rho_0^{(1)})^3. \tag{46}$$

The sign of $\rho_0^{(1)}$ is determined by the sign of μ^*.

At $\gamma = 1$ $Q = 0$, from (43) $\rho_0^{(1)} = \sqrt[3]{\mu^*/G}$, as well as because $\left(\frac{1}{4}\right)^{1/3}\left[1+\left(\frac{1}{4}\right)^{1/3} - \frac{1}{12} + \frac{\sqrt[3]{2}}{24} - \dots\right] = 1$ in (75).

The case $Q > 0$ means that

$$\left(\frac{\mu^*}{8G}\right)^2 > \left|\left(-\frac{B}{6G}\right)^3\right| \quad \text{and} \quad |\mu^*| > G\left(\frac{2}{3}\frac{B}{G}\right)^{3/2}.$$

Thus, at $Q > 0$, both μ^* and $\rho_0^{(1)}$ vary within

$$|\mu^*| \geq a, \quad \text{where} \quad a = G\left(\frac{2}{3}\frac{B}{G}\right)^{3/2},$$

$$|\rho_0^{(1)}| \geq b, \quad \text{where} \quad b = \left(\frac{2}{3}\frac{B}{G}\right)^{1/2}. \tag{47}$$

b) The case $Q = 0$

This equality describes intermediate surface between two regions $Q > 0$ and $Q < 0$. Equation (42) has three real roots:

$$\rho_1 = u + v, \quad \rho_2 = \rho_3 = -\frac{1}{2}(u + v),$$

where $u = \left[-\frac{W}{2} + \sqrt{Q}\right]^{1/3}$, $v = \left[-\frac{W}{2} - \sqrt{Q}\right]^{1/3}$. But only for the root ρ_1 we get a maximum for $E(\rho)$

$$E''(\rho_1) = -GB < 0; \quad E''(\rho_2 = \rho_3) = 0.$$

Therefore we take

$$\rho_0 = \rho_1 = 2\sqrt[3]{-\frac{W}{2}} = \sqrt[3]{\mu^*/G}.$$

Written explicitly the condition $Q = 0$ takes on the form:

$$\left(\frac{W}{2}\right)^2 = -\left(\frac{V}{3}\right)^3 \quad or \quad \mu^* = \pm a = \pm G\left(\frac{2}{3}\frac{B}{G}\right)^{3/2}. \tag{48}$$

When discriminant Q equals zero, we receive the value of chemical potential of the system.[6] From Eq. (43)

$$\rho_0^{(1)} = 2\sqrt[3]{-\frac{W}{2}} = \sqrt[3]{-\frac{\mu^*}{G}} = \sqrt[3]{-\frac{\pm a}{G}}. \tag{49}$$

Substituting μ^* from (48), we receive

$$\rho_0^{(0)} = \pm b, \quad here \quad b = \sqrt{\frac{2}{3}\frac{B}{G}}. \tag{50}$$

We have got the transitional points on the plane μ^*, ρ_0. The point $(-a, -b)$ corresponds to the solution $\rho_0^{(1)}$, defined in (45) at $\rho_0^{(1)} = -b$, the point (b, a) corresponds to solution $\rho_0^{(1)}$ at $\rho_0^{(1)} = b$. The slope of the curve $\mu^* = \mu^*(\rho_0)$ at point $Q = 0$

$$\left.\frac{\partial\mu^*}{\partial\rho_0^{(1)}}\right|_{Q=0} = \left.\left(\frac{\partial\rho_0^{(1)}}{\partial\mu*}\right)^{-1}\right|_{Q=0} = 6B. \tag{51}$$

To get this derivative we have to take for $\rho_0^{(1)}$ its expression from (43).

From the condition $Q = 0$ we receive also:

$$\mu^* = \pm\mu_0^*|\tau|^{5/2\nu}; \quad \mu_0^* = G_0\left(\frac{2}{3}\frac{B_0}{G_0}\right)^{3/2}$$

and

$$\rho_0 = \bar{\rho}_0|\tau|^{\nu/2}; \quad \bar{\rho}_0 = \sqrt{\frac{2}{3}\frac{B_0}{G_0}}.$$

We have here two mutually receiprocal parabolic cylinder surfaces. On the plane $\tau = -\tau_0$ the intersection figure is an rectangular with the vertices $(-a, b)$, $(-a, -b)$, $(a, -b)$, (a, b) as it is shown on the fig. 5 and fig. 10.

c) In the region $Q < 0$, the equation (41) has three real solutions. It is more convenient to write them in trigonometrical form:

$$\rho_{01} = 2\sqrt{\left|\frac{V}{3}\right|}\cos\varphi/3, \qquad \rho_{02} = 2\sqrt{\left|\frac{V}{3}\right|}\cos\frac{\varphi + 2\pi}{3},$$

$$\rho_{03} = 2\sqrt{\left|\frac{V}{3}\right|}\cos\frac{\varphi + 4\pi}{3}, \tag{52}$$

---

[6] Not from the generalized condition $\frac{\partial \ln \Xi}{\partial \mu^*} = N$.

$$\varphi = \arccos t, \;\; t = -\frac{W}{2\left(-\frac{V}{3}\right)^{3/2}} = \frac{\mu^*}{a}, \;\; \text{that is:}$$

$$\mu^* = a\cos\varphi, \;\; \rho_{01} = b\cos\varphi/3, \;\; \rho_{02} = b\cos\frac{\varphi+2\pi}{3}, \;\; \rho_{03} = b\cos\frac{\varphi+4\pi}{3}. \tag{53}$$

In the vicinity of the point $\mu^* = -a$ we have $-1 = \cos\varphi$, $\varphi = \pi$. Substituting the values $\varphi = \pi$ into the solution, we obtain

$$\begin{aligned}
\rho_{01} &= 2\sqrt{\left|\frac{V}{3}\right|}\cos\frac{\pi}{3} = b\cdot\frac{1}{2},\\
\rho_{02} &= b\cos\frac{3\pi}{3} = -b,\\
\rho_{03} &= b\cos\frac{\delta\pi}{3} = b\cos\left(2\pi - \frac{\pi}{3}\right) = b\cdot\frac{1}{2}.
\end{aligned}$$

As we see, only the solution ρ_{02} coincides with the solution $\rho_0^{(1)}$ at the point $(-b-a)$.

For the case $\mu^* = a$, $\cos\varphi = 1$, $\varphi = 0$ we have

$$\begin{aligned}
\rho_{01} &= b\cos 0 = b,\\
\rho_{02} &= b\cos\frac{2\pi}{3} = -\frac{1}{2}b,\\
\rho_{03} &= b\cos\frac{4\pi}{3} = b\cos\left(\pi + \frac{\pi}{3}\right) = -\frac{1}{2}b.
\end{aligned}$$

Thus, we take the solution ρ_{01}.

The generalized chemical potential μ^* varies within $-a \le \mu^* \le a$. At the point $\mu^* = -0$, $\varphi = \frac{\pi}{2}$

$$\begin{aligned}
\rho_{02} &= b\cos\frac{\pi/2 + 2\pi}{3} = -b\cos\frac{\pi}{6} = -b\frac{\sqrt{3}}{2} = -\sqrt{\frac{1}{2}\frac{B}{G}},\\
\rho_{01} &= b\cos\frac{\pi}{6} = b\frac{\sqrt{3}}{2} = \sqrt{\frac{1}{2}\frac{B}{G}}.
\end{aligned}$$

So, at $\mu^* = 0$ there is a jump in ρ_0 along the ρ_0 axis which equals $\sqrt{3}b = \sqrt{2B/G}$.

Let us find the slope of the isotherms of chemical potentials μ^* which can be obtained by studying the behavior of $\rho_0^{(1)}$, ρ_{02} and ρ_{01} at the points:

$$(-a,-b), \;\; \left(0, -\frac{\sqrt{3}}{2}b\right), \;\; \left(0, \frac{\sqrt{3}}{2}b\right) \;\; \text{and} \;\; (a,b).$$

From $(-a,-b)$ to the left, and from (a,b) to the right, $\frac{\partial\mu^*}{\partial\rho_0^{(1)}} = 6B$ (see (51)).

Within the interval $-a \le \mu^* \le 0$, $-b \le \rho_{02} \le -\frac{\sqrt{3}}{2}b$, according to (53), $\mu^* = a\cos\varphi$; $\varphi = 3\arccos(\rho_{02}/b) - 2\pi$ and

$$\frac{\partial\mu^*}{\partial\rho_{02}} = \frac{\partial\mu^*}{\partial\varphi}\frac{\partial\varphi}{\partial\rho_{02}} = a(\sin\varphi)\frac{3}{b}\frac{1}{\sqrt{1-\frac{\rho_{02}^2}{b^2}}} = 3\frac{a}{b}\frac{\sin\varphi}{\sin\frac{\varphi+2\pi}{3}},$$

close to $\mu^* = -a$, $\varphi = \pi$

$$\frac{\partial\mu^*}{\partial\rho_{02}} = 9\frac{a}{b}\frac{\cos\pi}{\cos\pi} = 6B,$$

close to $\mu^* = -0$, $\varphi = \frac{3}{2}\pi$

$$\frac{\partial\mu^*}{\partial\rho_{02}} = 3\frac{a}{b}\frac{\sin\frac{3}{2}\pi}{\sin\left(\pi + \frac{\pi}{6}\right)} = 4B.$$

For the root ρ_{01} we have, analogously, $\frac{\partial\mu^*}{\partial\rho_{01}} = 3\frac{a}{b}\frac{\sin\varphi}{\sin\varphi/3}$, around $\mu = a$, according to (53), $\varphi = 0$

$$\frac{\partial\mu^*}{\partial\rho_{01}} = 9\frac{a}{b}\frac{\cos\varphi}{\cos\varphi/3}\bigg|_{\varphi=0} = 6B$$

around $\mu^* = 0$, $\varphi = \frac{\pi}{2}$

$$\frac{\partial\mu^*}{\partial\rho_{01}}\bigg|_{\mu^*=0,\varphi=\frac{\pi}{2}} = 3\frac{a}{b}\frac{\sin\pi/2}{\sin(\pi/6)} = 4B.$$

The plot of the generalized chemical potential isotherm as a function of ρ has the form shown in Fig. 5. Here we have a smooth continuation of curves $\rho_0^{(1)}$ to ρ_{02} at the point $(-b, -\mu*)$ and $\rho_0^{(1)}$ to ρ_{01} at the point $(b, \mu*)$.

It is very important to note here, that among solutions (51) only solution ρ_{02} in region $-b < \rho_0 < -d$ and only solution ρ_{01} in region $d < \rho_0 < b$ obey conditions (41) for maximum of the function $E(\rho_0)$. For all other values of ρ_{01}, ρ_{02}, ρ_{03} maximum of $E(\rho_0)$ in (39) cannot be realised.

We have completed investigations of the generalized chemical potential μ^*.

Having studied the integral (39), $\int\exp(NE(\rho_0))d\rho_0$, and the function $E(\rho_0)$, given in (40), we revealed the most essential changes in the

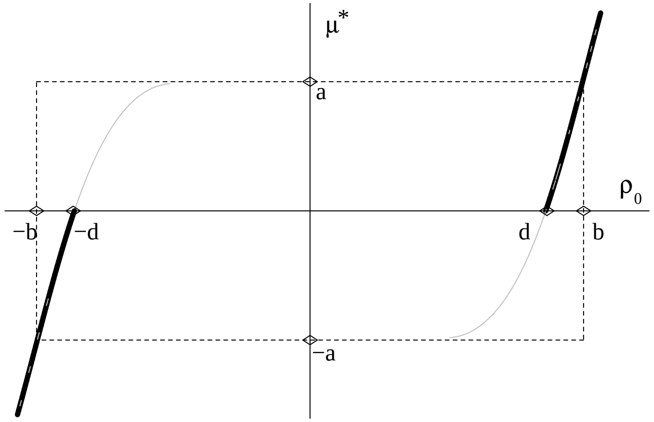


Figure 5. Chemical potential isotherm as a function of ρ_0. Here, $d = \frac{\sqrt{3}}{2}b$, $a = G\sqrt{\frac{2}{3}\frac{B}{G}}^{\,3} \sim \tau^{(5/2)\nu}$, $b = \sqrt{\frac{2}{3}\frac{B}{G}} \sim \tau^{\nu/2}$.

behavior of the partition function as well as in the behavior of the thermodynamic functions.

In order to describe the scenario of the phase transition at $T \leq T_c$, we have to extract from the entire set of integration results those that correspond to the integration as well as to the shift transformations of the variable ρ_0 and its Fourier transform ω_0. This will automatically concern the events connected with the generalized chemical potential μ^*.

Our main goal in this study is to describe what exactly is happening at $T < T_c$. Here, as well as in [21], we restrict ourselves to the narrow region around the critical point. The scenario of the phase transition is connected with the behavior of the generalized chemical potential μ^*. As it follows from Eq. (38), the plane $\mu^* = 0$ contains the coordinates of the critical point T_c, η_c.

Bringing together the obtained results, and taking the terms containing $\mu*$, let us write the initial partition function Ξ, according to Eqs. (19), (23), (25)-(28), and (32), (33), in the form of a product of two partition functions:

$$\Xi = \Xi^{(2)}\Xi_{\rho_0}, \tag{54}$$

where in $\Xi^{(2)}$ we included the results

$$\Xi^{(2)} = \Xi_0 \Xi_G Z(\tilde{\mathfrak{M}}_2, \tilde{\mathfrak{M}}_4)\Upsilon \exp -\beta(F_{cr} + F_{m_\tau}).$$

Expression $\Xi^{(2)}$ does not depend on μ^* (except for μ_0, which is considered to be a fixed function of density). All terms and effects connected with the behavior of μ^*, are gathered in the part Ξ_{ρ_0}. These terms enter the expression (26) in term $\exp(\sqrt{N}\mu^*(\rho_0 + \tilde{\mathfrak{M}}_1))$.

Partition function Ξ_{ρ_0} is of most interest to us. From (22) and (32)

$$\Xi_{\rho_0} = \exp\Big[\mu^*(1-\Delta)N\Big] \int e^{NE(\rho_0)} d\rho_0, \tag{55}$$

where

$$\begin{aligned}
&\Delta = -\Big(\mathfrak{M}_2\xi + \frac{1}{3}\mathfrak{M}_3\xi^2\Big);\\
&(1-\Delta)N = \sqrt{N}\tilde{\mathfrak{M}}_1;\\
&E(\rho_0) = \mu^*\rho_0 + B\rho_0^2 - G\rho_0^4.
\end{aligned}$$

In expression (55)

$$\ln \Xi_{\rho_0} = \frac{P_{\rho_0}(\mu^*, \eta, \tau)}{kT} V$$

pressure $P^{(2)}_{\rho_0}$ is the function of the generalized chemical potential μ^*, density η and temperature τ. Exclusion of the chemical potential is achieved by fulfilling the condition

$$\frac{\partial \ln \Xi_{\rho_0}}{\partial \mu^*} = N. \tag{56}$$

Depending on the regions where μ^* and ρ_0 are defined, shown in Fig. 5, the integral $\int\limits_{-\infty}^{\infty} \exp(NE(\rho_0))d\rho_0$ can be presented as a sum of integrals.

First, let us find its value for coexistence region (48)-(50)

$$\begin{aligned}
&\mu_0^* = \pm a = \pm G\left(\frac{2}{3}B/G\right)^{3/2}, \;\; a = a(\eta\tau),\\
&\rho_0 = \pm b = \pm\sqrt{\frac{2}{3}B/G}, \;\; b = b(\eta\tau).
\end{aligned} \tag{57}$$

Function $\exp(NE(\rho_0))$ has very sharp and large peaks at the points $\rho_0 = \pm b$

$$\begin{aligned}
&\exp\Big[NE(\rho_0 = b)\Big] = \exp\left[N\frac{2}{3}\frac{B^2}{G}\right],\\
&E''(\rho_0 = b) = -6B < 0.
\end{aligned}$$

Thus, for coexistence boundary we will have

$$\int \exp(NE(\rho_0))d\rho_0 =$$

$$= \exp(NE(b)) \int \exp\left[-\frac{1}{2}NE''(b)(b-\rho_0)^2\right] d\rho_0 =$$

$$= \exp(NE(b))|_{b=+b,-b}\sqrt{\frac{2\pi}{NE''(b)}}.$$

In $\ln \Xi$ we neglect the terms dependent on $\ln N$. The phase separation region will have the form:

$$\Xi_{\rho_0} = \exp N\left\{\mu^*(1-\Delta) + \mu^*\rho_0 + B\rho_0^2 - G\rho_0^4\right\}_{\substack{\mu^*=\pm a\\ \rho_0=\pm b}}. \tag{58}$$

We have here the value of $\Xi\rho_0$ in the general form, which will have the same external form at all maximum points of function $\exp NE(\rho_0)$.

The application of condition (56) also gives us a general relation for all subsequent calculations, valid at maximum points of the expression $\exp NE(\rho_0)$. From (55) we have:

$$N(1-\Delta+\rho_0)_{\rho_0=\rho_{max}} = N, \qquad \text{hence} \quad \rho_0|_{\rho_0=\rho_{max}} = \Delta. \tag{59}$$

Let us call Δ the order parameter. Substitution of $\rho_0 = \rho_{max} = \Delta$ in (58) leads to the cancellation of the terms $-\mu^*\Delta + \mu^*\rho_0 = 0$. The starting expression for determining $\Xi_{\rho_0}(\mu^*, \eta, \tau)$ will be

$$\Xi_{\rho_0} = \exp N\left\{\mu^* + B\rho_{max}^2 - G\rho_{max}^4\right\}_{\Delta=\rho_{max}}. \tag{60}$$

Returning to (57), we have two turning points:

$$\Delta = -b,\ \mu^* = -a \ \ \textit{and} \ \ \Delta = b,\ \mu^* = a;\ a = Gb^3,\ b = \sqrt{\frac{2}{3}\frac{B}{G}}. \tag{61}$$

Inserting them into (60), we get two turning points in the equation of state:

$$P_{\rho_0}(\eta\tau)_1 = \frac{NkT}{V}\left\{-Gb^3 + Bb^2 - Gb^4\right\} \tag{62}$$

and

$$P_{\rho_0}(\eta\tau)_2 = \frac{NkT}{V}\left\{Gb^3 + Bb^2 - Gb^4\right\}, \tag{63}$$

where

$$b = \sqrt{\frac{2}{3}\frac{B}{G}}. \tag{64}$$

According to (61) we have two particular values of parameter Δ and quantities b, namely,

$$\Delta = -\left(\mathfrak{M}_2\xi + \frac{1}{3}\mathfrak{M}_3\xi^2\right) = -b = -\sqrt{\frac{2}{3}\frac{B}{G}} \ \ \text{for} \ \ (62)$$

and

$$\Delta = -\left(\mathfrak{M}_2\xi + \frac{1}{3}\mathfrak{M}_3\xi^2\right) = b \ \ \text{for} \ \ (63).$$

Thus, for the range of densities for which $\rho_0 = \rho_0^{(1)}$, i.e., according to (59), function Δ varies within the ranges $\Delta = \rho_0^{(1)} < -b$ and $\Delta = \rho_0^{(1)} > b$, and μ^* is defined by Eq. (47). Partition function $\Xi_L^{(2)}$, according to (52), will have the form:

$$\Xi_{\rho_0} = \exp N\left\{qG\Delta^3 + B\Delta^2 - G\Delta^4\right\}, \ \ |\Delta| < \sqrt{\frac{2}{3}\frac{B}{G}}.$$

In expression (47) for

$$\mu^* = \Delta^3 4G\left(1 + \left(\frac{\gamma}{4}\right)^{1/3} - \frac{1}{12}|\gamma| + \frac{\sqrt{2}}{24}|\gamma|^{4/3} - \ldots\right)^{-3}$$

we have introduced the mean value of the fraction

$$4\left(1 + \left(\frac{\gamma}{4}\right)^{1/3} - \frac{1}{12}|\gamma| + \frac{\sqrt{2}}{24}|\gamma|^{4/3} - \ldots\right)^{-3} = q,$$

at $\mu^* = a$, $\gamma = 1$ and when $\mu \to \infty$, $\gamma \to 0$ quantity q varies in the range from one to four, $1 \le q \le 4$. So, we obtain the final expression for the equation of state in the range of densities

$$|\Delta| \ge b = \sqrt{\frac{2}{3}\frac{B}{G}},$$

$$P_{\rho_0}(\eta, \tau) = \frac{NkT}{V}\left\{B\Delta^2 + qG\Delta^3 - G\Delta^4\right\}. \tag{65}$$

On the phase separation boundary

$$\Delta = \pm b, \ \ q = 1.$$

Let us consider now the next regions (see Fig. 5). In the ranges of density

$$-a \le \mu^* < 0 \ \ \text{and} \ \ 0 < \mu^* \le a \tag{66}$$

for the integrated function in (55) we have two values ρ_0 that define the maxima of function $\exp(NE(\rho_0))$, namely (see (52)):

$$\rho_0 = \rho_{02} = b\cos\frac{\varphi + 2\pi}{3} \quad \text{for} \quad -a \le \mu^* < 0 \quad \text{and} \quad -b \le \rho_{02} < -\frac{\sqrt{3}}{2}b,$$

and

$$\rho_0 = \rho_{01} = b\cos\frac{\varphi}{3} \quad \text{for} \quad 0 < \mu^* \le a \quad \text{and} \quad \frac{\sqrt{3}}{2}b \le \rho_{01} \le b,$$

where $\varphi = \arccos\frac{\mu^*}{a}$.

From condition (56) or (59) we have:

$$\rho_{02} = \Delta, \quad \varphi = 3\arccos\frac{\Delta}{b} - 2\pi \quad \text{and} \quad -b \le \Delta \le -\frac{\sqrt{3}}{2}b, \tag{67}$$

and

$$\rho_{01} = \Delta \quad and \quad \varphi = 3\arccos\frac{\Delta}{b}, \quad \text{for} \quad \frac{\sqrt{3}}{2}b \le \Delta \le b. \tag{68}$$

We insert the above obtained expressions (67) and (68) into the form (60), valid for all regions, and get the equation of state for the densities that define the parameter Δ in the range $-b \le \Delta \le -\frac{\sqrt{3}}{2}b$:

$$P_{\rho_0}(\eta\tau) = \frac{NkT}{V}\left\{a\cos\varphi^* + B\Delta^2 - G\Delta^4\right\}, \tag{69}$$
$$\varphi^* = 3\arccos\frac{\Delta}{b} - 2\pi, \quad \Delta = b\cos\frac{\varphi + 2\pi}{3}, \quad \frac{3}{2}\pi \le \varphi \le \pi$$

and for densities $\frac{\sqrt{3}}{2}b < \Delta < b$

$$P_{\rho_0}(\eta\tau) = \frac{NkT}{V}\left\{a\cos\varphi^{**} + B\Delta^2 - G\Delta^4\right\},$$
$$\varphi^{**} = 3\arccos\frac{\Delta}{b}, \quad \Delta = b\cos\frac{\varphi}{3}; \quad 0 \le \varphi \le \frac{\pi}{2}. \tag{70}$$

Both regions of the curves of the equation of state meet at points $\Delta = -b$ and $\Delta = b$ with curves (65) which correspond to the values $\mu^* = -a$ and $\mu^* = a$ (see (53)). Indeed, in the first case (Eq. (69)) $\varphi = \pi$, in the second case (Eq. (70)) one takes $\varphi = 0$.

Finally, all we have to do is to compute in (55) the part of the isotherm that corresponds to the range

$$-\frac{\sqrt{3}}{2}b \le \rho_0 \le \frac{\sqrt{3}}{2}b$$

or, based on Eqs. (59), corresponds to the range

$$-\frac{\sqrt{3}}{2}b \le \Delta \le \frac{\sqrt{3}}{2}b, \quad \text{here} \quad \mu^* = 0.$$

We have the integral

$$J = \int\limits_{-\frac{\sqrt{3}}{2}b}^{\frac{\sqrt{3}}{2}b} \exp(NE(\rho_0))d\rho_0, \quad E(\rho_0) = B\rho_0^2 - G\rho_0^4. \tag{71}$$

The function to be integrated has a deep minimum at $\rho_0 = 0$, $\exp\left[NE(\rho_0)\right]|_{\rho_0=0} = 1$, $E''(\rho_0 = 0) = 2B > 0$ and two very high maxima at the edges at

$$\rho_0 = \rho_{max} = \frac{\sqrt{3}}{2}b, \quad E(\rho_{max}) = \frac{1}{4}\frac{B^2}{G}, \quad E''(\rho_{max}) = -4B < 0.$$

In the range $\left(-\frac{\sqrt{3}}{2}b \div \frac{\sqrt{3}}{2}b\right)$, the variable ρ_0 changes its sign. Parameter Δ changes its sign as well.

At the boundaries of the interval, $\exp(NE(\rho_0))$ sharply goes up and fuses on the left at $\rho_0 = \Delta = -\frac{\sqrt{3}}{2}b$ with $\exp(NE(\rho_{02}))$ and on the right at $\rho_0 = \Delta = \frac{\sqrt{3}}{2}b$ with $\exp(NE(\rho_{01}))$. The following condition is also satisfied:

$$\exp NE\left(-\frac{\sqrt{3}}{2}b\right)\Bigg|_{\mu^*=0} = \exp NE\left(\frac{\sqrt{3}}{2}p\right)\Bigg|_{\mu^*=0}.$$

The width of the interval: $\sqrt{3}b = \sqrt{2B/G} \sim |\tau|^{\nu/2}$. The larger is $|\tau|$, the wider is the interval. The slope of the curves at the edges of the interval is defined by the tangent lines, from the left side:

$$\left(\frac{dP_L}{d\rho_0}\right)_{\substack{\rho_0=\Delta\to-\frac{\sqrt{3}}{2}b \\ \Delta\leqslant-\frac{\sqrt{3}}{2}b}} = 4B$$

(this result coincides with the slope of the curve of $\mu^* \to -0$), and from the right side, $\mu^* = 0$,

$$\left(\frac{\partial P_L}{\partial\rho_0}\right)_{\rho_0=\Delta\to-\frac{\sqrt{3}}{2}b,\, \Delta\geqslant-\frac{\sqrt{3}}{2}b} = 2B\Delta - 4G\Delta^3 = 0,$$

and is horizontal.

The system passes from the stable state with the order parameter

$$\Delta = -\frac{\sqrt{3}}{2}b = -\sqrt{\frac{1}{2}\frac{B}{G}}$$

to another stable state with the order parameter

$$\Delta = \frac{\sqrt{3}}{2}b = \sqrt{\frac{1}{2}\frac{B}{G}},$$

"jumping over" the unstable state around $\Delta = 0$.

The integral J given in Eq.(71) splits into two integrals as follows:

$$J = \int_{-\frac{\sqrt{3}}{2}b}^{0} \exp\big(NE(\rho_0)\big)d\rho_0 + \int_{0}^{\frac{\sqrt{3}}{2}b} \exp\big(NE(\rho_0)\big)d\rho_0.$$

These integrals have the same magnitudes but opposite signs.

3. The equation of state

As it follows from (58) and (59), the starting expressions for the equation of state were

$$\frac{P_{\rho_0}V}{kT} = N\left\{\mu^* + B\rho_{max}^2 - G\rho_{max}^4\right\} \tag{72}$$

and

$$\rho_{max} = \Delta, \tag{73}$$

where ρ_{max} are the values of ρ_0 that maximize the integrated function in the integral $\int \exp[NE(\rho_0)]d\rho_0$ in (55). The integral is composed of a sum of integrals

$$\int\limits_{-\infty}^{\infty} \exp[NE(\rho_0)]d\rho_0 = \int\limits_{-\infty}^{-b} \cdots + \int\limits_{-b}^{-\frac{\sqrt{3}}{2}b} \cdots + \int\limits_{-\frac{\sqrt{3}}{2}b}^{\frac{\sqrt{3}}{2}b} \cdots + \int\limits_{\frac{\sqrt{3}}{2}b}^{b} \cdots + \int\limits_{b}^{\infty} \ldots, \tag{74}$$

where symbol "$\ldots$" denotes the exponential

$$\cdots \equiv \exp[NE(\rho_0)]d\rho_0.$$

All the integrals have already been done and given in Eqs. (61), (62) – for the curve $Q = 0$, in Eq. (64) – for $|\Delta| > b$ and in Eqs. (68), (69) for the regions $b \geq |\Delta| \geq \frac{\sqrt{3}}{2}b$ and integral J, given by (70) for the range $\left[-\frac{\sqrt{3}}{2}b, \frac{\sqrt{3}}{2}b\right]$. Now, we have to bring everything together.

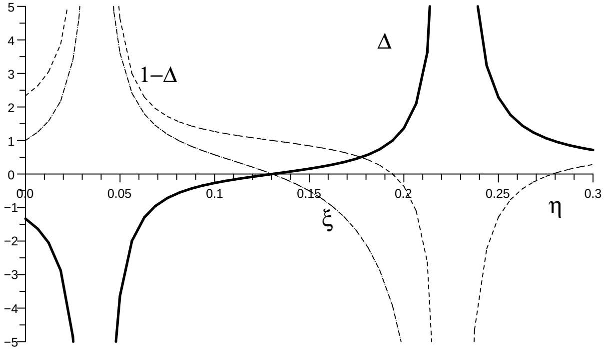


Figure 6. The dependence of Δ (solid line),$1-\Delta$ (dashed line), and ξ (dash-dotted line) on the density η. In the present work, the system is considered within the range $0.05 < \eta < 0.2$. In this interval, the values of cumulant $\mathfrak{M}_4$ are finite and negative.

In the starting Eq. (55) all quantities ξ, $\tilde{\mathfrak{M}}_1$, B and G (see Fig. 6) are continuous functions of density and temperature. The generalized chemical potential μ^* has the form of a smooth curve given in Fig. 5 as a function of ρ_0, and according to (59) as a function of Δ with two breaking points at $\mu* = 0$. As a consequence, the equation of state (72) and (74) will have the form of a broken curve as well.

Herein, one has a step-like change of the order parameter Δ from the value $-\frac{\sqrt{3}}{2}b$ to the value $\frac{\sqrt{3}}{2}b$ through the unstable improbable state $\Delta = 0$.

The work of the transition is a macroscopic quantity. Its value A equals the area of a rectangle with the height $\sqrt{3}b/2$ and the width equal to $\sqrt{3}b$ (see Fig. 7).

Now, we can gather the results together. Thus, from Eqs. (65), (69), (70) and from Fig. 7 we shall get the equation of state, P_{ρ_0} as a function

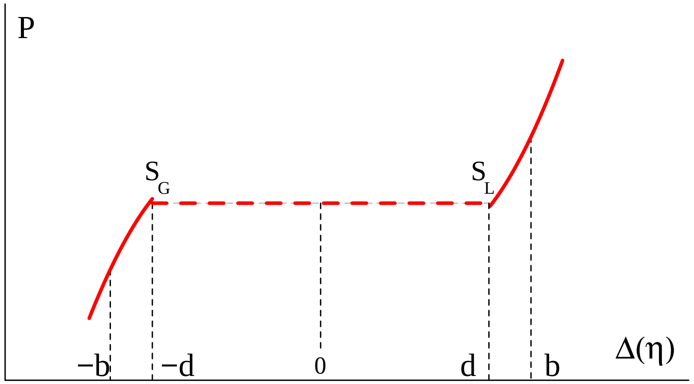


Figure 7. The isotherm of the equation of state, $d = \sqrt{3}b/2$.

of η and τ, $P_{\rho_0} = P_{\rho_0}(\eta,\tau)$:

$$\begin{aligned} P_{\rho_0} = kT\Big\{&\frac{N}{V}(\mathfrak{B}(\Delta) - qG\Delta^3)\Theta(-b-\Delta) + \\ &+\frac{N}{V}(\mathfrak{B}(\Delta) - a\cos\varphi^*)\Theta(\Delta+b)\Theta\Big(-\frac{\sqrt{3}}{2}b-\Delta\Big) + \\ &+\frac{N}{V}(\mathfrak{B}(\Delta) + a\cos\varphi^{**})\Theta\Big(\Delta\frac{\sqrt{3}}{2}b\Big)\Theta(b-\Delta) + \\ &+\frac{N}{V}(\mathfrak{B}(\Delta) + pG\Delta^3)\Theta(\Delta-b)\Big\} + \frac{A}{V}\Theta\Big(\Delta+\frac{\sqrt{3}}{2}b\Big)\Theta\Big(\frac{\sqrt{3}}{2}b-\Delta\Big); \end{aligned} \tag{75}$$

where $\mathfrak{B}(\Delta) = B\Delta^2 - G\Delta^4$, $\Delta = \Delta(\eta)$ according to (55), and factor $N/V = 6\eta/(\pi\sigma^3)$ ought to be taken for the densities corresponding to the value of $\Delta(\eta)$ (for example, see Fig. 7).

The isotherm curve of the equation of state will have the form given in Fig. 7.

The work of transition equals to the latent heat of vaporization. The latent heat is generated by the system at condensation and is supplied to the system at the boiling point under the gas-liquid transition or the liquid-gas

$$A_{GL} = \int_G^L P(\eta,\tau)dV.$$

The element of work is $dA = PdV$. Under transition between the points

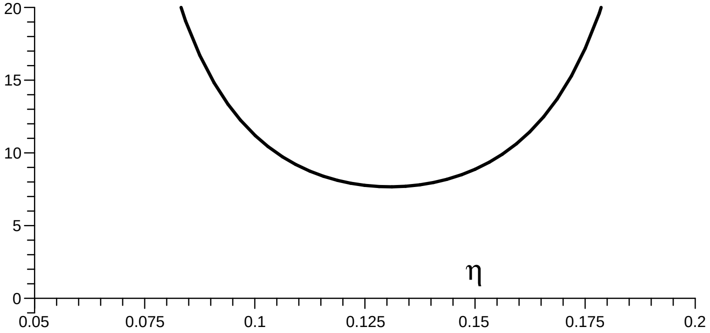


Figure 8. Plot of the derivative of Δ with respect to η.

$\Delta_G = -\frac{\sqrt{3}}{2}b$ and $\Delta_L = \frac{\sqrt{3}}{2}b$, the pressure and temperature of the system remain constant (see Fig. 8).

From equation of state (75) one obtains the pressure at points $\Delta_G = -\frac{\sqrt{3}}{2}b$ and $\Delta_L = \frac{\sqrt{3}}{2}b$ being equal to:

$$P_{GL} = \frac{NkT}{V}\frac{1}{4}\frac{B^2}{G}.$$

The element of work equals:

$$PdV = \frac{NkT}{V}\frac{1}{4}\frac{B^2}{G}dV,$$

where $dV = \frac{dV}{d\eta}\frac{d\eta}{d\Delta}d\Delta$. We take into account the simple correspondence between V and η, $\eta = \frac{N}{V}\frac{\pi}{6}\sigma^3$, here σ is diameter of elastic particle, hence $\frac{dV}{d\eta} = -\frac{V}{\eta}$.

The dependence between η and Δ is shown graphically in Fig. 6. Therein we also present the plot of the function $\xi(\eta) = \mathfrak{M}_3(\eta)/|\mathfrak{M}_4(\eta)|$. The system is considered in the density interval $\eta = 0,05 \div 0,2$. In this interval, the cumulant $\mathfrak{M}_4$ is finite and negative. (All the plots were built by V.O. Kolomiyets for argon Ar.) The critical density here corresponds to the values of $\eta_c \approx$ 0,13. In the narrow region close to η_c, a simple correspondence between η and Δ takes place. Thus, [7]:

$$dV = -\frac{V}{\eta}\frac{d\eta}{d\Delta}d\Delta = -\frac{V}{\eta}\frac{1}{\frac{d\Delta}{d\eta}}d\Delta.$$

---

[7] The plot of function $\frac{d\Delta}{d\eta}$ presented in Fig. 8, was kindly offered to us by V.O. Kolomiyets and R.Romanik

Now we can substitute the values of dV and rewrite the element of work in the integrable form:

$$dA_{GL} = P_{(G)}dV = \frac{NkT}{V}\frac{1}{4}\frac{B^2}{G}\left(-\frac{V}{\eta}\frac{1}{\frac{d\Delta}{d\eta}}\right)d\Delta.$$

As can be seen in Fig. 9, $\eta\frac{d\Delta}{d\eta}$ is a monotonous positive value, which at critical point has the exact value [8]

$$\eta_c\left(\frac{d\Delta}{d\eta}\right)_c = 1.$$

As a result, we receive for A_{GL}

$$\begin{aligned} A_{G,L} &= -Nk_BT\frac{1}{4}\frac{B^2}{G}\left(\eta\frac{d\Delta}{d\eta}\right)^{-1}\sqrt{3}b \\ &= -Nk_BT\frac{\sqrt{2}}{4}\left(\frac{B^5}{G^3}\right)^{1/2}\left(\eta\frac{d\Delta}{d\eta}\right)^{-1}. \end{aligned} \tag{76}$$

Very narrow to T_c one can write

$$A_{G,L} \simeq -Nk_BT\frac{\sqrt{2}}{4}\left(\frac{B^{5/2}}{G^{3/2}}\right). \tag{77}$$

This is the value of latent heat which is generated at the boiling point under the gas-liquid phase transition, as shown in Fig. 7.

Enclosing curves. Now, let us find the equations for the enclosing curves. They follow from the relations (48), (50) for the curve $Q = 0$, and from the relations (52-53) for the curve that encloses the area $\mu^* = 0$. The curve $Q = 0$ in expressions (72) and (75) means the points:

$$\rho_{0(max)} = |\Delta| = \pm b. \tag{78}$$

The curve that encloses the area $\mu^* = 0$ is given by the equation

$$\rho'_{0(max)} = |\Delta| = \frac{\sqrt{3}}{2}b, \tag{79}$$

that would correspond to the binodal equation as a function of τ and η.

In the explicit form, according to (55) and (65), for the curve (78):

$$\left|\mathfrak{M}_2\frac{\mathfrak{M}_3}{|\mathfrak{M}_4|} + \frac{1}{3}\mathfrak{M}_3\left(\frac{\mathfrak{M}_3}{\mathfrak{M}_4}\right)^2\right| = \sqrt{\frac{2}{3}\frac{B}{G}} \tag{80}$$

---

[8] The author is thankful to O.V. Patsahan for this information.

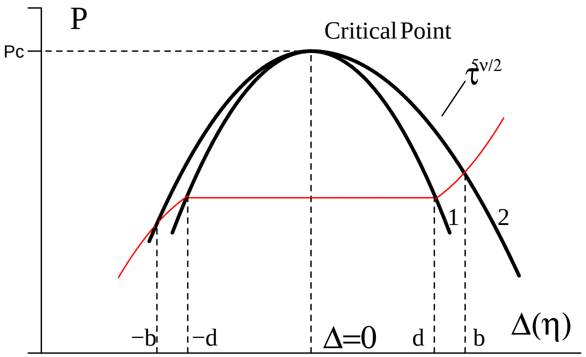


Figure 9. Curve 1 is the binodal curve as a function of the parameter Δ, Curve 2 denotes the states where $Q = 0$; here $d = \sqrt{3}b/2$.

and for the curve (79):

$$\left|\mathfrak{M}_2\frac{\mathfrak{M}_3}{|\mathfrak{M}_4|} - \frac{1}{3}\mathfrak{M}_3\left(\frac{\mathfrak{M}_3}{\mathfrak{M}_4}\right)^2\right| = \sqrt{\frac{1}{2}\frac{B}{G}}. \tag{81}$$

In order to get the curves corresponding to the condition $Q = 0$ in the plain (p, η), let us use the relation (59) between ρ_0 and Δ. In the case $\Delta = \rho_0^{(1)} = b$ it is given by relations (61-64), or by Eq. (75). We have two such points for $Q = 0$ [9]

$$\begin{aligned} P_{Q=0} &= \frac{NkT}{V}\left(\mathfrak{B}(\Delta) - G\Delta^3\right)_{\Delta=b}, \\ P_{Q=0} &= \frac{NkT}{V}\left(\mathfrak{B}(\Delta) + G\Delta^3\right)_{\Delta=b}, \end{aligned} \tag{82}$$

that are situated on different sides from the line $\Delta = 0$, and are on the cubic parabola $G\Delta^3$. Thus, this curve is asymmetrical with respect to the line $\Delta = 0$. At $\tau \to 0$, the locus of points corresponding to $Q = 0$ tend to the critical point as $\tau^{5/2\nu}$.

The binodal points correspond to the case $\mu^* = 0$ and $\Delta = \pm\frac{\sqrt{3}}{2}b$. On the curve of the equation of state (75), the following values of pressure correspond to them

$$P_{\text{binodal}} = \frac{NkT}{V}\left\{\mathfrak{B}(\Delta) - a\cos\varphi\right\}_{\Delta=-\frac{\sqrt{3}b}{2},\varphi=\frac{\pi}{2}}, \tag{83}$$

---

[9] Here the factor N/V is a function of Δ like it is in expression (75)

$$P_{\text{binodal}} = \frac{NkT}{V}\left\{\mathfrak{B}(\Delta) + a\cos\varphi\right\}_{\Delta=\frac{\sqrt{3}}{2}b,\varphi=\frac{\pi}{2}} .$$

The binodal points are situated symmetrically with respect to the line $\Delta = 0$.

The equality of chemical potentials. Equilibrium conditions. According to (23), the generalized chemical potential μ^* is equal to

$$\mu^* = h - \xi + |\alpha(0)|\frac{\tilde{\mathfrak{M}}_1}{\sqrt{N}},$$

where

$$h = \beta(\mu - \mu_0),\ \ \xi = \frac{\mathfrak{M}_3}{|\mathfrak{M}_4|},\ \ \tilde{\mathfrak{M}}_1 = \sqrt{N}(1-\Delta),\ \ \alpha(0) = \frac{N}{V}\frac{\tilde{\Phi}(0)}{k_BT}.$$

Near the points of the phase transition of the first order, $\Delta_{G,L} = \mp\sqrt{\frac{1}{2}B/G}$, the function μ^* tends to zero, and

$$\beta\mu = \beta\mu_0 + \xi - |\alpha(0)|(1-\Delta)|_{\Delta_G=-\sqrt{\frac{1}{2}B/G},\ \Delta_L=\sqrt{\frac{1}{2}B/G}} . \qquad (84)$$

Here all the functions on the right hand side are monotonous functions of density η, of the order parameter Δ, and of temperature τ. In the “jump”-points, according to (72), when $\mu^* = 0$, and according to (75), when$\varphi^* = \varphi^{**} = \frac{\pi}{2}$:

$$P_{\rho_0} = \frac{NkT}{V}\mathfrak{B} = \frac{NkT}{V}(B\Delta^2 - G\Delta^4). \qquad (85)$$

The pressure P_{ρ_0} has the same value on both points. When we were calculating the pressure P_{ρ_0}, we got a situation of two quite identical maximum-points on the curves $\exp N(B\Delta^2 - G\Delta^4)$ (see fig. 6). Thus, the probabilities of both states are identical.

Owing to a monotonous and continuous dependence between P_{ρ_0} and η, ξ, $|\alpha(0)|$, Δ in (85), we arrive at a conclusion that the chemical potential μ in (84) is a simple function P_{ρ_0}. So, when in the points $\Delta = \pm\sqrt{\frac{1}{2}B/G}$ we have the same vales of pressure and temperature, then in both points along (85) the values of chemical potential are also the same

$$\mu(P_{\rho_0}(\Delta_G,\tau),\tau) = \mu(P_{\rho_0}(\Delta_L,\tau),\tau)\ . \qquad (86)$$

The points $\Delta = \pm\sqrt{\frac{1}{2}B/G}$ are those points on the binodal between which there occurs a gas-liquid phase transition of the first order.

We have got all the three equilibrium conditions for the phase transition of the first order located on the binodal curve in the points $\Delta_G = -\sqrt{\frac{1}{2}B/G}$; $\Delta_L = \sqrt{\frac{1}{2}B/G}$:

$$\tau_G = \tau_L,\ \ P_G = P_L,\ \ \mu_G = \mu_L. \qquad (87)$$

Overheated liquid and overcooled gas. Making calculations in (39)–(41), we used the method of the steepest descent. Therefore we were looking for such values of ρ_0 for which the function $\exp(NE(\rho_0))$ in (39) possessed an absolute maximum.

We had three solutions in formula (51). From those we were obliged to take only one part of the solution ρ_{02}, i.e., its values in the area $\frac{\pi}{2} \le \varphi \le \pi$, and only one part of the solution ρ_{01}, i.e., its values in the area $0 \le \varphi \le \frac{\pi}{2}$. We altogether rejected the solution ρ_{03}, as well as parts for solutions ρ_{02} for $0 \le \varphi \le \frac{\pi}{2}$ and ρ_{01} for $\frac{\pi}{2} \le \varphi \le \pi$.

Now we shall analyse the shapes of ρ_{01}, ρ_{02}, ρ_{03} in the whole area $0 \le \varphi \le \pi$. We have

$$\rho_{01} = b\cos\frac{\varphi}{3};\ \ \rho_{02} = b\cos\frac{\varphi+2\pi}{3};\ \ \rho_{03} = b\cos\frac{\varphi+4\pi}{3};$$

$$b = \sqrt{\frac{3}{2}\frac{B}{G}};\ \ \mu^* = a\cos\varphi;\ \ 0 \le \varphi \le \pi,$$

$$-a \le \mu^* \le a;\ \ a = G(b)^{3/2}.$$

Instead of Figs. 5 and 7, where we have only two parts of solutions $\rho_{02}\left(\frac{\pi}{2} \le \varphi \le \pi\right)$ and $\rho_{01}\left(0 \le \varphi \le \frac{\pi}{2}\right)$, we present in Fig. 10 a complete picture of all isoterms (87) within the area $Q = 0$, for $Q < 0$.

We shall translate these curves into the equation of state $P_{\rho_0}(\eta\tau)$, see Fig. 8, for whole intervals $-b \le \Delta \le b$, $0 \le \varphi \le \pi$. Therefore, we have to extend the curve $a\cos\varphi$ in formula (69) to the interval $0 \le \varphi \le \frac{\pi}{2}$, and extend the curve $a\cos\varphi$ in formula (70) to interval $\frac{\pi}{2} \le \varphi \le \pi$ and add the curve ρ_{03}. As a result, we obtain Fig. 11, an *a la* Van der Waals curve for equation of state.

Now we shall show that these additional parts cannot be really realised.

An initial form used for equation of state (75) was the formula (55) for the partition function Ξ_{ρ_0}

$$\int \exp\Big(NE(\rho_0)\Big)d\rho_0,$$

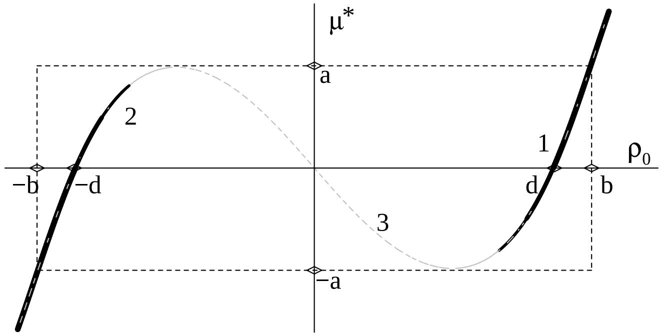


Figure 10. Function μ^* in the whole region $Q < 0$.

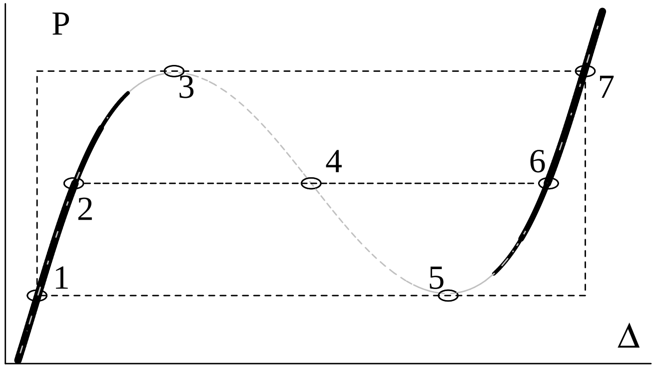


Figure 11. A complete set of the curve of equation of state given in fig. 7 with some new parts (which cannot be realised).

where $E(\rho_0) = \mu^*\rho_0 + B\rho_0^2 - G\rho_0^4$. Owing to the fact that in exponent we have the factor N, for calculation we used the steepest descent method. We were going along the lines of maxima of the function $\exp\Big(NE(\rho_0)\Big)$. The result is shown in Fig. 7 where the isotherm of the equation of state $P(\tau,\eta)$ is shown. Starting with the small values of Δ, we come from the left to the point $\Delta = -\frac{\sqrt{3}}{2}b$ where a jump to the point $\Delta = \frac{\sqrt{3}}{2}b$ occurs with a further smooth continuation along the lines of maxima of $\exp\Big(NE(\rho_0)\Big)$. In all these cases, the integrand was a measure of probability. We were going along the most probable states.

Now we shall estimate the measures of probabilities of the states marked in fig. 11 by numbers 1, 2, 3, 4, 5, 6, 7.

According to (57a) in points 1 and 7, for the function $\exp\Big(NE(\rho_0)\Big)$, we have very high maxima equal to:

$$\max\ \exp\Big(NE(\rho_0)\Big)\Big|_{\rho_0=b,-b} = \exp\Big(N\frac{2}{3}\frac{B^2}{G}\Big).$$

In points 2 and 6, according to the formula (71), the function $\exp\Big(NE(\rho_0)\Big)$ has also got two very high maxima equal to

$$\max\ \exp\Big(NE(\rho_0)\Big)\Big|_{\rho_0=\pm\frac{\sqrt{3}}{2}b} = \exp N\frac{1}{4}\frac{B^2}{G}.$$

However, in points $\rho_0 = \pm\frac{1}{2}b$, the probability density is vanishing small:

$$\exp\Big(NE(\rho_0)\Big)_{\rho_0=\pm\frac{1}{2}b} = \exp\Big(-N\frac{1}{12}B^2/G\Big).$$

Thus, points $\rho_0 = \Delta = \pm\frac{1}{2}b$ are unattainable for the system. In the point $\rho_0 = \Delta = 0$ we have $\exp\Big(NE(\rho_0)\Big) = 1$.

Therefore, the curve ρ_{03} can be never realised. And the path marked in Fig. 11 by a thin line should not be regarded.

Nevertheless, if we have very high maxima in the points 2 and 6, there may exist some probable states in a very close vicinity to those points along the curves $\rho_0(1,2)$ and $\rho_0(7,6)$. They are superheated and supercooled states.

Concluding remarks

We solved the problem of the critical point of liquid-gas transition.

An equation of state is obtained, which demonstrates an interdependence between the pressure p, temperature τ and density η in the critical region in the vicinity of T_c and η_c.

The shape of isotherm curve in vicinity of T_c, $T < T_c$ is presented on Fig. 7.

Between the points Δ_G and Δ_L on the "binodal" there occurs the first-order phase transition from the gas state S_G into the liquid state Δ_L. The corresponding value of the latent heat (76) is proportional to the area of a rectangular with apexes Δ_G, Δ_L (Fig. 7).

The equilibrium conditions at the phase transition of the first order as well as overheated and overcooled states are presented. In Fig. 11 we described the real situation of the process of the phase transition of the first order. We have got two boundary curves, Fig.9. The first one is the curve corresponding to the condition $Q = 0$. The second one is the curve where the generalized chemical potential is equal to zero, $\mu^* = 0$. The locus of its points describes is related to the beginning and to the end of the first order phase transition. This is the binodal curve.

It is also shown that the points belonging to the spinodal curve are not realistic at all.

The points which correspond $\Delta = 0$ (rectilinear diameter) are of a very small probability. Therefore, those may be regarded as some transition points when the system undergoes a phase transition from vapour to liquid or vice versa, supported be the latent heat.

In the way the problem is stated, we are restricted to the region of minimum of the Fourier-image of attraction potential (the wave vectors $k \leqslant B$). We assume that the main events concerning the phase transition concentrate in this region. We supposed that the problem at $k > B$ had a known solution, which can be presented, e.g., in the form of the virial series with convergent integrals. More accurate results could have been produced by renormalization of the quantities B in G in the region of $k < B$. However, as shown in [20], the correction is inessential.

To describe the interaction between the particles at short-range distances, the reference system of elastic particles is introduced with the corresponding cumulant values $\mathfrak{M}_1$, $\mathfrak{M}_2$, $\mathfrak{M}_3$, $\mathfrak{M}_4$. A principal question in solving the problem in general is the discovery of wide plateaus in cumulants $\mathfrak{M}_n$ at small values of k in the vicinity to the point $k = 0$. Corresponding calculations, permitting us to reduce the problem of gas-liquid point to the Ising model in external field, have been carried out by my collaborators I. Idzyk and V.O. Kolomiyets.

The effect of short-range interactions concentrated in a reference system is essential in solving our problem. The values $\mathfrak{M}_2(0)$, $\mathfrak{M}_3(0)$ and $\mathfrak{M}_4(0)$ produce an expression for the order parameter $\Delta = -\Big(\mathfrak{M}_2(0)\xi + \frac{1}{3}\mathfrak{M}_3(0)\xi^2\Big)$, $\xi = \frac{\mathfrak{M}_3(0)}{|\mathfrak{M}_4(0)|}$, which is the main variable of the equation of state. The natural "crossing" of the short-range and long-range interactions takes place in the equation $\frac{\partial \ln \Xi_L}{\partial \mu^*} = N$ (see (59) and (60)) under substitution of the generalized chemical potential μ^* by its values as functions of τ and η.

As it was already mentioned, our analysis is correct in the region of densities η, where the cumulant $\mathfrak{M}_4$ is finite and negative, namely at $0{,}02 \leqslant \eta \leqslant 0{,}2$. The widening of density region is possible at a different choice of short-range interactions $\psi(r_{ij})$ in the starting equations (4), (5). Let us note that integration is carried out in the region of collective variables $\rho_{\mathbf{k}}$, ρ_0. That is why the values of initial coefficients a_2 and a_4, presented in Table 2, are essential.

In our problem, the equation of state of the reference system as a part of general equation of state is not separated. It is probable, however, that adding $-p_0V = -\mu_0N + dF_0$ after separating the contribution of free energy, F_0 of the reference system may be canceled.

The equation of state $P_{\rho_0} = P(\tau, \eta)$ below $T = T_c$ is obtained by separately studying the short-range and long-range interaction forces in different phase spaces. The short-range interaction was considered in Descartes space of particle coordinates, whereas the long-range attraction was studied on the basis of collective variables $\rho_{\mathbf{k}}$ defined on the space of wave vectors $\mathbf{k}$. This was the idea proposed by N. N. Bogolyubov in his work [37] and in his suggestions given to us in mid 50-ies of the last century. They have led then to virial expansions for electrolyte solutions.

In general, after a twenty-year long break, connected with my political activities, I would like to express the heartfelt gratitude to my dear friends, collaborators at the Institute for Condensed Matter Physics of the NAS of Ukraine, in particular to I.M. Mryglod and O.L. Ivankiv, for permanent assistance in my returning to the "liquid-gas critical point" problem and for the first discussion of this work at the Institute seminar. I am sincerely grateful to L.A. Bulavin for discussion of this work at the seminar of the physics faculty at T. Shevchenko Kiev National university and to A.G. Zagorodni for the discussion of the work at the seminar of the Bogolubov Institute for Theoretical Physics NAS of Ukraine.

I am sincerely grateful to M.P. Kozlovsky and especially to R. Romanik for fruitful discussions and for assistance in proof-reading of the

paper and for the preparation of illustrations.

I heartily thank Yu. Holovatch for useful discussions of the results and for assistance in preparing an English version of the paper.

I heartily thank O.V. Patsahan for proof-reading the paper and for useful pieces of advice concerning calculations of latent heat of transition.

And my special thanks to V.O. Kolomiyets and I.M. Idzyk for successful formulation of the results of Refs. [13–17] in temperature region $T > T_c$ and $T = T_c$, presented in [19], for analysis of the functions Δ and ξ, performed also by R. Romanik and presented graphically in Figs. 5 and 7, and for the willingness to come back to phase transitions problems.

References

1. Yukhnovskii I.R., Idzyk I.M., Physics of Many Particle Systems, Kiev, Naukova Dumka, 1983, **3**, 18 (in Russian).
2. Zubarev D.M., Dokl. Acad. Nauk SSSR, 1954, **47**, N 8, 2856-2861.
3. Hubbard J., Phys. Rev. Lett., 1954, **3**.
4. Hubbard J., Proc. R. Soc. A, 1957, **A240**, 539.
5. Yukhnovskii I.R., Zhurn. Eksp. Theor. Phys., 1958, **34**, 379 (in Russian).
6. Yukhnovskii I.R., Golovko M.F., Statistical Theory of Classical Equilibrium Systems, Kiev, Naukova Dumka, 1980, 372 p. (in Russian).
7. Yukhnovskii I.R. Partition Function for the Three-dimensional Ising Model, Dokl. Akad. Nauk USSR, 1977, **232**, N 2, 312-315.
8. Yukhnovskii I.R. Three-dimensional Ising Model. Integration of the Partition Function in the Collective Variable Method. Part 1. Ukr. Phys. Journ., 1977, **22**, N 2, 325-335; Part 2. Ukr. Phys. Journ., 1977, **22**, N 3, 483-492.
9. Yukhnovskii I.R., Phase Transitions of the Second Order. Collective Variables Method, Kiev, Naukova Dumka, 1985, 252 p. (in Russian). See also World Scientific. Singapore, 1987, 327p.; La Rivista del Nuovo Cimento, 1989, **12**, N 1, 119.
10. Ginzburg V.L., Landau L.D., Zhurn. Eksp. Theor. Phys., 1960, **72**, 1064.
11. Braut R., Phase Transitions, Benjamin New York, 1963; Moscow, Mir, 1967.
12. Patashinskii G.V. and Pokrovskii V.L., Fluctuation Theory of Phase Transitions, Moscow, Nauka, 1975 (in Russian).
13. Ma S.K., Modern Theory of Critical Phenomena, Benjamin New York, 1976.

14. Yukhnovskii I.R., Kozlovskii M.P., Pylyuk I.V., Microscopic Theory of Phase Transitions in Three-Dimensional Systems, Lviv, Eurosvit, 2001, 592 p. (in Ukrainian).
15. Yukhnovskii I.R., On the statistical theory for condensed systems with long-range and short-range interparticle interactions, Prepr. Inst. Theor. Phys., ITP-79-133P, Kiev, 1979, 34 p. (in Russian).
16. Yukhnovskii I.R., Idzyk I.M., Thermodynamical limit near the critical-point liquid-vapour, Prepr. Inst. Theor. Phys., ITP-85-97P, Kiev, 1985 (in Russian).
17. Yukhnovskii I.R., Idzyk I.M., Kolomiets V.O., The Formulation of the Problem of a Liquid-Gas Critical Point in Collective Variables Method, Prepr. Inst. Theor. Phys., ITP-87-15P, Kiev, 1987, 29 p. (in Russian).
18. Idzyk I.M., Kolomiets V.O., Yukhnovskii I.R., Critical point on the liquid-vapour system in collective variables method, Theor. Math. Phys., 1987, **73**, N 2, 264-280.
19. Yukhnovskii I.R. The grand partition functional in collective variables method and its application for investigations on the liquid-gas phase transition, Proc. of the Steklov Inst. of Mathematics, 1992, Iss.2, 223p.
20. Yukhnovskii I.R. The Chemical Potential Isotherm in the Region of the Liquid-Gas Phase Transition, Prepr. Inst. Theor. Phys., ITP-88-43P, Kiev, 1988, 35 p. (in Russian).
21. Yukhnovskii I.R., Idzyk I.M., Kolomiets V.O., Investigation of a Homogeneus Many-Particle System in the Vicinity of the Critical Point, Journ. Stat. Phys., 1995, **80**, Nos 1/2, 405.
22. Yukhnovskii I.R., Patsahan O.V., Grand Canonical Distribution for Multicomponent Systems in the Collective Variables Method with a Distinquished Reference System, Prepr. Inst. Theor. Phys., ITP-87-163P, Kiev, 1987, 28 p.
23. Yukhnovskii I.R., Idzyk I.M., Kolomiets V.O., Liquid-gas critical point. Proc. of the First Confer. on Renorm. Group. Edited by D.Y.Shirkov, Singapore, World Sci. Pub., 1988, 430-446.
24. Hubbard I. and Scofield P., Phys. Lett. A., 1972, **40**, 245.
25. Vause C. and Sac J., Phys. Rev. A, 1980, **21**, 2099.
26. Pelissetto, Vicari E., Critical Phenomena and Renormalization-Group Theory, Physics Reports, 2002, **368**, 549-727.
27. Parisi G., Statistical Field Theory, Persens Books, 1998, 352.
28. Fisher M.E., Orkoulas G., The Yang-Yang Anomaly in Fluid Criticality. Eksperiment and Scaling Theory, Phys. Rev. Lett., 2000, **85**, 696-699.

29. Kim Y.C., Fisher M.E., Orkoulas G., Asymmetric fluid criticality. I. Scaling with pressure mixing, Phys. Rev. E., 2003, **67**, 061506.
30. Wang I., Anisimov M.A., Nature of vapour-liquid asymmetry in fluid criticality, Phys. Rev. E., 2007, **75**, 051107.
31. Johannes D. van der Waals, The equation of state for gases and liquids, Nobel Lecture, December 12, 1910.
32. Juan J. de Pablo, Qiliang Yan, Fernando A. Escovedo, Ann. Rev. Phys. Chem., 1999, **50**, 377-411.
33. Wilson K.G. Renormalisation Group and Critical Phenomena. 1. Renormalisation group and Kadanoff scaling picture, Phys. Rev. B, 1971, **4**, N 9, 3174-3183. 2. Phase-space cell analisis of critical behaviour, Ibid, 3184-3205.
34. Wilson K.G., Quantum field-theory models in less than 4 dimensions, Phys. Rev. D, 1973, **7**, N 10, 2911-2926.
35. Wilson K. and Kogut J., Phys. Rev., 1974, **75**, 12.
36. Wilson K. and Kogut J. Renormalisation Group and ε-expansion, Moscow, Mir, 1975, 254 (in Russian).
37. Kadanoff L.P., Scaling Laws for Ising Models near T_c, Physics, 1966, **2**, N 6, 263.
38. Landau L.D., Livshits E.M., Statistical Physics. Part 1, Moscow, Nauka, 1976, 584 (in Russian).
39. Bogolubov N.N., Selected works, Kiev, Naukova Dumka, 1970, **2**, 129, 194 (in Russian).
40. Carnahan N.F. and Starling K.E., J. Chem. Phys., 1969, **51**, 635.

CONDENSED MATTER PHYSICS

The journal **Condensed Matter Physics** is founded in 1993 and published by Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine.

AIMS AND SCOPE: The journal **Condensed Matter Physics** contains research and review articles in the field of statistical mechanics and condensed matter theory. The main attention is paid to physics of solid, liquid and amorphous systems, phase equilibria and phase transitions, thermal, structural, electric, magnetic and optical properties of condensed matter. Condensed Matter Physics is published quarterly.

ABSTRACTED/INDEXED IN: Chemical Abstract Service, Current Contents/Physical, Chemical&Earth Sciences; ISI Science Citation Index-Expanded, ISI Alerting Services; INSPEC; “Referatyvnyj Zhurnal”; “Dzherelo”.

CONTACT INFORMATION:
Institute for Condensed Matter Physics
of the National Academy of Sciences of Ukraine
1 Svientsitskii Str., 79011 Lviv, Ukraine
Tel: +38(032)2761978; Fax: +38(032)2761158
E-mail: cmp@icmp.lviv.ua   http://www.icmp.lviv.ua