# Investigation in the Vicinity of the Critical Point

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It is shown that the events occuring in the vicinity of the critical point can be described in full by means of the collective variables with the appropriate reference system. The partition function containing the explicit form for the quartic measure density is obtained and integrated. Expressions for the critical temperature, critical density and critical chemical potential surfaces are calculated.

After having solved the three dimensional Ising model [1] and having obtained expressions for the free energy and other thermodynamical functions, we are going to describe the critical point phenomena in the liquid-gas system [2].

To solve the problem we use the method of collective variables (CV) with a reference system (RS). The background of the method was set forth in the monography [3] and in the papers [4, 5] concerned with electrolyte theory. But there we did not pay ample attention to the thermodynamical limit $V \to \infty$, $N \to \infty$, $N/V = \text{const}$. At that time the phase transition problems were not within the scope of our interest, and therefore there was no reason for introducing the collective variable $\varrho_0$ connected with the number of particles in the system and the order parameter arising in the vicinity of the critical point.

The method proposed here is essentially different from the previous statistical methods described in the papers [6, 7] also pertaining to certain reference systems. In those papers the attractive part of the interaction potential is considered as a perturbation. This assumption is not correct in the phase transition region, where collective effects induced by attractive forces predominate.

In our method the attractive forces are regarded in a collective variables phase space, and the Jacobian that describes the transition to the CV phase space is modulated by the RS measure density. In the CV phase space there exists the possibility to include automatically in the description the indirect attractive interactions between particles. This leads to screened interactions that become long-range in the vicinity of the critical point, this being the main reason for the phase transition phenomena.

The application of the methods recently worked out for the three dimensional Ising model allowed us to get explicit forms for the free energy and other thermodynamical functions and to give a complete description of the thermodynamics in the vicinity of the critical point.

## 1. Statement and Treatment of the Problem

Consider a system of $N$ particles in the volume $V$ at the temperature $T$. From the equation of state point of view we distinguish between three (or four) domains on the $P$, $N/V$ plane. The first is the one above the critical isotherm. There any increase of pressure will not lead to the liquid state. Below the critical isotherm, in the region of great pressure we have the liquid state and in the region of small pressure the gaseous state. Besides there is a region of thermodynamical instability, where the gas-liquid transition occurs.

Our aim is to perform calculations in the vicinity of the critical point. We have to find expressions for the critical point and the free energy $F - F_{\text{id}} = -kT \ln Z$. All other functions are then obtained in the known way.

The system under consideration belongs to an Ising universality class, so we shall get Ising critical indices.

The main aim is to compute the partition function

$$Z = \int \exp(-\beta V)\, \mathrm{d}\Gamma_N \tag{1.1}$$

$$\beta = 1/kT,\ \mathrm{d}\Gamma_N = \mathrm{d}\boldsymbol{r}_1 \ldots \mathrm{d}\boldsymbol{r}_N,\ \mathrm{d}\boldsymbol{r} = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,.$$

The potential energy $\mathscr{V}$ consists of two parts:

$$\mathscr{V} = \chi + \phi\,.$$

$$\chi = \frac{1}{2} \sum_{i,j=1}^{N} \chi(\boldsymbol{r}_{ij})$$

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is the sum of pair interactions between hard spheres,

$$\chi(r) = \begin{cases} \infty & \text{when} \quad r < \sigma \\ 0 & \text{when} \quad r \geq \sigma \end{cases}, \tag{1.2}$$

and $\phi = \frac{1}{2} \sum_{i,j=1}^{N} \phi(r_{ij})$, where $\phi(r)$ is a regular function of $r$; it contains an attraction at large distances. $\phi(r)$ must belong to the $\mathrm{L}_2$ space and possesses a Fourier transform $\tilde{\phi}(k) = \int \phi(r)\, e^{-i\boldsymbol{k}\boldsymbol{r}}\, \mathrm{d}r$. We adopt for $\phi(r)$ Morse's potential

$$\phi(\boldsymbol{r}) = \varepsilon \cdot \left[\exp\left(-2\frac{r - R_0}{\alpha}\right) - 2\exp\left(-\frac{r - R_0}{\alpha}\right)\right],$$

which is suitable for our calculations. Its Fourier transform is

$$\begin{aligned} \tilde{\phi}(k) &= 16\pi\alpha^3 \varepsilon \varphi\, [\varphi(k^2\alpha^2 + 4)^{-2} - (1 + k^2\alpha^2)^{-2}], \\ \tilde{\phi}(0) &= -16\pi\varepsilon\alpha^3 \varphi(1 - \varphi/16), \\ \tilde{\phi}(B) &= 0, \\ (B\alpha)^2 &= (4 - \sqrt{\varphi})(\sqrt{\varphi} - 1)^{-1}; \end{aligned} \tag{1.3}$$

here

$$\varphi = \exp R_0/\alpha, \quad R_0/\alpha < \ln 16;$$

$$\tilde{\phi}(k) < 0, \quad 0 \leq k \leq B, \quad \tilde{\phi}(k) \geq 0, \quad k > B.$$

It is easy to see that consideration of a chain of interactions of the type

$$\phi(r_{12}) - \beta\frac{N}{V}\int \phi(r_{13})\,\phi(r_{32})\,\mathrm{d}\boldsymbol{r}_3 + \beta^2\frac{N^2}{V^2}\int \phi(r_{13})\,\phi(r_{34})\,\phi(r_{42})\,\mathrm{d}\boldsymbol{r}_3\,\mathrm{d}\boldsymbol{r}_4 + \ldots$$

leads to a screened potential

$$g(\boldsymbol{r}) = \sum_{\boldsymbol{k}} \frac{1}{V}\,\frac{\tilde{\phi}(k)}{1 + \beta N/V\,\tilde{\phi}(k)}\,\exp(i\boldsymbol{k}\boldsymbol{r}),$$

which can take a long-range character like $\sim 1/r$ near the critical point.

This is the reason why we have to treat the potentials $\chi$ and $\phi$ by different statistical techniques.

The partition function $Z$ is written in an extended phase space. It consists of the space of Cartesian coordinates, which is connected with hard sphere interactions, and the collective variables space, connected with the attractive interactions:

$$Z = \int \exp(-\beta\phi(\varrho))\exp(-\beta\chi(r))\,J(\varrho\, r)\,\mathrm{d}\Gamma_N \prod_{\boldsymbol{k}} \mathrm{d}\varrho_{\boldsymbol{k}}, \tag{1.4}$$

where $\{\varrho_k\}$ is the set of collective variables (CV). Each variable $\varrho_k$ is a quantity connected with a magnitude of density fluctuations mode in the following manner:

$$\begin{aligned} &\frac{1}{\sqrt{N}} \sum_{i=1}^{N} \exp(-i\boldsymbol{k}\boldsymbol{r}_i) \\ &\quad = \int \varrho_{\boldsymbol{k}}\,\delta\left(\varrho_{\boldsymbol{k}} - \frac{1}{\sqrt{N}}\sum_{i=1}^{N}\exp(-i\boldsymbol{k}\boldsymbol{r}_i)\right)\mathrm{d}\varrho_{\boldsymbol{k}}, \end{aligned} \tag{1.5}$$

where $\delta(\ldots)$ is Dirac's delta function. There is an additional important reason for introducing the CV phase space. Among these variables there is one connected with the order parameter. For the regarded problem this variable is $\varrho_0 \sim \sqrt{N}$. The subscript $k = 0$ corresponds to the minimum of the potential $\tilde{\phi}(k)$.

Insertion on of the CV $\varrho_0$ in the canonical partition function $Z$ (see (1.4)) is not a trivial operation. It means a transition to the great canonical ensemble. The rigourous way to introduce $\varrho_0$ in integral (1.4) is the following:

$$\begin{aligned} Z = \int &\exp\{-\beta\phi(\varrho) - \beta\chi(r) + \mu(\sqrt{N}\varrho_0 - N)\} \\ &\cdot J(\varrho\, r)\,\delta(\varrho_0 - \sqrt{N})\,\mathrm{d}\varrho_0 \prod_{\boldsymbol{k}} \mathrm{d}\varrho_{\boldsymbol{k}}\,\mathrm{d}\Gamma_N. \end{aligned} \tag{1.6}$$

To get coincidence with the great canonical ensemble we have to look for $\mu$ from the equation

$$\partial \ln Z/\partial\mu = 0 \tag{1.7}$$

and have to take the thermodynamical limit $V \to \infty$, $N \to \infty$, $N/V = \text{const}$.

We shall consider the hard spheres system with the potential energy $\chi(r)$ as the reference system (RS).

Let us extract in (1.6) the partition function $Z_0$ of the RS and integrate over the set of Cartesian coordinates. We come to the functional form

$$Z = Z_0 \int \exp\left[\frac{1}{2}\sum_{\boldsymbol{k}} \alpha(k)\,(\varrho_{\boldsymbol{k}}\varrho_{-\boldsymbol{k}} - 1)\right] \tag{1.8}$$

$$Z = Z_0 \int w_6(\varrho)(\mathrm{d}\varrho). \tag{1.16}$$

where $\alpha(k) = N/V\,\beta\tilde{\phi}(k)$. $J(\varrho)$ is the transition Jacobian from the Cartesian coordinates to collective variables:

$$\begin{aligned} J(\varrho) = &\lim_{\substack{N\to\infty \\ V\to\infty \\ N/V = \text{const}}} \int Z_0^{-1}\exp(-\beta\chi(r)) \\ &\cdot \prod_{\boldsymbol{k}} \delta\left(\varrho_{\boldsymbol{k}} - \frac{1}{\sqrt{N}}\sum_{i=1}^{N}\exp(-i\boldsymbol{k}\boldsymbol{r}_i)\right)\mathrm{d}\Gamma_N. \end{aligned} \tag{1.9}$$

It differs from the usual from of a Jacobian by the RS's density of probability $Z_0^{-1}\exp(-\beta\chi(r))$. One may say that the Jacobian is modulated by the RS's distribution. The free energy of the RS,

$$F_0 = -kT\ln Z_0,$$

is to be known as well as the RS's equation of state and the RS's pair distribution function:

$$\frac{F_0 - F_{\mathrm{id}}}{NkT} = \frac{4\eta - 3\eta^2}{(1-\eta)^2};\quad \frac{p_0 V}{NkT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \tag{1.10}$$

$$\begin{aligned}\mathcal{M}_2(\boldsymbol{k}_1,\boldsymbol{k}_2) &= \delta_{\boldsymbol{k}_1+\boldsymbol{k}_2}\left(1 + \frac{N}{V}\int e^{-i\boldsymbol{k}_1\boldsymbol{r}}(F_2(\boldsymbol{r})-1)\,\mathrm{d}\boldsymbol{r}\right)\\ &= \delta_{\boldsymbol{k}_1+\boldsymbol{k}_2}\{1 + A(\eta)/\varkappa^3(\sin\varkappa - \varkappa\cos\varkappa) - B(\eta)/\varkappa^4\\ &\qquad\cdot[2\varkappa\sin\varkappa - (\varkappa^2-2)\cos\varkappa - 2] + C(\eta)/\varkappa^6\\ &\qquad\cdot[(4\varkappa^3 - 24\varkappa)\sin\varkappa - (\varkappa^4 + 12\varkappa^2 + 24)\cos\varkappa + 24]\}^{-1},\end{aligned} \tag{1.11}$$

$$A = \frac{24\eta(1+2\eta)^2}{(1-\eta)^4},\quad B = \frac{36\eta^2(2+\eta)^2}{(1-\eta)^4},\quad C = \frac{12\eta^2(1+2\eta)}{(1-\eta)^4};$$

here

$$\eta = \pi/6\,\sigma^3 N/V,\quad \varkappa = k\sigma.$$

The main problem now is the evaluation of the Jacobian $J(\varrho)$. When we write $\delta$-functions in their explicit integral form and perform integration over all $\mathrm{d}\boldsymbol{r}_1\ldots\mathrm{d}\boldsymbol{r}_N$, we shall get for $Z$ the following initial functional form:

$$\begin{aligned}Z = Z_0\int\exp\Bigg\{&\sum_k\left[-\frac{1}{2}\alpha(k)(\varrho_{\boldsymbol{k}}\varrho_{-\boldsymbol{k}}-1) + i2\pi\omega_{\boldsymbol{k}}\varrho_{\boldsymbol{k}} - \frac{1}{2}\mathcal{M}_2(k)\omega_{\boldsymbol{k}}\omega_{-\boldsymbol{k}}\right] - i2\pi\sqrt{N}\omega_0 + \mu(\sqrt{N}\varrho_0 - N)\\ &+ \sum_{n\geq 3}\sum_{\boldsymbol{k}_1\ldots\boldsymbol{k}_n}\mathcal{M}_n(\boldsymbol{k}_1,\ldots,\boldsymbol{k}_n)\omega_{\boldsymbol{k}_1}\ldots\omega_{\boldsymbol{k}_n}\Bigg\}(\mathrm{d}\varrho)(\mathrm{d}\omega).\end{aligned} \tag{1.12}$$

Here the $\{\omega_{\boldsymbol{k}}\}$ are variables conjugated to the CVs $\{\varrho_{\boldsymbol{k}}\}$. They may be interpreted as variables connected with fluctuations of some internal stress field;

$\mathcal{M}_n(\boldsymbol{k}_1,\ldots,\boldsymbol{k}_n)$ are semiinvariants which consist of the RS's correlation functions; e.g. $\mathcal{M}_2(\boldsymbol{k}_1,\boldsymbol{k}_2)$ is given by (1.11), $\mathcal{M}_3(\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3) = \sqrt{N}^{-1}\delta_{\boldsymbol{k}_1+\boldsymbol{k}_2+\boldsymbol{k}_3}\cdot(1+3\mu_2(\boldsymbol{k}_1)+\mu_3(\boldsymbol{k}_2,\boldsymbol{k}_3))$, and $\mathcal{M}_n(\boldsymbol{k}_1,\ldots,\boldsymbol{k}_n)$ is a function of $\mu_1$, $\mu_2,\ldots,\mu_n(\boldsymbol{k}_1,\ldots,\boldsymbol{k}_n)$, where $\mu_n(\boldsymbol{k}_1,\ldots,\boldsymbol{k}_n)$ is the $n$-th correlation function of the RS.

We say that $w_n(\varrho)$ is the $n$-th basic measure density if all momenta $\int w_n(\varrho)\varrho_{\boldsymbol{k}_1}\ldots\varrho_{\boldsymbol{k}_m}(\mathrm{d}\varrho)$ are convergent at the given temperature and density. It was proved [1] that for the description of events in the vicinity of the critical point it is sufficient to keep only $\mathcal{M}_1$, $\mathcal{M}_2$, $\mathcal{M}_3$, $\mathcal{M}_4$, $\mathcal{M}_5$, and $\mathcal{M}_6(\boldsymbol{k}_1,\ldots,\boldsymbol{k}_6)$ in the exponent in (1.12). All the rest terms may be moved down in a series. In such a way we come to the sixfold basic density measure

$$\begin{aligned}w_6(\varrho) = \int\exp\Bigg[&\sum_{\boldsymbol{k}}\left(-\frac{1}{2}\alpha(k)(\varrho_{\boldsymbol{k}}\varrho_{-\boldsymbol{k}}-1) + i2\pi\omega_{\boldsymbol{k}}\varrho_{\boldsymbol{k}}\right)\\ &+ \mu(\sqrt{N}\varrho_0 - N) + \sum_{1\leq n\leq 6}\sum_{\boldsymbol{k}_1,\ldots,\boldsymbol{k}_n}\mathcal{M}_n(\boldsymbol{k}_1,\ldots,\boldsymbol{k}_n)\omega_{\boldsymbol{k}_1}\ldots\omega_{\boldsymbol{k}_n}\Bigg](\mathrm{d}\omega).\end{aligned} \tag{1.13}$$

Let us denote $\mathcal{D}_6 = \sum_{n>6}\sum_{\boldsymbol{k}_1,\ldots,\boldsymbol{k}_n}\mathcal{M}_n(\boldsymbol{k}_1,\ldots,\boldsymbol{k}_n)\,\omega_{\boldsymbol{k}_1}\ldots\omega_{\boldsymbol{k}_n}$. Then the complete expression for the partition function may be written as a sum of momenta of the basic density measure

$$Z = Z_0\int w_6(\varrho)(1 + \mathcal{D}_6 + \tfrac{1}{2}(\mathcal{D}_6)^2 + \ldots)(\mathrm{d}\varrho).$$

Each of them is convergent at arbitrary temperatures and densities including the critical point.

Above the critical point the Gaussian density measure

$$w_2(\varrho) = \int \exp\left( -\frac{1}{2} \sum_k [\alpha(k)(\varrho_{\boldsymbol{k}} \varrho_{-\boldsymbol{k}} - 1) - i 4\pi \omega_{\boldsymbol{k}} \varrho_{\boldsymbol{k}} + \mathscr{M}_2(\boldsymbol{k}) \omega_{\boldsymbol{k}} \omega_{-\boldsymbol{k}}] + \mu(\sqrt{N} \varrho_0 - N) \right) (\mathrm{d}\omega)$$

is a basic one.

In the phase transition area we have to deal with the zero approximation

$$Z = Z_0 \int w_6(\varrho)(\mathrm{d}\varrho). \tag{1.16}$$

To describe the vicinity of the critical point the quartic measure $w_4(\varrho)$ is sufficient. The quartic measure consists of the semiinvariants $\mathscr{M}_1$, $\mathscr{M}_2$, $\mathscr{M}_3$ and $\mathscr{M}_4(\boldsymbol{k}_1, \boldsymbol{k}_2, \boldsymbol{k}_3, \boldsymbol{k}_4)$.

Expressions (1.12), (1.13), (1.16) remind us of some phenomenological forms of Ginsburg-Landau and Wilson [8]. But the main distinction is that the explicit form of $\mathscr{M}_n(\boldsymbol{k}_1, \ldots, \boldsymbol{k}_n)$ has become known.

The problem now turns out to be very difficult. The semiinvariants $\mathscr{M}_n(\boldsymbol{k}_1, \ldots, \boldsymbol{k}_n)$ are so complicated functions of $\boldsymbol{k}_1, \ldots, \boldsymbol{k}_n$ that it seems to be quite hopeless to take the integral (1.16) or even the much simpler integral

$$Z = Z_0 \int w_4(\varrho)(\mathrm{d}\varrho) \tag{1.17a}$$

and to solve the problem of the critical point and of the liquid-gas phase transition.

Nevertheless, Nature gives us some chance: As it follows from formula (1.3), the function $\alpha(k) = N/V\, \beta \tilde{\phi}(k)$ is positive in region $k > B$ and negative in region $k < B$. For that reason in (1.12) and (1.13) we may perform integration over all $\varrho_{\boldsymbol{k}}$ and $\omega_{\boldsymbol{k}}$ with Gaussian basic density measure*. We get a new basic density measure. Its form is like (1.13) but the coefficients $\tilde{\mathscr{M}}_1, \tilde{\mathscr{M}}_2, \ldots, \tilde{\mathscr{M}}_6$ are renormalised and the sums over $\boldsymbol{k}$ run from $k = 0$ to $k = B$.

Thus this new measure $\tilde{w}_6(\varrho)$ describes a distribution of a limited number of $\varrho_{\boldsymbol{k}}$ with the indices $0 \le k \le B$.

Here $B$ may be considered as a boundary of the Brillouin semizone of some lattice with a period $C = \pi/B$. Further, it is necessary to consider $\alpha(k)$ to be a periodic function with $2B$ period setting $\alpha(k) = \sum_n \alpha(\boldsymbol{k} + B\boldsymbol{n})$, $\tilde{\mathscr{M}}_n(\boldsymbol{k}_1, \ldots, \boldsymbol{k}_n)$ is to be treated in the same way. The number of lattice sites in periodicity volume $V$ is equal to

$$N_B = V/c^3 = V(B/\pi)^3.$$

For example, for the Morse's potential

$$N_B = N \frac{V}{N} \left( \alpha^{-2} \frac{4 - \sqrt{\varphi}}{\sqrt{\varphi} - 1} \right)^{3/2} < N \frac{(\ln 16)^3 \sigma^3}{6\pi^2 R_0^3 \eta} < N. \tag{1.17b}$$

We have received an essential result: The problem of the calculation of the configurational integral of a spatially homogeneous system of particles may be reduced to the problem formulated on an adequate space lattice**.

To come to a final result we shall extremely simplify the interaction potential $\tilde{\phi}(k)$. We shall use for $\tilde{\phi}(k)$ a parabolic approximation, setting

$$\alpha(k) = \begin{cases} \alpha(0)(1 - 2b^2 k^2), & k < B, \\ 0, & k > B. \end{cases} \tag{1.18}$$

Then we neglect renormalising of semiinvariants and set $\tilde{\mathscr{M}}_1 = \mathscr{M}_1, \ldots, \tilde{\mathscr{M}}_6 = \mathscr{M}_6$.

From the plot of $\mathscr{M}_2(k)$ one can see that in a "Brillouin zone" $(0 \le k \le B)$ the functions $\mathscr{M}_2(k), \ldots, \mathscr{M}_6(k)$ may be replaced by parabolas or even by constants: $\mathscr{M}_2(k) \approx \mathscr{M}_2(0), \ldots, \mathscr{M}_6(k) \approx \mathscr{M}_6(0)$ when $k < B$ and $\eta > 0{,}1$, where $\eta = \frac{\pi}{6} \frac{N}{V} \sigma^3$ is the dimensionless density. Then it is easy to show that

$$\begin{aligned} \mathscr{M}_2(0) &= \frac{\langle (N - \langle N \rangle)^2 \rangle}{N} = \frac{1}{N} \frac{\partial \langle N \rangle}{\partial \mu} \\ &= k T \chi_T N/V, \end{aligned} \tag{1.19}$$

where $\chi_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$ is the compressibility of the reference system;

$$\mathscr{M}_3(0) = \frac{1}{N} \frac{\partial^2 \langle N \rangle}{\partial \mu^2};$$

$$\mathscr{M}_4(0) = \frac{1}{N} \frac{\partial^3 \langle N \rangle}{\partial \mu^3} - 3 \langle (N - \langle N \rangle)^2 \rangle^2.$$

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* It may be shown that for every attractive potential of the type $\phi(r) = -\phi_0 r^{-6}(1 - \exp(-q r^n))$ there exists such a point $B$ that for $k > B$ holds $1/\mathscr{M}_2(k) > |\tilde{\phi}(k)|$ and there exists the possibility to integrate with the Gaussian measure density for all $\varrho_{\boldsymbol{k}}$ and $\omega_{\boldsymbol{k}}$ with $k > B$.

** Here we do not discuss the problem of the most suitable type of the lattice.

And from thermodynamics it follows that

$$\begin{aligned} \mathcal{M}_3(0) &= \mathcal{M}_2^2(0) + \eta\, \mathcal{M}_2(0)\frac{\partial \mathcal{M}_2(0)}{\partial \eta} \\ \mathcal{M}_4(0) &= \mathcal{M}_2^3(0) + 4\eta\, \mathcal{M}_2^2(0)\frac{\partial \mathcal{M}_2(0)}{\partial \eta} + \eta^2 \mathcal{M}_2(0)\left(\frac{\partial \mathcal{M}_2(0)}{\partial \eta}\right)^2 + \eta^2 \mathcal{M}_2^2(0)\frac{\partial^2 \mathcal{M}_2(0)}{\partial \eta^2}\,. \end{aligned} \tag{1.20}$$

As a result, the initial form of the integrand in the partition function is completely determined.

Now the problems of the phase transition and of the critical point can be solved.

We start with the expression

$$Z = Z_0\, e^{\mu N} Z_\mu ,$$

where

$$\begin{aligned} Z_\mu = \int \exp\Bigg\{ &-(a_1 + \mu\sqrt{N})\varrho_0 - \frac{1}{2}\sum_{k<B}\alpha(k)(\varrho_k\varrho_{-k} - 1) - i2\pi \sum_{k<B}\omega_{\boldsymbol{k}}\varrho_{\boldsymbol{k}} - \frac{1}{2}\tilde{\mathcal{M}}_2(0)\sum_{k<B}\omega_{\boldsymbol{k}}\omega_{-\boldsymbol{k}} \\ &- \frac{(i2\pi)^4}{4!}\frac{1}{N_B}|\tilde{\mathcal{M}}_4(0)| \sum_{\substack{\boldsymbol{k}_1,\ldots,\boldsymbol{k}_4 \\ k_i<B}} \omega_{\boldsymbol{k}_1}\ldots\omega_{\boldsymbol{k}_4}\delta_{\boldsymbol{k}_1+\ldots+\boldsymbol{k}_4}\Bigg\}(\mathrm{d}\omega)^{N_B}(\mathrm{d}\varrho)^{N_B}. \end{aligned} \tag{1.21}$$

Here we have the possibility to separate the variables $\{\omega_{\boldsymbol{k}}\}$ and to integrate over them. As a result we get an expression for $Z_\mu$* ready for further investigations

$$Z_\mu = C\int \exp\Bigg[-(a_1 + \mu\sqrt{N})\varrho_0 - \frac{1}{2}\sum_{k<B}(a_2 + \alpha(k))\,\varrho_{\boldsymbol{k}}\varrho_{-\boldsymbol{k}} - \frac{1}{4!}\frac{1}{N_B}a_4 \sum_{\substack{k_1,\ldots,k_4 \\ k_i \leqq B}} \varrho_{\boldsymbol{k}_1\ldots\boldsymbol{k}_4}\Bigg](\mathrm{d}\varrho)^{N_B}. \tag{1.22}$$

Here (see [2])

$$\tilde{\mathcal{M}}_2(0) = \mathcal{M}_2(0) - \mathcal{M}_3^2(0)/2|\mathcal{M}_4(0)|,\ \tilde{\mathcal{M}}_4 = \frac{N}{N_B}\mathcal{M}_4,\quad a_1 = \sqrt{N}\,\mathcal{M}_3(0)/|\mathcal{M}_4(0)| + \alpha(0)\,\tilde{\mathcal{M}}_1,$$

$$\tilde{\mathcal{M}}_1 = \sqrt{N}\left(1 + \frac{\mathcal{M}_2(0)\,\mathcal{M}_3(0)}{|\mathcal{M}_4(0)} + \frac{\mathcal{M}_3^3(0)}{3|\mathcal{M}_4(0)|^2}\right).$$

## 2. Free Energy in the Vicinity of the Critical Point

Formula (1.21) for $Z_\mu$ coincides with the partition function of an Ising model in an external field. The method of integration is already known. One can use the results previously obtained for the three dimensional Ising model in [1].

In the process of integration of the partition function over the CVs $\varrho_k$ one may distinguish three regions with respect to $k$: the first one is $B_{m_\tau} < k < B$, here the measure density is quartic (or sixfold) and the recursion equation's solutions are of the renormalisation group type; the second one $0 < k < B_{m_\tau}$ is the region of the limit Gaussian regime (LGR), where we can integrate with some special Gaussian measure, as a basic one; and the third region consists of the $k = 0$ point, here we perform integration over $\varrho_0$.

While the measure density and the manner of integration in the first domain is known at the present time and is widely discussed now because of the nonlinear form of the recursion equations, the integration in the LGR is not so popular.

Note that the probability density over the CVs $\varrho_{\boldsymbol{k}}$ in the domain $0 < k \le B_{m_\tau}$ is of the form

$$w_{\mathrm{LGR}}(\varrho) = \exp\Bigg\{-(a_1 + \mu\sqrt{N})\varrho_0 - \frac{1}{2}\sum_{k<B_{m_\tau}}\mathrm{d}^{(m_\tau)}(k)\,\varrho_{\boldsymbol{k}}\varrho_{-\boldsymbol{k}} - \frac{1}{4!}\frac{a_4^{(m_\tau)}}{N_{m_\tau}}\sum_{\substack{\boldsymbol{k}_1\ldots\boldsymbol{k}_4 \\ k_i<B_{m_\tau}}}\varrho_{\boldsymbol{k}_1}\ldots\varrho_{\boldsymbol{k}_4}\delta_{\boldsymbol{k}_1+\ldots+\boldsymbol{k}_4}\Bigg\}\,. \tag{2.1}$$

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* We have used shifts such that the quantity $\omega_0 = \omega_0' + [i/2\pi]\,\mathcal{M}_3(0)/|\mathcal{M}_4(0)|$ and $\varrho_0 = \varrho_0' + \tilde{\mathcal{M}}_1$.

Here the coefficients have a non analytical dependence on the relative temperature $\tau$, namely

$$d^{(m_\tau)}(k) \sim \tau^{2\nu}, a_4^{(m_\tau)}/N_{m_\tau} \sim \tau^{\nu}, \quad \tau = \left| \frac{T - T_c}{T_c} \right|;$$

$\nu$ is the critical exponent of the correlation length,

$$\left.\begin{array}{l} d^{(m_\tau)}(k) > 0 \\ d^{(m_\tau)}(0) = 0 \end{array}\right\} \text{ when } T > T_c,$$
$$\left.\begin{array}{l} d^{(m_\tau)}(B_{m_\tau}) = 0 \\ d^{(m_\tau)}(0) \quad < 0 \end{array}\right\} \text{ when } T < T_c, \tag{2.2}$$
$$m_\tau = -\ln|\tau|/\ln E_1 + \text{const}.$$

It is very instructive to investigate first the function $F_\mu = -kT\ln Z_\mu$ and after that the free energy $F = -kT\ln Z$.

The thermodynamic potential $F_\mu$ depends on $\mu$, the density $N/V$ and the temperature $T$. From (1.21) one can readily see that on the surface $\mu = -a_1/\sqrt{N}$ we get a pure problem of a second order phase transition, we have the genuine Ising model in zero external field.

The results of the integration over $\varrho_k$ in the region $B_{m_\tau} < k < B$ yield the equation for $T_c$:

$$k T_c = 2\frac{N}{V}\tilde{\phi}(0)\left\{a_2 + \left[a_2^2 + 4\frac{a_4 R_{12}}{\bar{u}^{1/2}(R_{11} - E_2)} \cdot \left(1 - \bar{r} + \frac{R_{12}^0 \bar{u}^{1/2}}{R_{11} - E_2}\right)\right]^{1/2}\right\}^{-1}$$
$$(1 - \bar{r} + R_{12}^0 (R_{11} - E_2)^{-1} \bar{u}^{1/2}), \tag{2.3}$$

where $r^* = \beta\tilde{\phi}(0)\bar{r}$, $u^* = (\beta\tilde{\phi}(0))^2\bar{u}$ are the coordinates of the fixed point, $R_{ij}$, $E_1$, $E_2$ are the matrix elements and eigenvalues which arrive when we apply the fixed point method for the solution of the recursion equations. The expression for $T_c$ is valid for all $\mu$, because $\mu$ refers to the integration over the $\varrho_0$ variable, which is not involved in the integration over the first region.

As it follows from our computations, the dependence of $T_c$ on the density is very weak. The surface (2.3) is the plane $T = T_c$ parallel to the $\mu$, $N/V$ coordinate plane. The plane $T = T_c$ intersects the surface $\mu_0 = -a_1/\sqrt{N}$ along the line of the critical temperatures. On this surface, moving across the critical temperatures line, in arbitrary direction, we shall have to do with a phase transition of the second order (with respect to the function $F_\mu = -kT\ln Z_\mu$).

But the surface $\mu_0$ is not physical. To obtain $\mu$ we have first to integrate $Z_\mu$ over all $\varrho$, including $\varrho_0$, and then find the true value of the chemical potential from the condition $\partial \ln Z\mu/\partial\mu = N$. In the result for $T > T_c$ we get

$$\sqrt{N}\mu = -a_1 + 2(\tilde{\mathscr{M}}_1 - \sqrt{N})A, \tag{2.5}$$

where

$$A = \frac{a_4^{(m_\tau)}}{4N_{m_\tau}} \sum_{k<B_{m_\tau}} \langle \varrho_{\boldsymbol{k}} \varrho_{-\boldsymbol{k}} \rangle \simeq \frac{1}{4}\alpha(0)\tau^{2\nu}.$$

The chemical potential surface (2.5) intersects the surface $\mu_0 = -a_1/\sqrt{N}$ along the line $(\tilde{\mathscr{M}}_1 - \sqrt{\mathrm{N}})/\sqrt{\mathrm{N}} = 0$, where $\tilde{\mathscr{M}}_1$ is given by (1.22). The surface

$$\Delta = (\tilde{\mathscr{M}}_1 - \sqrt{N})/\sqrt{N} = 0 \tag{2.6}$$

is the critical concentrations surface. If we neglect a weak dependence on temperature, it turns into a plane parallel to the $\mu - T$ coordinate plane.

The intersection of the (2.3) and (2.6) surfaces gives the coordinate of the critical point.

At $T < T_c$ on the $\mu_0$ surface we have three values of the order parameter:

$$\varrho_0^{(1)} = 0, \quad \varrho_0^{(2)} = \sqrt{-v}, \quad \varrho_0^{(3)} = -\sqrt{-v}, \tag{2.7}$$

where

$$v = -3\frac{|d^{(m_\tau)}(0)|}{a_4^{(m_\tau)} N} N_{m_\tau} \sim \tau^{\nu}.$$

The curve of the thermodynamic potential $F_{\mu_0}$vs. $\varrho_0$ has the form corresponding to a second order phase transition (see Figure 1).

In fact, there are three values of the chemical potential at $T < T_c$:

$$\mu_1 = -a_1/\sqrt{N} + 4\mathscr{B}\Delta, \text{ corresponding to } \varrho_0^{(1)},$$
$$\mu_2 = -a_1/\sqrt{N} + 4\mathscr{B}(\varrho_0^{(2)} + \Delta),$$

and

$$\mu_3 = -a_1/\sqrt{N} + 4\mathscr{B}(\varrho_0^{(3)} + \Delta), \tag{2.8}$$

where

$$\mathscr{B} \simeq 1/2\,|d^{(m_\tau)}(0)| \sim \tau^{2\nu}.$$

For each of them we have to find an expression for the free energy. It occurs that all three values of $\varrho_0^{(i)}$ and,

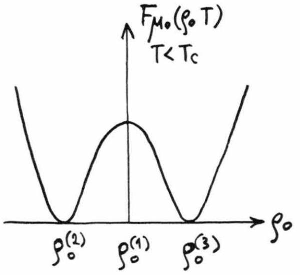

Fig. 1. The thermodynamic potential $F_{\mu_0}(\varrho_0)$ below the critical point.

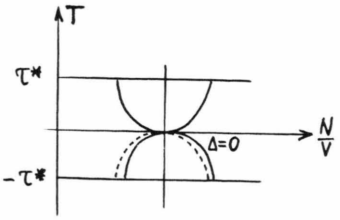

Fig. 2. The boundary curves of the critical region in the vicinity of the critical point.

correspondingly, $\mu_i$ inserted in the formula

$$F = -kT \ln Z_\mu(\varrho_0^{(i)}) - \mu N k T$$

lead to the same value of the free energy,

$$F - F_{\mathrm{id}} - F_0 = F_1 + F_2(\Delta),$$

where $F_1$ is the part of the free energy connected with the integrals in the critical region* ($B_{m_\tau} < k \leq B$) and in the LGR region ($0 < k \leq B_{m_\tau}$). $F(\Delta)$ is the part of the free energy containing the contributions from integration over $\varrho_0$ and from chemical potential,

$$F(\Delta) = -NkT\left[(\alpha(0) + \mathscr{B})\Delta^2 - \frac{a_4^{(m_\tau)} N}{4 N_{m_\tau}} \Delta^4\right]. \tag{2.9}$$

The curves $F(\Delta)$ and $F_\mu(\varrho_0)$ differ in shape. As $\mathscr{B} \sim \tau^{2\nu}$ and $\alpha(0)$ is negative and independent on $\tau$, the minimum of $F(\Delta)$ takes place at $\Delta = 0$, while the other two roots of $F'(\Delta) = 0$ are imaginary.

Thus it seems to be true that for the description of the system below $T_c$, where the first order phase transition occurs, it is necessary to consider the integral of the sixfold basic measure density.

Finally, let us consider the size of the critical region. It is located around the critical density line $\Delta = 0$. The boundary of the critical region is determined from the condition that the discriminant of the equation $F_\mu'(\varrho_0) = 0$ is equal to zero:

$$\left|\frac{v}{3}\right|^3 = \left|\frac{w}{2}\right|^2, \text{ where } w = \frac{(a_1/\sqrt{N} + \mu_i)4!\, N_{m_\tau}}{a_4^{(m_\tau)} N}.$$

After substitution of the chemical potential values it takes the form (see Fig. 2)

$$\Delta = \pm \frac{4}{3}\left(A \frac{N_{m_\tau}}{N} a_4^{(m_\tau)}\right)^{1/2} = \pm \Delta^{>} \tau^{\nu/2} \quad \text{when} \quad T > T_c,$$

and

$$\Delta = \left(\frac{12 B N_{m_\tau}}{a_4^{(m_\tau)} N}\right)^{1/2} [\pm 1 + (27)^{-1/2}] = \pm \Delta^{<} \tau^{\nu/2}$$

when $T < T_c$.

The critical region is bounded from above and below by the straight lines [1] $|\tau| < \tau^*$. For $|\tau| > \tau^*$ the events connected with the renormalization group symmetry are absent, $\tau^* \approx 0,1$.

In this way, starting from first principles, we have shown the possibility to obtain a complete description of the thermodynamics in the near vicinity of the critical point.

[1] I. R. Yukhnovskii, Phase Transitions of the Second Order. The Collective Variable Method, Singapore: World Scientific 1987, 327 pp.

[2] I. R. Yukhnovskii, I. M. Idzyk, and V. A. Kolomiets, Preprint ITP-87-15P, Kiev 1987; Preprint ITP-87-16P, Kiev 1987.

[3] I. R. Yukhnovskii and M. F. Golovko, Statistical Theory of Classical Equilibrium Systems. Kiew: Naukova Dunika 1980 (in Russian).

[4] I. R. Yukhnovskii, Preprint ITP-74-149P, Kiev 1974.

[5] I. R. Yukhnovskii and I. M. Idzyk, Phys. of Many-Particle Systems, Kiev **3**, 18 (1983).

[6] R. W. Zwanzig, J. Chem. Phys. **22**, 1420 (1954).

[7] J. A. Barker and D. Henderson, J. Chem. Phys. **47**, 2856 (1967).

[8] J. Hubbard and P. Schofield, Phys. Lett. A **40**, 245 (1972).

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* That is, in the region where the renormalization group symmetry appears.