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FIRST-ORDER PHASE TRANSITION  
BASED ON QUARTIC BASIC DENSITY MEASURE

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**Фазовий перехід першого роду на основі четвірної базисної густини міри**

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**Анотація.** Запропоновано теорію фазового переходу першого роду на основі четвірної базисної густини міри. Показано, що стрибок густини під час ізотермічного процесу фазового переходу першого роду пара-рідина починається і відбувається у нововиниклій двофазній системі між материнською фазою пари та краплею рідини. Умовою зародження нової фази у формі краплі рідини є виникнення під дією зовнішнього тиску ситуації рівних ймовірностей, що дорівнюють  $1/2$ , для найбільш ймовірних станів пари і найбільш ймовірних станів рідини. Теорія побудована з перших принципів: задаються потенціали взаємодії між частинками системи. Прототипом для міркувань є ізотерма ван дер Ваальса. Здійснено поетапні розрахунки великої статистичної суми у взаємно пов'язаних фазових просторах, відповідно до малих параметрів притаманним діючим силам.

**First-order phase transition based on quartic basic density measure**

I.R. Yukhnovskii, V.O. Kolomietz, I.M. Idzyk

**Abstract.** The theory of the first-order phase transition based on the quartic density measure is proposed. It is shown that the jump of density during the isothermal process of the vapor-liquid phase transition of the first order starts and occurs in a newly arisen two-phase system between the parent phase of vapor and the droplet of liquid. The condition of a new phase nucleation in the form of a liquid droplet is the appearance under the high external pressure of equal probabilities  $1/2$  for the most probable vapor states and the most probable liquid states. The theory is developed from the first principles: the potentials of interaction between particles are set. The van der Waals isotherm is a prototype for consideration. According to small parameters inherent in active forces, respective phase spaces are chosen. A staged calculation of the grand partition function in mutually connected phase spaces is performed.

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ФАЗОВИЙ ПЕРЕХІД ПЕРШОГО РОДУ НА ОСНОВІ ЧЕТВІРНОЇ  
БАЗИСНОЇ ГУСТИНИ МІРИ

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## 1. Introduction

The wide-spread phenomenon of the first order phase transitions remains topical nowadays. Brilliant ideas and papers by van der Waals [1, 2] and by the authors of the classical nucleation theory [3–5], the computer simulations within the Monte Carlo and molecular dynamics methods [6–8], as well as the experimental efforts in the nucleation science have formed a firm basis for establishing a potentially more and more precise statistical theory of those events. The collective variables method was very effective in describing the Ising model [9–11]. In the present paper, we propose a compound method for calculating the grand partition function aiming on description of the first order phase transitions (FOPT).

*Problem statement. Initial arguments. The grand partition function*  $\Xi(T, V, \mu)$ . Consider an isothermal quasistatic process of compressing the vapor system persisting from the beginning of the FOPT to the end, where the vapor transit into an equilibrium liquid phase. The potential energy  $\Psi_N(\mathbf{r}_1, \dots, \mathbf{r}_N)$  of the system of  $N$  interacting particles consists of a sum of attraction potentials  $\Phi(r_{ij})$ , let's say of the van der Waals type, and of the potentials of a short-range repulsive interaction  $\varphi(r_{ij})$ , such as the interaction between hard spheres. The function  $\Phi(r)$  has a Fourier transform

$$\Phi(r) = \frac{1}{V} \sum_{\mathbf{k}} \tilde{\Phi}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}}, \text{ and } \min \tilde{\Phi}(\mathbf{k}) = \tilde{\Phi}(0) < 0.$$

This condition means that expanding the integrand of  $\Xi$  in series over  $\tilde{\Phi}(\mathbf{k})$  the most important are series of the polarization diagrams, which summation leads to substituting a screened potential for  $\Phi(r)$ . The radius of screening becomes the radius of effective interactions of the attractive forces.

Since the hard-sphere-like potential and the attraction potential of van der Waals-type produce parameters that inversely depend on the density, the calculation of  $\Xi$  is carried out within an extended phase space, consisting of the Cartesian subspace of individual particle coordinates for description of a short-range repulsion [in what follows referred to as the reference system (RS)], and of the subspace of collective variables  $\rho_{\mathbf{k}}$  for a description of a long-range attractions. The subspace of  $\rho_{\mathbf{k}}$  is the subspace of values connected with the modes

$$\hat{\rho}_{\mathbf{k}} = \sum_{i=1}^N e^{-i\mathbf{k} \cdot \mathbf{r}_i}$$

of the operator  $N(\mathbf{r})$  of the number of particles

$$N(\mathbf{r}) = \frac{1}{V} \sum_k \hat{\rho}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} = \sum_i \delta(\mathbf{r} - \mathbf{r}_i).$$

The overloading of the phase spaces is removed by introducing products of the corresponding generalized functions, which forms the Jacobian of transition from the Cartesian's phase space to the phase space  $\{\rho_{\mathbf{k}}\}$  of the collective variables (CV). After integration in the Cartesian phase space,  $\Xi$  is reduced to a functional integral over the set  $\{\rho_{\mathbf{k}}\}$ . The analysis of the Euler equations shows that the maximum of the integrand in  $\Xi$  is achieved for  $\rho_{\mathbf{k}} = 0$  for all  $k \neq 0$  and  $\rho_0 = \rho_0^{\max} \neq 0$  for  $\mathbf{k} = 0$ . As a result, the calculation of  $\Xi$  in  $\{\rho_{\mathbf{k}}\}$  space splits into two macroscopic tasks [10, 13, 14]: (i) integration over all variables  $\rho_{\mathbf{k}}$  with  $\mathbf{k} \neq 0$  and (ii) doing single integral of the Landau type [15, 16] with respect to  $\rho_0$ . The integrations over the CV for all  $\mathbf{k} \neq 0$  was reduced to the typical Ising problem. To get it the third semiinvariant  $\mathfrak{M}_3(\eta)$  of the RS has been taken equal to zero.

From the latter two steps of integration in the Cartesian and in the  $\{\rho_{\mathbf{k}}\}$ ,  $k \neq 0$  spaces two important concepts had been got:

- the universal quantity for the dimensionless critical density

$$\eta_{\text{cr}} = \left( \frac{N}{V} \right)_{\text{cr}} \times \frac{\pi \sigma^3}{6} = 0,13044 \quad (1.1)$$

$N$  is the number of particles,  $V$  is the volume,  $\sigma$  is the diameter of a hard sphere, modeling the size of a particle. The values of  $\sigma$  for different systems are represented in Table 1;

- an expression for  $\Delta$  which is the mean density (MD) parameter,  $\Delta = -(\mathfrak{M}_2 \xi + \frac{1}{3} \mathfrak{M}_3 \xi^2)$ ,  $\xi = \mathfrak{M}_3 / |\mathfrak{M}_4|$ ,  $\mathfrak{M}_2$ ,  $\mathfrak{M}_3$ ,  $\mathfrak{M}_4$  the semi-invariants of the RS [13, 14] and the linear dependence of  $\Delta$  on the density

$$\Delta = \frac{1}{\eta_c} (\eta - \eta_c). \quad (1.2)$$

It seems to be obligatory to introduce the Ising model in the tasks connected with phase transition phenomena and with the calculation of the partition function  $\Xi$ . Because in that case we get the right expressions, connected with the renormalization group symmetry, the right values for the critical indexes, for the thermodynamical functions etc. Calculation of the Ising model in the CV phase space consist of two

Table 1. The effective hard sphere diameter  $\sigma$  and the critical temperature  $T_c$  for several systems [13, 14].

System	$T_c$ , °C (exp.)	$T_c$ , °C (this work)	$\sigma_0$ , Å (exp.)	$\sigma$ , Å	$\sigma/\sigma_0$	$\varepsilon/k_B$ , K
CO-CO	-140.23	-138.46	3.76	3.37	0.898	100.2
Ar-Ar	-122.65	-123.27	3.405	3.14	0.922	119.8
Kr-Kr	-63.1	-67.84	3.6	3.367	0.935	171
Xe-Xe	16.62	16.84	4.1	3.71	0.905	221
O <sub>2</sub> -O <sub>2</sub>	-118.84	-110.8	3.58	3.18	0.89	117.5
N <sub>2</sub> -N <sub>2</sub>	-147.05	-150.02	3.698	3.365	0.91	95.05

successive basic density measures: the critical — non-Gaussian one, containing a polynomial function of degree four in the indeterminate  $\rho_{\mathbf{k}}$  in the exponent for description of the renormalization group symmetry events, and the limiting Gaussian-density measure to get in summary a stable thermodynamics. Here, exhaustive results have been reached. All thermodynamic functions, critical exponents, critical temperature have been calculated starting from the first principles [11, 17, 18]. Some of them are demonstrated in Table 2.

Finally, following the calculations, we have obtained:

$$\Xi = \Xi' \times \Xi_{\rho_0}, \quad \Xi' = \Xi_0 \times \Xi_{\{\rho_{\mathbf{k}}\}}, \quad (1.3)$$

where  $\Xi_0$  is the partition function of the RS,  $\Xi_{\{\rho_{\mathbf{k}}\}}$  is the result of the integrations over  $\{\rho_{\mathbf{k}}\}$ ,  $\mathbf{k} \neq 0$  [17–19]. For  $\Xi'$  in [25–27] we have obtained explicit expressions.

Calculations in Cartesian and in  $\{\rho_{\mathbf{k}}\}$ ,  $\mathbf{k} \neq 0$ , phase spaces do not affect the chemical potential. The chemical potential  $\mu$  or the generalized chemical potential  $\mu^*(\Delta)$ , where  $\Delta$  is the mean density parameter, is present in the calculation of the Landau-type integral over the macroscopic variable  $\rho_0$ . Here the main events of the first order phase transition process are located.

## 2. The single integral over $\rho_0$ . The most probable trajectories

Now, we start to solve the last task, the calculation of  $\Xi_{\rho_0}$  which is the objective of the present paper. One has the following initial form for

$\Xi_{\rho_0}$  [13, 19]:

$$\Xi_{\rho_0} = \exp\left[N\mu^*(1 - \Delta)\right] \int \exp[NE(\rho_0)] d\rho_0, \\ E(\rho_0) = \mu^* \rho_0 + D\rho_0^2 - G\rho_0^4. \quad (2.1)$$

The coefficients  $D$  and  $G$  were calculated in detail in [9, 10, 14] while solving a problem of the Ising model:

$$D = \frac{|d^{(n_\tau)}(0)|}{2} - \frac{a_4^{(n_\tau)}}{4N_{(n_\tau)}} \sum_{k < B_{n_\tau}} \frac{1}{\bar{d}(k)}, \quad G = \frac{1}{4!} \frac{N}{N_{(n_\tau)}} a_4^{(n_\tau)},$$

where  $d^{(n_\tau)}(0)$  and  $a_4^{(n_\tau)}$  are the values of the coefficients  $d(k)$  and  $a_4$  in the initial Hamiltonian after integration over  $\rho_{\mathbf{k}}$  in  $n_\tau$  consecutive block systems (consisting of  $N_{(n_\tau)} = N/s^{3n_\tau}$  lattice sites), which is being performed till in the resulting expression for the block Hamiltonian  $H_{n_\tau}(\rho_{\mathbf{k}})$  the values of the correlation lengths calculated both in the quartic and in the Gaussian basic density measures mutually coincide; the sum  $\sum_{k < B_{n_\tau}} 1/\bar{d}(k)$  arises from the displacement transformation and the integration over  $\rho_{\mathbf{k}}$ ,  $0 < k \leq B/s^{n_\tau}$ ;  $B$  is the point, where  $\tilde{\Phi}(B) = 0$ ;  $s$  is the factor of dividing the initial Brillouin zone  $B$  into layers (the optimal value  $s = s_0 = 3, 58$ ) [9, 10]. Here we use the resulting values of  $G$  and  $D$  for  $s = s_0$ ,  $D = D_0\tau^{2\nu}$ ,  $G = G_0\tau^\nu$  and  $D_0 \approx 1.19$ ,  $G_0 \approx 1.67$ ,  $\nu \approx 0.605$ .

In the characteristic function  $kT \ln \Xi(T, V, \mu) = VP(T, \mu)$  at a fixed

Table 2. The critical indexes of the Ising model; The renormalization group symmetry of vapor-liquid system belongs to the same universality class the Ising model.

Valu- es	Collective variables method		Field theories [21, 22]	High temperature series [23, 24]
	model $\rho^4$ [17, 18]	model $\rho^6$ [19, 20]		
$\nu$	0.605	0.637	0.630	0.638
$\alpha$	0.185	0.088	0.110	0.125
$\beta$	0.303	0.319	0.325	0.312
$\gamma$	1.210	1.275	1.241	1.250
$\Delta_1$	0.463	0.525	0.498	0.50

temperature and  $\langle N \rangle = N = \text{const}$ , the differential  $dP(T, \mu)$  is a complete differential of  $\mu$  [12].

Due to the factor  $N$  in the exponent of the integrand in (2.1), to solve the integral we use the method of steepest descend, showing the most probable trajectories of evolution of the process.

The quasi-static process of the isothermal compression of vapor will move along the most probable thermodynamic trajectories. So we have to look for the values of  $\rho_0$  providing the maximum of  $E(\rho_0)$  in (2.1):

$$\frac{\partial E}{\partial \rho_0} = 0; \quad \frac{\partial^2 E}{\partial \rho_0^2} < 0. \quad (2.2)$$

That leads to the equation

$$\mu^* = -2D\rho_0 + 4G\rho_0^3; \quad 2D - 12G\rho_0^2 > 0 \quad (2.3)$$

or in a standard form  $\rho_0^3 + V\rho_0 + W = 0$ ,  $V + 3\rho_0^2 < 0$ , with the discriminant

$$Q = \frac{W^2}{4} + \frac{V^3}{27}, \quad (2.4)$$

where  $V = \frac{-D}{2G}$ ,  $W = -\frac{1}{4}\frac{\mu^*}{G}$ . The first item in  $Q$  is always positive, the second one is always negative, therefore there can be three cases  $Q > 0$ ,  $Q < 0$ , and  $Q = 0$ .

At  $Q > 0$  equation (2.2) has one real and two complex-conjugated roots.  $Q > 0$  means, that  $\frac{W^2}{4} > \left|\frac{V^3}{27}\right|$  and  $\left|\frac{W}{2}\right| > \sqrt{Q}$ . The real solution along with Cardano method equals:

$$\rho_0^{(1)} = \sqrt[3]{\frac{1}{4}\frac{\mu^*}{2G}} = \frac{1}{2}\sqrt[3]{\frac{\mu^*}{G}}. \quad (2.5)$$

The quantities  $\mu^*$  and  $\rho_0^{(1)}$  change on the boundaries (see Fig. 1)

$$|\mu^*| \geq a, \quad a = G \left(\frac{2}{3}\frac{D}{G}\right)^{\frac{2}{3}Db}; \quad |\rho_0^{(1)}| \geq b, \quad b = \left(\frac{2}{3}\frac{D}{G}\right)^{1/2}. \quad (2.6)$$

We get similar results for  $T \geq T_c$ , but without any restriction on  $\mu^*$ , here always  $Q > 0$ .

In case  $Q = 0$

$$\left(\frac{W}{2}\right)^2 = -\left(\frac{V}{3}\right)^3 \quad \text{and} \quad \mu^* = \pm a, \quad \rho_0 = \pm b, \quad (2.7)$$

we get the points of bifurcation of the solutions in a plane  $(\mu^*, \rho_0)$ .

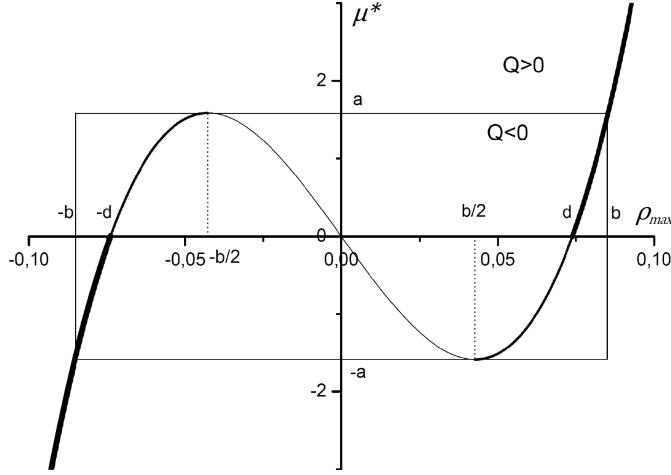


Figure 1. The most probable thermodynamic trajectories  $\rho_0^{\max} = \rho^{(1)}$ ,  $\rho_{01}$ ,  $\rho_{02}$ ,  $\rho_{03}$ ,  $|\rho_0^{(1)}| \geq b$ ,  $|\rho_{0i}| \leq b$ ,  $i = 1, 2, 3$ , either as a functions of variable  $\varphi$ , or of the chemical potential  $\mu^*$ . The curve between the points  $(-b, -a)$  and  $(-b/2, a)$  corresponds to the solution  $\rho_{02} = b \cos \frac{\varphi+2\pi}{3}$ , the curve between  $(b, a)$  and  $(b/2, -a)$  corresponds to  $\rho_{01} = b \cos \frac{\varphi}{3}$ , the curve between  $(-b/2, a)$  and  $(b/2, -a)$  corresponds to  $\rho_{03} = b \cos \frac{\varphi+4\pi}{3}$ . The main maxima are denoted by bold lines, the relative maxima — by thin lines;  $\rho_{03}$  describes unstable states;  $\mu^* = a \cos \varphi$ ,  $0 \leq \varphi \leq \pi$ ,  $b = (\frac{2}{3} \frac{D}{G})^{1/2} \sim \tau^{\nu/2}$ ,  $a = Gb^3 \sim \tau^{5\nu/2}$ ,  $d = (\frac{1}{2} \frac{D}{G})^{1/2} \sim \tau^{\nu/2}$ . We shall call points  $-d$ ,  $d$ ,  $\mu^* = 0$  as the van der Waals points.

When  $Q < 0$  equation (2.2) has three real roots. It is more advantageously to write them in a trigonometric form, putting in (2.5):  $r = \sqrt{-V^3/27}$ ;  $\cos \varphi = -\frac{W}{2r}$ , then we get  $\rho_0 = 2\sqrt[3]{r} \cos \frac{\varphi+2n\pi}{3}$ ,  $n = 0, 1, 2$ , or

$$\begin{aligned} \rho_{01} &= b \cos \frac{\varphi}{3}, \quad \rho_{02} = b \cos \frac{\varphi+2\pi}{3}, \quad \rho_{03} = b \cos \frac{\varphi+4\pi}{3}, \\ \mu^* &= a \cos \varphi, \quad 0 \leq \varphi \leq \pi, \end{aligned} \quad (2.8)$$

that is an important relation between  $\mu^*$  and  $\varphi$ .

Here, we get a new explicit expression (2.3) for the generalized chemical potential  $\mu^*(\rho_0) = \mu^*(\rho_0^{\max})$ , which is of great significance in our consideration.

The initial expression for  $\mu^*$  is realized while integrating over all  $\rho_{\mathbf{k}}$  for  $k \neq 0$ , and analyzing the Ising-like model behavior inside the system. Then,  $\mu^*$  was equal to:  $\mu^* = \mu - \mu_0 - \xi + \frac{N}{V} \tilde{\Phi}(0)(1 - \Delta)$ , where

Table 3. The values of  $\rho_{01}$ ,  $\rho_{02}$ ,  $\rho_{03}$  and of  $E(\rho_0)$  (in (2.1)) and of  $\mu^*(\rho_0)$  at the nodal-points of the argument  $\varphi$ ;  $\varphi = 0, \pi/2, \pi$ .

$\varphi$	$\rho_{01}(\varphi)$	$\rho_{02}(\varphi)$	$\rho_{03}(\varphi)$	$\mu^*(\varphi) = -2D\rho_0 + 4G\rho_0^3$		
				$\rho_{01}$	$\rho_{02}$	$\rho_{03}$
0	$b$	$-\frac{b}{2}$	$\frac{b}{2}$	$a$	$a$	$-a$
$\pi/2$	$d$	$-d$	0	0	0	0
$\pi$	$\frac{b}{2}$	$-b$	$-\frac{b}{2}$	$-a$	$-a$	$a$

$\varphi$	$E(\rho_0) = \mu^*(\rho_0)\rho_0 + D\rho_0^2 - G\rho_0^4$		
	$\rho_{01}$	$\rho_{02}$	$\rho_{03}$
0	$Db^2$	$-\frac{1}{8}Db^2$	$-\frac{1}{8}Db^2$
$\pi/2$	$\frac{1}{2}Dd^2 = \frac{3}{8}Db^2$	$\frac{1}{2}Dd^2 = \frac{3}{8}Db^2$	0
$\pi$	$-\frac{1}{8}Db^2$	$Db^2$	$-\frac{1}{8}Db^2$

$\xi = \mathfrak{M}_3/|\mathfrak{M}_4|$ ,  $\Delta = -\mathfrak{M}_2\xi - \frac{1}{3}\mathfrak{M}_3\xi^2$ ,  $\mathfrak{M}_2$ ,  $\mathfrak{M}_3$ ,  $\mathfrak{M}_4$  are the values of cumulants of the RS (we have taken them at  $k = 0$ ),  $\mu_0$  is the chemical potential of the RS. To take into account the Ising model we have to put  $\mathfrak{M}_3(\eta) = 0$ . We get the universal value for the critical density

$$\eta_c = \left(\frac{N}{V}\right)_c \frac{\pi\sigma^3}{6} = 0.14044,$$

$(N/V)_c$  is the experimental value of the critical density of particular system,  $\sigma$  is the diameter of a hard sphere of the particle of that particular system (see Table 1) [13]. It was proved [13, 19] that  $\Delta|_{\eta=\eta_c} = 0$ , and for  $\Delta = \Delta(\eta)$  it is rigorously linear dependence  $\Delta = \frac{1}{\eta_c}(\eta - \eta_c)$ ,  $\eta = \frac{N}{V} \frac{\pi\sigma^3}{6}$ .

As a result of searching for the most probable trajectory at  $Q < 0$ ,  $\mu^*$  transforms into

$$\mu^* = a \cos \varphi = a \sin \left[ \frac{\pi}{2} - \varphi \right], \quad (2.9)$$

$0 \leq \varphi \leq \pi$ ,  $-a \leq \mu^* \leq a$ . The main values of the roots (2.8) are in the following intervals: for  $\rho_{01}(\varphi)$ :  $0 \leq \varphi \leq \frac{\pi}{2}$ , and for  $\rho_{02}(\varphi)$ :  $\frac{\pi}{2} \leq \varphi \leq \pi$ . From (2.9) we see that between  $0 \leq \varphi \leq \pi$  and  $-a \leq \mu^* \leq a$ , there is a full mutual correspondence:

$$\frac{\pi}{2} - \varphi = \arcsin \frac{\mu^*}{a} = \frac{\mu^*}{a} - \frac{1}{2 \cdot 3} \left( \frac{\mu^*}{a} \right)^2 - \dots, \quad \left| \frac{\mu^*}{a} \right| \leq 1$$

and for  $\left| \frac{\mu^*}{a} \right| < 1$ ,  $\varphi \approx \frac{\pi}{2} - \frac{\mu^*}{a}$ .

In (2.3) we have

$$\mu^* = -2D\rho_0^{\max} + 4G(\rho_0^{\max})^3. \quad (2.10)$$

Here, we can be quite close to the results of applying the Monte Carlo methods [6, 8].

It is worthy to investigate the behavior of the roots (2.8) in the expressions (2.1) for  $E(\rho_0)$  and for the  $\exp N(E(\rho_0))$ . In Table 2 the values of  $\rho_{01}$ ,  $\rho_{02}$ ,  $\rho_{03}$ ,  $\mu^*(\varphi)$  and  $E(\rho_0)$  in nodal points of the argument  $\varphi = 0, \frac{\pi}{2}, \pi$ ;  $0 \leq \varphi \leq \pi$  (see Fig. 1) are given.

Only the expression (2.1) is of great importance in the analysis of the phase transition events. It is important to investigate zeros of the function  $E(\rho_0)$  in order to know the limiting areas of the validity of the obtained solutions (2.5), (2.8). For the zeros of  $E(\tilde{\rho}_0) = 0$  we have equation

$$\mu^* \tilde{\rho}_0 + D\tilde{\rho}_0^2 - G\tilde{\rho}_0^4 = 0, \quad (2.11)$$

with one — the trivial — root  $\tilde{\rho}_0 = 0$ , it is the straight — line perpendicular to the abscissa  $\mu^* = 0$  (see Fig. 2). The three another roots of (2.11) arise from the equation  $\mu^* + D\tilde{\rho}_0 - G\tilde{\rho}_0^3 = 0$  or in a standard form

$$\tilde{\rho}_0^3 + p\tilde{\rho}_0 + q = 0, \quad (2.12)$$

where  $p = -D/G$ ,  $q = -\mu^*/G$  with the discriminant  $R$ :

$$R = \frac{p^3}{27} + \frac{q^2}{4} = -\frac{1}{27}(D/G)^3 + \frac{1}{4} \frac{(\mu^*)^2}{G^2} \quad (2.13)$$

and solutions, at  $R < 0$ :

$$(\tilde{\rho})_{1,2,3} = 2\sqrt[3]{r} \cos \frac{\varphi + 2\pi n}{3} = 2f \cos \frac{\varphi + 2\pi n}{3}, \quad n = 0, 1, 2, \quad (2.14)$$

$$\text{where } r = \sqrt{-p^3/27} = \sqrt{(D/G)^3/27}, \quad \cos \varphi = -\frac{q}{2r} = \frac{\mu^*}{2/3 \cdot Df},$$

$$f = \sqrt{(1/3)D/G}; \quad f/b = 1/\sqrt{2} \quad \text{and}$$

$$\tilde{\mu}^* = \frac{2}{3}Df \cos \varphi. \quad (2.15)$$

The function  $\tilde{\mu}^*(\varphi)$  is a curve of the boundary values of the chemical potential, according to  $R = 0$ ,

$$-\frac{2}{3}Df \leq \tilde{\mu}^*(\varphi) \leq \frac{2}{3}Df. \quad (2.16)$$

Table 4 contains the nodal points of  $\tilde{\rho}_{1,2,3} = 2f \cos \frac{\varphi + 2\pi n}{3}$ ,  $n = 0, 1, 2$ .

Table 4. The nodal points of  $\tilde{\rho}_1$ ,  $\tilde{\rho}_2$ ,  $\tilde{\rho}_3$ .

$\varphi$	$\tilde{\rho}_1, n = 0$	$\tilde{\rho}_2, n = 1$	$\tilde{\rho}_3, n = 2$
0	$2f$	$-f$	$-f$
$\pi/2$	$\sqrt{2}d$	$-\sqrt{2}d$	0
$\pi$	$f$	$-2f$	$f$

In Fig. 2 the limiting curves of the area of the positive values of  $E(\rho_0)$ , as well as the curves of the maximal values of  $E(\rho)$  and the rectangular  $R = 0$  for  $\tilde{\rho}_{1,2,3}$  and  $Q = 0$  for  $\rho_{01,02,03}$  are demonstrated.

In Fig. 3 we demonstrate the volumetric pictures for  $E(\rho_0)$  (left) and for  $\exp NE(\rho_0)$  (right).

In Fig. 3 only the positive part of  $E(\rho)$  is seen. The abscissa  $\mu^* = 0$  divides the parts of  $\rho_{01}$  and  $\rho_{02}$  to the main and relative maxima. One

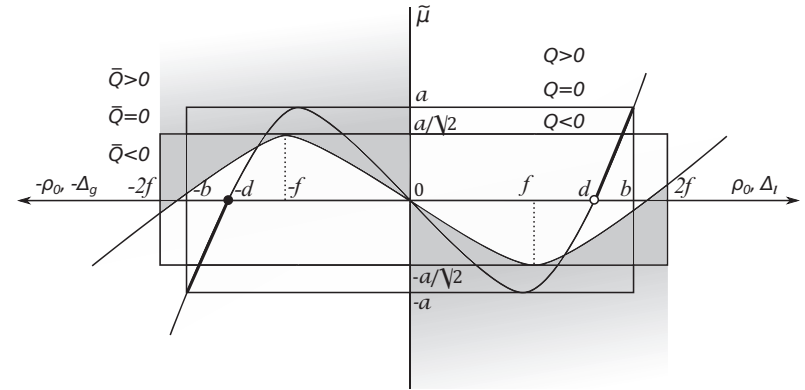


Figure 2. The curves of zero-values of  $E(\rho)$  (solid lines):  $(-2f, -\frac{a}{\sqrt{2}}) \leq \tilde{\rho}_1 \leq (-f, \frac{a}{\sqrt{2}})$ ,  $(-f, \frac{a}{\sqrt{2}}) \leq \tilde{\rho}_2 \leq (f, \frac{-a}{\sqrt{2}})$ ,  $(f, \frac{-a}{\sqrt{2}}) \leq \tilde{\rho}_3 \leq (2f, \frac{a}{\sqrt{2}})$  — the boundary lines of the positive values of  $E(\rho_0)$ ; and of the maximal values of  $E(\rho)$  (bold lines) as functions of  $\mu^*(\varphi)$  on the interval  $0 \leq \varphi \leq \pi$ . The bold thick lines represent the main maxima of  $\rho_{01}$  and  $\rho_{02}$ , the bold thin lines — the relative maxima  $(\frac{b}{2}, -a) \leq \rho_{01} \leq (b, a)$ ;  $(-b, -a) \leq \rho_{02} \leq (-\frac{b}{2}, a)$ . The area of the unrealized states is shaded. Therefore, the contribution of the relative maxima to  $E(\rho)$  may only be considered if  $d < \rho_{01} \leq f$  and  $-d > \rho_{02} > -f$ . The states of  $E(\rho_{03})$  for all values of  $\rho_{03} = b \cos \frac{\varphi + 4\pi}{3}$   $(-\frac{b}{2}, a) \geq \rho_{03} \geq (\frac{b}{2}, -a)$  are unrealizable and may be excluded from the investigations.



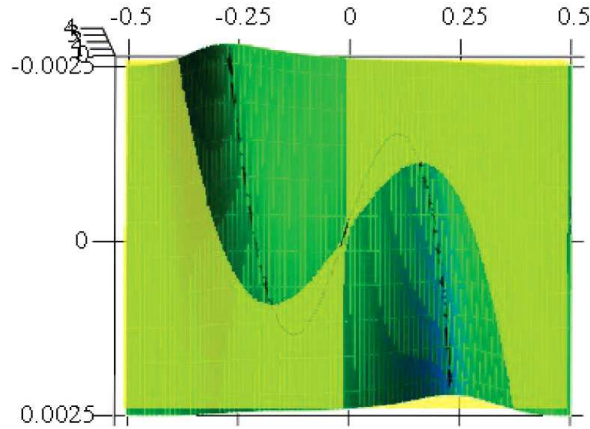


Figure 3. The volumetric pictures for  $\exp NE(\rho_0)$ . A confirmation of the results given in Fig. 2. The curves for  $\rho_{0i}$  are marked with the dashed curve.

may make sure that the behavior of those maxima with the increasing  $N$  is different: the main maximum part grows rapidly up, the growing of relative maximum is weak.

Summing up the investigations of  $E(\rho_0)$  and of  $\exp NE(\rho_0)$  we can say following. The trajectory  $\rho_{03}$  doesn't play any role in the process of the FOPT, and we can investigate only the behavior of  $E(\rho_{01}, \rho_{02})$  and of  $\exp NE(\rho_{01}, \rho_{02})$  as a behavior of a two phase system. In the TL  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V = \text{const}$  the principal meaning in the  $\exp NE(\rho_{01}, \rho_{02})$  is connected only with the main values of  $\rho_{01}$  and of  $\rho_{02}$ .

So in the TL values of the integrals

$$\int_0^\infty \dots \exp(NE(\rho_0)) d\rho_0 \quad \text{and} \quad \int_{-\infty}^0 \dots \exp(NE(\rho_0)) d\rho_0$$

will be contributed from the main values of trajectories  $\rho_{01}$  and  $\rho_{02}$  respectively. Both of these integrals are functions of  $\varphi$  or  $\mu^*/a$ , along (2.12). The influence of  $\rho_{03}$  can not be taken into consideration.

### 3. Investigation of the envelope of curves (2.8) in the region $Q < 0$

Continue to study equations for the envelope in case  $T < T_c$  and  $Q < 0$ :

$$\frac{PV}{\Theta} = \ln \Xi_0 = N\mu^*(1 - \Delta) + \ln \int_{-\infty}^{\infty} \exp[NE(\rho_0)] d\rho_0, \quad (3.1)$$

$$\frac{\partial \ln \Xi_{\rho_0}}{\partial \mu^*} - N = 0, \quad (3.2)$$

$\mu^*$  is treated as a parameter in these equations.

Let us consider in detail the equation (3.2). Taking into account (3.1) and (2.1) we get

$$\frac{\int_{-\infty}^{\infty} \rho_0 \exp(NE(\rho_0)) d\rho_0}{\int_{-\infty}^{\infty} \exp(NE(\rho_0)) d\rho_0} = \Delta. \quad (3.3)$$

On the left hand we have the mean value of  $\rho_0$ , the equations (3.2), (3.3) take on the form

$$\langle \rho_0 \rangle = \Delta. \quad (3.4)$$

Fig. 4 shows, that at big values of  $N$ ,  $N > 10^5$ , the main values of  $\rho_{01}$  and  $\rho_{02}$  coincide with the mean values  $\langle \rho_0 \rangle$ . As a result for all expressions

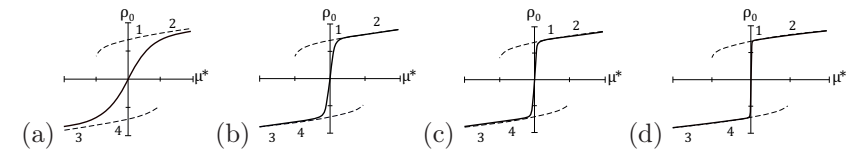


Figure 4. The curves for  $\langle \rho_0 \rangle$  direct from (3.3) (solid line) and the most probable  $\rho_0^{\max}$ -functions of  $\mu^* = -2D\Delta + 4G\Delta^3$  at different values of  $N$ . The arcs 1–2 and 3–4 (dashed lines) correspond to the absolute maxima of  $\exp[NE(\rho_0)]$ . The absolute maxima of  $\exp NE(\rho_0)$  one obtains only at  $\rho_0 = \rho_{02}(\varphi)$ ,  $\frac{\pi}{2} \leq \varphi \leq \pi$  and at  $\rho_0 = \rho_{01}(\varphi)$ ,  $0 \leq \varphi \leq \frac{\pi}{2}$ . Overshooted parts — the dashed lines — correspond to the relative maxima of  $\rho_0^{\max}$  (see Fig. 1). In the TL they are needless and may be dropped. Here (a)  $N = 1000$ , (b)  $N = 5000$ , (c)  $N = 10000$ , (d)  $N = 100000$ .

in (3.1) and (3.3), as well as in the initial one (2.1), one may state that for large  $N$  the following equalities take place

$$\Delta = \langle \rho_0 \rangle = \bar{\rho}_0^{\max}, \quad (3.5)$$

where  $\bar{\rho}_0^{\max}$  means the main maxima of  $\rho_{01}^{\max}$  and  $\rho_{02}^{\max}$  (see Fig. 1).

So in Fig. 4 we can see, that for  $N > 10^5$  the curves  $\langle \rho_0 \rangle$  and  $\rho_0^{\max}(\mu^*)$  behave the same way and the following equalities take place:

$$\begin{aligned} \mu^*(\Delta) &= \mu^*(\langle \rho_0 \rangle) = \mu^*(\bar{\rho}_0^{\max}), \\ E(\Delta) &= E(\langle \rho_0 \rangle) = E(\bar{\rho}_0^{\max}). \end{aligned} \quad (3.6)$$

Here  $\rho_{01} = \bar{\rho}_0^{\max}$  for  $0 \leq \varphi \leq \frac{\pi}{2}$ ,  $1 \geq \mu^*/a \geq 0$ , and for  $\rho_{02} = \bar{\rho}_0^{\max}$  we have  $\frac{\pi}{2} \leq \varphi \leq \pi$ ,  $0 \geq \mu^*/a \geq -1$ .

We bear in mind that the maxima of the integrand in (3.3) go along the lines  $\rho = \rho_{02}$  and  $\rho = \rho_{01}$  and that the curve  $\rho_{02}$ ,  $-b \leq \rho_{02} \leq -b/2$  corresponds to the vapor phase and the curve  $\rho_{01}$ ,  $b/2 \leq \rho_{01} \leq b$ , corresponds to the liquid phase.

Formula (3.3) may be written in the form:

$$\Delta = \frac{I_g + I_l}{\mathcal{K}_g + \mathcal{K}_l}, \quad (3.7)$$

where

$$\begin{aligned} I_g &= \int_{-\infty}^0 \rho_0 \exp(NE(\rho_0)) d\rho_0, & I_l &= \int_0^{\infty} \rho_0 \exp[NE(\rho_0)] d\rho_0, \\ \mathcal{K}_g &= \int_{-\infty}^0 \exp(NE(\rho_0)) d\rho_0, & \mathcal{K}_l &= \int_0^{\infty} \exp[NE(\rho_0)] d\rho_0. \end{aligned}$$

In the limit of a very large  $N$  the mean values of  $\rho_{01}$  and  $\rho_{02}$  coincide with the main maximal values of  $\rho_{01}^{\max}$  and  $\rho_{02}^{\max}$ , as it is shown in Fig. 4.

In the TL, practically for  $N > 10^5$ , we find:

$$\begin{aligned} I_g &= \rho_{02} e^{NE(\rho_{02})} \frac{\sqrt{\pi}}{\sqrt{\frac{N}{2} |\ddot{E}(\rho_{02})|}}, & I_l &= \rho_{01} e^{NE(\rho_{01})} \frac{\sqrt{\pi}}{\sqrt{\frac{N}{2} |\ddot{E}(\rho_{01})|}}, \\ \mathcal{K}_g &= \left[ \exp[NE(\rho_{02})] \frac{\sqrt{\pi}}{\sqrt{\frac{N}{2} |\ddot{E}(\rho_{02})|}} \right], \\ \mathcal{K}_l &= \left[ \exp[NE(\rho_{01})] \frac{\sqrt{\pi}}{\sqrt{\frac{N}{2} |\ddot{E}(\rho_{01})|}} \right]. \end{aligned} \quad (3.8)$$

For MD parameter  $\Delta$  in formula (3.4) we write:

$$\Delta = \rho_{02} w_g + \rho_{01} w_l, \quad \Delta = \Delta_g + \Delta_l, \quad (3.9)$$

where  $\Delta_g = \rho_{02} w_g$ ,  $\Delta_l = \rho_{01} w_l$ .

$$\begin{aligned} w_g &= \frac{c_g \exp(NE(\rho_{02}))}{c_g \exp(NE(\rho_{02})) + c_l \exp(NE(\rho_{01}))} = \frac{\mathcal{K}_g}{\mathcal{K}_g + \mathcal{K}_l}, \\ w_l &= \frac{c_l \exp(NE(\rho_{01}))}{c_g \exp(NE(\rho_{02})) + c_l \exp(NE(\rho_{01}))} = \frac{\mathcal{K}_l}{\mathcal{K}_g + \mathcal{K}_l}, \end{aligned} \quad (3.10)$$

$c_g = |\ddot{E}(\rho_{02})|^{-1/2}$ ;  $c_l = |\ddot{E}(\rho_{01})|^{-1/2}$ ,  $w_g + w_l = 1$ . The functions  $w_g$  and  $w_l$  are positive simple functions of  $\varphi$  in the area  $\frac{\pi}{2} \leq \varphi \leq \pi$  — for  $\rho_{02}$  and  $0 \leq \varphi \leq \frac{\pi}{2}$  — for  $\rho_{01}$ , they play the role of probabilities of either vapor or liquid state, respectively.

For  $N \rightarrow \infty$  the functions  $w_g$  and  $w_l$  become the Heaviside step functions

$$w_g = \begin{cases} 1 & \text{for } -b \leq \rho_{02} < -d, & \frac{\pi}{2} < \varphi \leq \pi \\ 0 & \text{for } -d < \rho_{02} < -\frac{b}{2}, & 0 \leq \varphi < \frac{\pi}{2} \\ \frac{1}{2} & \text{for } \rho_{02} = -d, & \varphi = \frac{\pi}{2} \end{cases}, \quad (3.11)$$

$$w_l = \begin{cases} 0 & \text{for } \frac{b}{2} \leq \rho_{01} < d, & \frac{\pi}{2} < \varphi \leq \pi \\ 1 & \text{for } d < \rho_{01} \leq b, & \frac{\pi}{2} > \varphi \geq 0 \\ \frac{1}{2} & \text{for } \rho_{01} = d, & \varphi = \frac{\pi}{2} \end{cases}.$$

And the expression (3.5) is been completely proved.

Now how we should deal with the nonstable trajectory  $\rho_{03}$  in expressions (3.1)–(3.5). Table 3 and especially Figs. 3 and 4 show that the contribution of  $\rho_{03}$  into the values of  $\mu^*(\Delta)$  or  $E(\Delta)$  is always negative. The area of influence of  $\rho_{03}$  in the integral (3.3) is located inside of the expressions

$$\int_{-b/2}^{b/2} \exp(NE(\rho_0)) d\rho_0$$

and in the integrals (3.6) of expressions

$$\int_{-b/2}^0 \dots \exp NE(\rho_0) d\rho_0$$



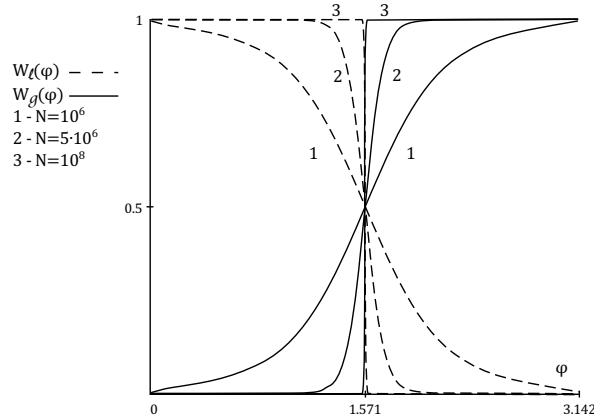


Figure 5. Probabilities (3.10) of the vapor and liquid states as functions of the angle  $\varphi$ ,  $\varphi = \arccos \frac{\mu^*}{a}$ ,  $a = Gb^3$ , in dependence on the number of particles  $N$ . Transformation of the curves  $w_g$  and  $w_l$  into the Heaviside step function as  $N$  increases is clearly seen. The point  $w_g = w_l = 1/2$  is of fundamental importance as a point of equal probabilities and of transition from the main maximum of the vapor phase to the main maximum of the liquid phase.

inside the  $\mathcal{I}_g$  and  $\mathcal{K}_g$  and in

$$\int_0^{b/2} \exp(NE(\rho_0)) d\rho_0$$

inside the  $\mathcal{I}_l$  and  $\mathcal{K}_l$ . Here everywhere  $E(\rho_0)$  is always negative. In any way of evaluating those integrals, taking into consideration the numbers in Table 3 and Figs. 2 and 3, we get the quantities of type  $\exp(-NDb^2/16)$  which rapidly tend to zero at large  $N$ , and are equal zero in TL.

Moving from those results to future we do not to take into account the influence of the nonstable trajectory  $\rho_{03}$ .

The probabilities along the main maxima tend to unity and along the relative maxima tend to zero. We turn special attention to the point  $\varphi = \pi/2$ . Here  $w_g = w_l = 1/2$ ,  $\mu^* = 0$ . This is a qualitatively new moment for the whole study at  $T < T_c$ , at this point the probability of appearance of the vapor state equals the probability of appearance of the liquid one. Simultaneously, for the probability curves this is a point of transition from vapor-phase-probability curve to the liquid-phase-probability curve

and vice versa. The main maxima of

$$\rho_{02} = b \cos \frac{\varphi + 2\pi}{3} \Big|_{\frac{\pi}{2}} = -d \quad \text{and} \quad \rho_{01} = b \cos \frac{\varphi}{3} \Big|_{\frac{\pi}{2}} = d$$

terminate on the line  $\mu^* = 0$ .

In case  $Q > 0$  we have two single solutions

$$|\rho_0^{\max}| = |\rho_0^{(1)}| \geq b,$$

and two different dependencies on density:

$$\begin{aligned} \rho_0^{(1)} &= \frac{1}{\eta_c}(\eta_g - \eta_c) \quad \text{and} \quad \eta_g = \eta_c(\rho_0^{(1)} + 1), \quad \text{when} \quad \rho_0^{(1)} \leq -b, \\ \rho_0^{(1)} &= \frac{1}{\eta_c}(\eta_l - \eta_c) \quad \text{and} \quad \eta_l = \eta_c(\rho_0^{(1)} + 1), \quad \text{when} \quad \rho_0^{(1)} \geq b. \end{aligned} \quad (3.12)$$

At the points  $-b$  and  $b$  there are smooth transitions from the area  $Q \geq 0$  to the area  $Q \leq 0$ , and  $\rho_0^{(1)}(-b) = \rho_{02}(-b) = -b$ ,  $\rho_0^{(1)}(b) = \rho_{01}(b) = b$ , and along (3.11):  $\rho_{02}(-b) = \frac{1}{\eta_c}(\eta_g(-b) - \eta_c)$ ,  $\rho_{01}(b) = \frac{1}{\eta_c}(\eta_l(b) - \eta_c)$ . At those points  $w_g(-b) = 1$ ,  $w_l(-b) = 0$ ;  $w_l(b) = 1$ ,  $w_g(b) = 0$ . Then in (3.8):

$$\Delta_g(-b) = w_g(-b)\rho_{02}(-b) = -b, \quad \Delta_l(b) = w_l(b)\rho_{01}(b) = b.$$

In general for  $\Delta_g(\rho_0)$  and  $\Delta_l(\rho_0)$  from (3.9) and (3.11) we get the following dependencies on densities

$$\begin{aligned} \Delta_g &= w_g \frac{1}{\eta_c}(\eta_g - \eta_c), \quad \eta_g = \eta_c(\rho_{02} + 1) \quad \text{and} \\ \Delta_l &= w_l \frac{1}{\eta_c}(\eta_l - \eta_c), \quad \eta_l = \eta_c(\rho_{01} + 1). \end{aligned} \quad (3.13)$$

So likely to the case  $Q > 0$ , at  $Q \leq 0$  we have two trajectories of density, one  $\Delta_g$  is for the vapor and another  $\Delta_l$  is for the liquid.

Taking into account (3.9) and (3.13) for the mean density (MD) parameter  $\Delta$  we have the following

$$\Delta = \frac{1}{\eta_c}(w_g\eta_g + w_l\eta_l - \eta_c) = \frac{1}{\eta_c}(\langle \eta \rangle - \eta_c) \quad (3.14)$$

because  $w_g + w_l = 1$ .

Inside the area  $Q \leq 0$ , we have the mean density

$$\langle \eta \rangle = w_g\eta_g + w_l\eta_l. \quad (3.15)$$

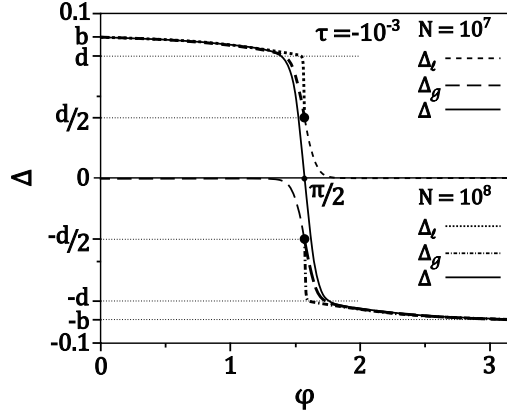


Figure 6. Curves for the mean density parameter  $\Delta(\varphi) = \Delta_g(\varphi) + \Delta_l(\varphi)$  and curves  $\Delta_g = w_g \rho_{02}$  and  $\Delta_l = w_l \rho_{01}$ ;  $\rho_{02} = b \cos \frac{\varphi+2\pi}{3}$ ;  $\rho_{01} = b \cos \frac{\varphi}{3}$ ,  $w_g(\varphi) + w_l(\varphi) = 1$ . The region  $0 \leq \varphi \leq \pi$  is divided into two parts: for  $\frac{\pi}{2} < \varphi \leq \pi$  the main maximum corresponds to vapor phase  $\rho_{02}$ ; for  $0 \leq \varphi < \frac{\pi}{2}$  the main maximum corresponds to liquid phase  $\rho_{01}$ . Bold lines correspond to the main maxima (compare Fig. 1), thin lines correspond to the relative maxima. In the TL a phase transition occurs along the line  $\mu^* = a \cos \varphi|_{\varphi=\pi/2} = 0$  between the points  $\Delta_g = -d/2$  and  $\Delta_l = d/2$  (independent of the magnitude of  $N$ ). In the TL, only bold lines remain, while thin lines (as well as the relative maxima) disappear (see Fig. 4).

Now about the densities  $\eta_g$  and  $\eta_l$  at the limiting points  $\Delta_g = -d/2$  and  $\Delta_l = d/2$ .

Along the considerations (3.11)–(3.14) and formula (3.13),

$$w_g \eta_g = (\Delta_g + w_g) \eta_c, \quad w_l \eta_l = (\Delta_l + w_l) \eta_c$$

during the FOPT, when  $\Delta_g = -\frac{1}{2}d$ ,  $\Delta_l = \frac{1}{2}d$  the densities for  $\eta_g$  and  $\eta_l$  will be:

$$\frac{1}{2} \eta_g = \left(-\frac{1}{2}d + \frac{1}{2}\right) \eta_c, \quad \frac{1}{2} \eta_l = \left(\frac{1}{2}d + \frac{1}{2}\right) \eta_c.$$

It means, that

$$\eta_g|_{\Delta_g=-d/2} = \eta_c(1-d), \quad \eta_l|_{\Delta_l=d/2} = \eta_c(1+d) \quad (3.16)$$

like at the van der Waals points  $\Delta_g = -d$ ,  $\Delta_l = 0$  and  $\Delta_g = 0$ ,  $\Delta_l = d$ .

As it follows in the process of pressing the vapor along the intervals  $\Delta_g = -d \div \Delta_g = -\frac{d}{2}$ ;  $\Delta_l = d \div \Delta_l = \frac{d}{2}$ , the densities of the vapor

do not change. The droplet of liquid is arising. The corresponding work is performed due to the change of the chemical potential  $\mu^*$  as well as a two-phase system vapor–liquid appears, a first-order phase transition occurs.

Here we face the following specific peculiarity: the function  $\Delta$ , given in (3.3), is in fact the envelope of the maxima  $\rho_{02}$  and  $\rho_{01}$ , which we have found in (2.8); the function  $\Delta$  is the mean density, and as a sum  $\Delta = \Delta_g + \Delta_l$  is zero at the point of equal probabilities  $w_g = w_l = 1/2$  (here  $\Delta_g = -\frac{d}{2}$ ,  $w_g = \frac{1}{2}$ ,  $\rho_{02} = -d$ ; and  $\Delta_l = \frac{d}{2}$ ,  $w_l = \frac{1}{2}$ ,  $\rho_{01} = d$ ), the mean density given by (3.14) is equal to  $\eta_c$ . The densities  $\eta_g = \eta_c(1-d)$  and  $\eta_l = \eta_c(1+d)$  remain unchanged up to the end of the transition from vapor to liquid (or vice versa). It happens because the point  $\Delta_g = -\frac{1}{2}d$  corresponds to the end of the main maximum of a vapor phase

$$\rho_{02}(\varphi) \Big|_{\varphi=\pi/2} = b \cos \frac{\varphi+2\pi}{3} \Big|_{\varphi=\pi/2} = -d$$

(the probability of further motion along the relative maximum of  $\rho_{02}$  in accordance with (3.9), (3.10) is zero), the point  $\Delta_l = \frac{1}{2}d$  corresponds here to the beginning of the main maximum of a liquid phase

$$\rho_{01}(\varphi) \Big|_{\varphi=\pi/2} = b \cos \frac{\varphi}{3} = d.$$

In TL for  $\varphi > \pi/2$  we have  $w_l = 0$ , and for  $\varphi < \pi/2$ , it is  $w_g = 0$ . At arbitrary  $N$  at the point  $\varphi = \pi/2$ ,

$$w(\varphi) \Big|_{\varphi=\pi/2} = 1/2,$$

both of the thermodynamic states have the same probability  $w_g = w_l = 1/2$  (see Fig 4). But they are disconnected:

$$\Delta_g|_{-d/2} = -\frac{1}{2}d, \quad \Delta_l|_{d/2} = \frac{1}{2}d.$$

Along (3.13) between those points there must be a jump of density

$$\eta_{d/2} - \eta_{-d/2} = 2d\eta_c.$$

The vertical segment  $\frac{d}{2} \div -\frac{d}{2}$  in Fig. 6 links the points of the vapor – liquid first-order phase transition. The Heaviside point  $1/2$  on the curves for  $w_g$  and  $w_l$  (see Fig. 5) transforms into two points  $\Delta_l = (1/2)d$  and  $\Delta_g = (-1/2)d$  on the vertical segment of the curve for  $\Delta$  in Fig. 6.

In formulas (3.8), (3.9)  $\Delta_g$  and  $\Delta_l$  are composed from products of the probabilities  $w_g$  and  $w_l$  given in (3.9) and the quantities  $\rho_{02}$  and  $\rho_{01}$  given in (2.8). These pairs of quantities  $w_g$  and  $w_l$ ,  $\rho_{02}$  and  $\rho_{01}$  come from different sources. The roots  $\rho_{02}$  and  $\rho_{01}$  are the coordinates of maxima (see formula (2.2)) of the function  $E(\rho_0)$  in the integral (2.1). The probabilities  $w_g$  and  $w_l$  follow from equations (3.1), (3.2) for the envelope.

As it is clearly seen from Fig. 4 for any finite  $N$  the points  $-d$  for  $\Delta_g$  and  $d$  for  $\Delta_l$  are not reachable. That can happen only in the thermodynamical limit  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V = \text{const}$ .

But for all curves  $w_g$  and  $w_l$  at any value of  $N$  there is one common point, the point of mutual intersection  $w_l = w_g = 1/2$ . This is the point of equal probability of being at either vapor,  $\rho_{02}$ , or liquid,  $\rho_{01}$ , thermodynamical trajectory.

From the “density” point of view, the points  $-\frac{1}{2}d$  and  $-d$  for  $\Delta_g$ , the points  $\frac{1}{2}d$  and  $d$  for  $\Delta_l$  are the same. *They can not be seen in the “mean density – temperature” theory.*

But what is different about them? The chemical potentials  $\mu_{-d/2}^*$  and  $\mu_{-d}^*$ ;  $\mu_{d/2}^*$  and  $\mu_d^*$  are different. The combinations of their differences describe the work of arising a nucleus of new phase inside the maternal phase. In our problem this nucleus is a droplet of liquid inside the vapor phase. The moment of arise of the droplet means the real beginning of the FOPT.

The functions  $\Delta_g$  and  $\Delta_l$  along (3.9) characterizes distribution of the densities inside the MD parameter  $\Delta$ , their curves are shown in Fig. 6. In the thermodynamic limit (TL)  $w_g$  and  $w_l$  become the Heaviside step functions. This means that *the probabilities for the processes along the main maxima (Fig. 1) tend to unity while the probabilities along the relative maxima tend to zero.* We pay special attention to the point  $w_g = w_l = \frac{1}{2}$ ,  $\mu^* = 0$  which refer to the endpoint of the main maxima  $\rho_{02} = -d$  and  $\rho_{01} = d$ . The latter are reached in the FOPT simultaneously.

#### 4. The generalized chemical potentials $\mu_g^*(\Delta_g, \Delta_l)$ and $\mu_l^*(\Delta_g, \Delta_l)$ and their role in the droplet formation

Recall the expressions (2.1). Here we have to take into account all previous results, with the following restriction: the two phase system appears and exists only in the thermodynamical limit. In this case the equalities

(3.4) take place:

$$\begin{aligned} \langle \rho \rangle &= \rho_{\max} = \Delta, \\ \Delta &= w_g \rho_{02} + w_l \rho_{01} = \Delta_g + \Delta_l. \end{aligned} \quad (4.1)$$

Due to that, in the last item in (3.1) we may write

$$\ln \int_{-\infty}^{\infty} \exp(N E) d\rho = N E(\Delta) = N [\mu^*(\Delta) \Delta + D \Delta^2 - G \Delta^4]$$

(without taking into account  $\ln[\pi/N|\ddot{E}|]$ ).

The whole expression (2.1) takes the form:

$$\ln \Xi_{\rho_0} = N \mathcal{E}(\Delta) \approx N \mu^*(\Delta), \quad (4.2)$$

where

$$\mathcal{E}(\Delta) = \mu^*(\Delta) \Delta + D \Delta^2 - G \Delta^4, \quad \mu^*(\Delta) = -2D\Delta + 4G\Delta^3, \quad \mathcal{E}(\Delta) \simeq \mu^*(\Delta).$$

In the critical region  $\mu^* \sim \tau^{5/2\nu}$ , and the expressions  $D\Delta^2 - G\Delta^4 \sim \tau^{3\nu}$ . Therefore, for the sake of simplicity in our following calculations for  $\mathcal{E}(\Delta)$  we use  $\mathcal{E}(\Delta) \simeq \mu^*(\Delta)$ , and for the equation of state  $P_{\rho_0} V = \Theta N \mathcal{E}(\Delta)$  we write:

$$P_{\rho_0} V \simeq \Theta N \mu^*(\Delta), \quad -b \leq \Delta \leq b, \quad (4.3)$$

where  $\Delta$  equals (4.1),  $\Delta = \Delta_g + \Delta_l$ . Fig. 7 represents plots of the curves  $\mathcal{E}(\Delta)$ ,  $E(\Delta)$  and  $\mu^*(\Delta)$ . The form of the isotherm in (4.3) is likely to that in the van der Waals theory.

We have got the situation of  $Q < 0$  with a compound argument  $\Delta$  in (4.1), consisting of two different thermodynamical trajectories:  $\rho_{02}(\varphi)$  describing evolution of vapor and  $\rho_{01}(\varphi)$  describing evolution of liquid. Both are functions of the single variable  $\varphi$ . The equations (3.1) and (3.2) for the envelop describe probabilities of the system to evolve as  $\rho_{02}$  and  $\rho_{01}$ . The probabilities are also functions of  $\varphi$ . The arguments  $\varphi$  and  $\mu^*$  are tightly connected by the expression (2.9).

Initially we have a vapor. Then we were continuously isothermally press on vapor. We move along a single trajectory  $\rho_0^{(1)}$  for  $\mu^* \leq -a$ , given in (2.5), here everywhere  $Q > 0$ . Then we come to the point  $\rho_0^{(1)} = -b$ ,  $\mu^* = -a$ , the point of the bifurcation, and while continue to press, we go inside the area  $Q < 0$  along the trajectory of the main maximum of  $\rho_{02}(\varphi)$  with the aim to reach the endpoint  $\rho_{02} = -d$ . In the area  $Q < 0$  going along the curve  $\rho_{02}$ , we have to compensate the

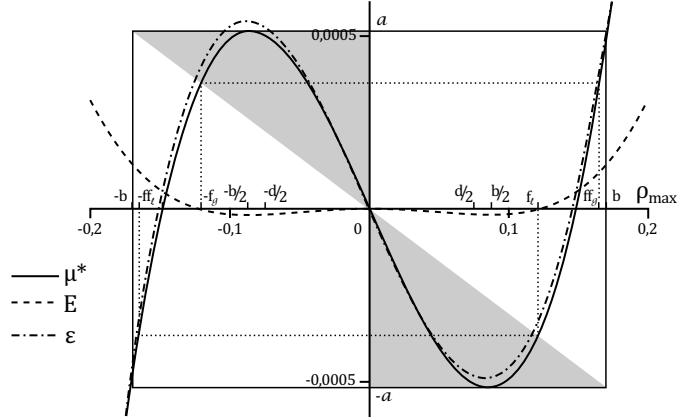


Figure 7. Plots of the functions  $\mathcal{E}(\Delta)$ ,  $\mu^*(\Delta)$  and  $E(\Delta)$ ,  $\Delta = \frac{1}{\eta_c}(\eta - \eta_c)$  inside the rectangular  $Q = 0$ . It is clear, that  $\mathcal{E}(\Delta) \approx \mu^*(\Delta)$ ;  $E(\Delta) = \mu^*(\Delta)\Delta + D\Delta^2 - G\Delta^4 = -D\Delta^2 + 3G\Delta^4$ ;  $\exp NE(\Delta)$  plays the role of density measure of the distribution of  $\Delta$ . The main points  $b, f, d, d/2$  are given. Obviously, in the region  $(-b/2, -a; b/2, a)$  the function  $E(\Delta)$  is negative and in TL the contribution of  $\rho_{03}$  is zero. Shaded areas are not subject to consideration (see Figs. 2 and 3).

inner work (the reaction of the system in form of the fluctuations of the density of a liquid type which have been started at the point  $(b/2, -a)$ ) going along the relative maximum  $\rho_{01}$  to the point  $(d, 0)$ . In the TL the probability of those fluctuations is zero, they disappear, except the point  $(d, 0)$  where the probability to be a liquid is equal to the probability to be a vapor, and is  $1/2$ .

Let us estimate the external work of pressing on the vapor system which take place along the isotherm  $\mu^*(\Delta)$ ,  $\Delta = w_g\rho_{02} + w_l\rho_{01}$  in TL. The process begins at a “pure” vapor state  $w_g = 1$ ,  $\Delta = \Delta_g(-b) = \rho_{02} = -b$  and ends for  $\Delta_g$  at the end of the main maximum of  $\rho_{02}$ ,  $\rho_{02} = -d$ , it means  $\Delta_g = w_g(-d)\rho_{02}(-d) = 1/2(-d)$ . We denote by  $A_{\text{out}}^{(1)}$  the value of this work per one particle:

$$A_{\text{out}}^{(1)} \simeq \Theta[\mu^*(\Delta_g(-d/2)) - \mu^*(\Delta_g(-b))] = \Theta Dd \left[ \frac{3}{4} + \frac{4}{3\sqrt{3}} \right], \quad (4.4)$$

here  $\mu^*(\Delta) = -2D\Delta + 4G\Delta^3$ ,  $\Delta_g(-b) = -b$ ,  $\Delta_g(-d/2) = -d/2$ ,  $b = \sqrt{(2/3)D/B}$ ,  $d = \sqrt{(1/2)D/B}$ . One has to add to this quantity the energy that compensates the internal work of the liquid type density

fluctuations, emerging spontaneously along the trajectory  $\frac{b}{2} \leq \rho_{01} \leq d$  with the probability  $w_l \approx 0$  everywhere but at the point  $\rho_{01} = d$  the probability is  $w_l(d) = \frac{1}{2}$ ,

$$A_{\text{out}}^{(2)} = -\Theta[\mu^*(\Delta_l(d/2)) - \mu^*(\Delta_l(b/2))] = -\Theta\mu^*\Delta_l(d/2) = \frac{3}{4}\Theta Dd \quad (4.5)$$

since  $w_l(b/2) = 0$ . As a result

$$A_{\text{out}} = A_{\text{out}}^{(1)} + A_{\text{out}}^{(2)} = \left( \frac{3}{2} + \frac{4}{3\sqrt{3}} \right) \Theta Dd. \quad (4.6)$$

The same relations at  $Q < 0$  may be written for the process of an isothermal stretching of the liquid to the boiling state which starts with the formation of a bubble of vapor in the liquid phase. In this case instead of (4.4) we have to write

$$\tilde{A}_{\text{out}}^{(1)} \simeq \Theta[\mu^*(\Delta_l(d/2)) - \mu^*(\Delta_b)] = \Theta Dd \left[ -\frac{3}{4} + \frac{4}{3\sqrt{3}} \right]. \quad (4.7)$$

Here  $\Delta_b = b$ ,  $w_b = 1$ ;  $\Delta_l(d/2) = d/2$ . We have to add to this energy the work  $\tilde{A}_{\text{out}}^{(2)}$  which compensates the internal work of the gas-type fluctuations, emerging spontaneously in the liquid phase along the relative maximum of the gas branch. Then:

$$\tilde{A}_{\text{out}}^{(1)} + \tilde{A}_{\text{out}}^{(2)} = \Theta Dd \left( -\frac{3}{2} + \frac{4}{3\sqrt{3}} \right). \quad (4.8)$$

In the TL the argument  $\Delta = \Delta_g$  of the main maximum of the isotherm  $\mu^*(\Delta)$  of the vapor phase varies in the intervals  $-b \leq \Delta \leq -d$  and  $-d \leq \Delta \leq -\frac{d}{2}$  (see Figs. 5 and 6) and takes a broken form. The van der Waals point  $\Delta = -d$  becomes a turning point of the thermodynamic trajectory of the vapor phase.

The part of the isotherm  $\mu^*(\Delta)$ , which refers to the relative maximum of the liquid phase, is nonzero only at the point  $\Delta_l = \frac{1}{2}d$ , since only here  $w_l = 1/2$ ,  $\rho_{01} = d$ , whereas everywhere within the interval  $\frac{b}{2} \leq \rho_{01} < d$  we have  $w_l = 0$ .

In the TL, the work along the trajectory of the main maximum of a vapor phase  $A_{\text{out}}^{(1)}$  in (4.6) has the form:

$$A_{\text{out}}^{(1)} = \Theta(\mu^*(\Delta)_{\Delta=-\frac{1}{2}d} - \mu^*(\Delta)_{\Delta=-d}) + \Theta(\mu^*(\Delta)_{\Delta=-d} - \mu^*(\Delta)_{\Delta=-b}). \quad (4.9)$$

However, one can easily make sure that

$$\mu^*(\Delta)_{\Delta=\pm d} = 0, \mu^*(\Delta)_{\Delta=-\frac{1}{2}d} = \frac{3}{4}Dd\Theta \text{ and } \mu^*(\Delta)_{\Delta=-b} = \frac{4}{3\sqrt{3}}\Theta Dd.$$

Therefore the term  $\frac{4}{3\sqrt{3}}\Theta Dd$  in expressions (4.4) and (4.6) can be treated as the work necessary to reach the axis  $\mu^* = 0$ , and the term  $(3/2)\Theta Dd$  in (4.6) describes an external work as a sum of two works along the axis  $\mu^* = 0$  (namely the sum of the first term of (4.9) and of the term (4.5)) *that result the creation of a nucleated liquid droplet in a vapor phase. Moreover, the thermodynamic trajectories which leads to such creation go along the axis  $\mu^* = 0$  inside the vapor phase states from the van der Waals point  $\Delta = \Delta_g = -d$  with probability 1 to the point  $\Delta_g = -\frac{1}{2}d$  with probability 1/2, and from the liquid phase states from the point  $\rho_{01} = d$ ,  $\Delta_l = 0$  with probability 0 to the point  $\Delta_l = \frac{1}{2}d$  with probability 1/2.*

After reaching at the line  $\mu^* = 0$  the state  $\rho_{02} = -d$ ,  $\Delta_g = -1/2d$ ,  $\rho_{01} = d$ ,  $\Delta_l = 1/2d$ , a phase transition starts: a droplet of liquid and two-phase system emerge. (This is the first stage of the FOPT, announced in the headline of the present work.)

The latent work (per one particle) of the transition of a particle from the gas phase to the liquid phase in full agreement with (4.4)–(4.8) equals:

$$A = \Theta(\mu^*(\Delta_{d/2}) - \mu^*(\Delta_{-d/2})) = -\frac{3}{2}\Theta Dd. \quad (4.10)$$

The creation of a liquid droplet in a vapor phase is equivalent to the work  $A_{\text{int}}$  spent for creation of an additional internal pressure inside the liquid droplet, which is equal to  $2\alpha/R_{\text{dr}}$  and for the energy of the surface tension  $\alpha S_{\text{dr}}$ , where  $\alpha$  is the surface tension coefficient,  $R_{\text{dr}}$  is the radius of the emerged droplet,  $S_{\text{dr}}$  is the surface of the droplet, all together gives  $-(\alpha/R_{\text{cr}})(4\pi/3)R_{\text{dr}}^3$ , and, recalculated per unity volume of the droplet,

$$A_{\text{int}} = -\frac{\alpha}{R_{\text{dr}}}. \quad (4.11)$$

As a result, for the balance of the performed densities of the work, after gathering (4.10) and the first term in (4.6) for  $A_{\text{out}}$  multiplied by  $n_l$ , here  $n_l$  is the density of particles in the droplet, we obtain an explicit value of the density of the surface energy of the droplet of liquid:

$$A_{\text{int}} = -\frac{\alpha}{R_{\text{dr}}} = -\frac{3}{2}\Theta n_l dD. \quad (4.12)$$

where, along (3.16),

$$n_l = n_l \frac{6}{\pi\sigma^3} = \eta_c(1+d) \frac{6}{\pi\sigma^3}. \quad (4.13)$$

Then the energy of the surface tension per one particle,  $A_{\text{int}}/n_l$ , is:

$$\frac{A_{\text{int}}}{n_l} = -\frac{3}{2}\Theta Dd = -\frac{\alpha}{R_{\text{dr}}} \frac{\pi\sigma^3}{6} \frac{1}{\eta_c(1+d)}. \quad (4.14)$$

When  $\Delta_g = -\frac{1}{2}d$ ,  $\Delta_l = \frac{1}{2}d$  it is easy see that for (4.12) one can write:

$$-3/2\Theta Dd = 12G[\Delta_g\Delta_l^2 - \Delta_l\Delta_g^2]. \quad (4.15)$$

This expression describes the structure of a surface layer, the mantel of the droplet. It's localization is in a narrow area of  $\varphi = \pi/2$  of arguments of the quantities  $\Delta_l$  and  $\Delta_g$ , namely  $\Delta_l(\varphi)$  for  $\varphi = \pi/2 + \gamma$ ,  $\Delta_g(\varphi)$  for  $\varphi = \pi/2 - \gamma$ . In TL the limit of  $\gamma$  is zero, which means that the mantel does not have any size, but the density of the energy of its surface is (4.15).

#### 4.1. Equality of the vapor and liquid chemical potentials at the jump points $\Delta_g = -d/2$ , $\Delta_l = d/2$

At that points the value of  $\Delta = \Delta_g + \Delta_l$  is equal to zero. This means that the mean density  $\eta$  in the whole expressions for  $\Xi = \Xi_0, \Xi_{\{\rho_k\}}, \Xi_{\rho_0}$  has to be put equal to  $\eta = \eta_c$ . Therefore in terms of the mean density

$$\mu_g \Big|_{\substack{\Delta=0 \\ \eta=\eta_c}} = \mu_l \Big|_{\substack{\Delta=0 \\ \eta=\eta_c}}. \quad (4.16)$$

The mean density equals  $\eta_c$ . The densities of vapor and liquid in the growing droplet remain unchanged from the beginning to the end of the phase transition. The volume of the vapor decreases, the volume of the droplet increases, the chemical potentials of both phases are equal,  $\mu_g = \mu_l$ . As a result of the latent work of pressure, a jump-like change of the density  $\eta_l - \eta_g = \eta_c 2d$  occurs. It occurs in all cases independent on  $N$ : for the *finite*  $N$  and in the *thermodynamic limit*  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V = \text{const}$ .

## 5. Two-phase systems

In the expressions (4.4)–(4.16) we have prepared a picture of a two-phase system: vapor + droplet of liquid.

In the TL the interface between those two phases is volumeless, there is no particles inside. In result the total number of particles  $N$  consists now of two terms  $N = N_g + N_l$ , the volume equals  $V_g + V_l$ . The numbers



$N_g$  and  $N_l$  as well as the volumes  $V_g$  and  $V_l$  do change continually. Therefore we have to take here all quantities estimated per one particle.

In the situation (4.2), or more simple (4.3)

$$\ln \Xi_{\rho_0} = \frac{PV}{\Theta}, \quad \ln \Xi_{\rho_0} = N\mathcal{E}(\Delta_g, \Delta_l) \approx N\mu^*(\Delta_g, \Delta_l) \quad (5.1)$$

we have to write:

$$Pv = \Theta\mu^*(\Delta_g, \Delta_l),$$

where  $v = V/N$  is the volume per one particle,  $\tau \leq 0,01$ . The independent variable is  $\varphi$ ,  $0 \leq \varphi \leq \pi$ .

Taking into account the sum (3.9) for  $\Delta$  we can write down the expressions for  $\mathcal{E}(\Delta)$  and  $\mu^*(\Delta)$  in the forms, which refer to two single phases, the vapor phase and the liquid phase:

$$\mathcal{E}(\Delta) = \mathcal{E}_g(\Delta_g, \Delta_l) + \mathcal{E}_l(\Delta_g, \Delta_l),$$

where

$$\begin{aligned} \mathcal{E}_g(\Delta_g, \Delta_l) &= \mu_g^*(\Delta_g, \Delta_l) + D\Delta_g^2 - G\Delta_g^4 + D\Delta_g\Delta_l - \\ &\quad - G[2(\Delta_g^3\Delta_l + \Delta_g\Delta_l^3) + 3\Delta_g^2\Delta_l^2], \\ \mathcal{E}_l(\Delta_g, \Delta_l) &= \mu_l^*(\Delta_g, \Delta_l) + D\Delta_l^2 - G\Delta_l^4 + D\Delta_g\Delta_l - \\ &\quad - G[2(\Delta_g^3\Delta_l + \Delta_g\Delta_l^3) + 3\Delta_g^2\Delta_l^2]; \end{aligned}$$

$$\begin{aligned} \mu^*(\Delta_g, \Delta_l) &= \mu_g^*(\Delta_g, \Delta_l) + \mu_l^*(\Delta_g, \Delta_l), \\ \mu_g^*(\Delta_g, \Delta_l) &= -2D\Delta_g + 4G\Delta_g^3 + 12G\Delta_g\Delta_l^2, \\ \mu_l^*(\Delta_g, \Delta_l) &= -2D\Delta_l + 4G\Delta_l^3 + 12G\Delta_l\Delta_g^2. \end{aligned} \quad (5.2)$$

These equalities are exact. The ends of the main maxima of  $\rho_{02}|_{\varphi=\pi/2} = -d$  and  $\rho_{01}|_{\varphi=\pi/2} = d$  are simultaneously the starting points of the relative maxima of  $\rho_{02}$  and  $\rho_{01}$ . Automatically that concerns to the quantities  $\Delta_g$  and  $\Delta_l$  in (5.2).

The dependence of  $\mu_g^*$  and  $\mu_l^*$  from the  $\Delta_g$  and  $\Delta_l$  is “mixed”: every one of them possesses mixed items  $\Delta_g\Delta_l^2$  or  $\Delta_l\Delta_g^2$  accordingly. In the TL (Fig. 8) mixed items are localized at the point  $\varphi = \frac{\pi}{2}$  or  $\mu^* = 0$ , along (2.12) that is the point of the end of the main maximum of  $\rho_{02}$ ,  $\rho_{02} = -d$ ,  $\Delta_g = -\frac{1}{2}d$ , and of the origin of the main maximum of  $\rho_{01}$  at  $\rho_{01} = d$ , or  $\Delta_l = \frac{1}{2}d$ .

The mixed product  $12G\Delta_g\Delta_l^2$  in (5.2) “pushes” the vapor branch  $\mu_g^*(\Delta_g, \Delta_l)$  to the point  $\mu_g^* = 0$ ,  $\Delta_g = -d/2$ . The product  $12G\Delta_l\Delta_g^2$

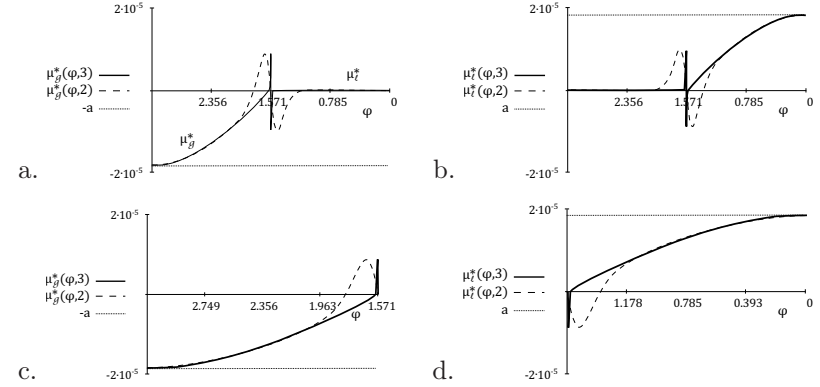


Figure 8. The plots of  $\mu_g^*(\Delta_g, \Delta_l)$  and  $\mu_l^*(\Delta_g, \Delta_l)$  and of their items, along (5.2), as functions of  $\varphi$  in area  $Q < 0$ ,  $0 \leq \varphi \leq \pi$  upper row and their main values, lower row at different  $N$ . The last items:  $12G\Delta_g\Delta_l^2$  in  $\mu_g^*(\Delta_g, \Delta_l)$  and  $12G\Delta_l\Delta_g^2$  in  $\mu_l^*(\Delta_g, \Delta_l)$  differ from zero only at the  $\varphi = \pi/2$ . Their difference  $\Theta 12G(\Delta_g\Delta_l^2 - \Delta_l\Delta_g^2)$  equals energy (per one particle) of the mantel of the droplet. The variation of the forms of curves  $\mu_g^*(\Delta_g, \Delta_l)$  and  $\mu_l^*(\Delta_g, \Delta_l)$  with growing  $N$ , starting from  $N = 10^5$  (dashed lines) to  $N = 10^7$  (solid lines) (that’s practically TL) is given.

“pushes” (for any  $N$ ) the trajectory of the liquid branch  $\mu_l^*(\Delta_g, \Delta_l)$  to the point  $\mu_l^* = 0$ ,  $\Delta_l = d/2$ . In the TL when pressing the vapor along the way  $\pi \geq \varphi \geq \pi/2$  the probabilities of all points of the relative maxima of the liquid branch are zero except the point,  $\rho_{01} = d$ , where  $w_l = 1/2$ .

Now we are ready to describe the whole process of the FOPT. Repeating the beginning of the previous section we start with the quasistatic isothermal pressing of a pure vapor. The description is in the TL. The discriminant  $Q > 0$ . The system of vapor moves along the trajectory  $\Delta = \rho^{(1)}$ ,  $\Delta < -b$ ,  $\mu^* < -a$ . The equation of state

$$\begin{aligned} Pv &= \Theta\mu^*(\rho^{(1)}) = -2D\Delta + 4G\Delta^3 = -2D\rho^{(1)} + 4G(\rho^{(1)})^3, \\ Pv &= \Theta \left[ -2D\frac{1}{\eta_c}(\eta - \eta_c) + 4G\frac{1}{\eta_c^3}(\eta - \eta_c)^3 \right], \\ \eta &< \eta_c(1 - b), \quad Pv/\Theta < -a. \end{aligned} \quad (5.3)$$

Then, continue to press we come to the points of bifurcation  $Q = 0$ ,  $\rho^{(1)} = \rho_{02} = -b$ ,  $\mu^* = -a$ . Inside the region  $Q < 0$  we (continue to) move along  $\rho_{02}$ , it is described in (4.9), we come close to the point



$\rho_{02} = -d$ ,  $\Delta_g = -\frac{1}{2}d$ ,  $\mu_g^* = 0$ ,  $\mu^* = 0$ . Along that way the equation of state is similar to (5.3), because in TL  $\Delta_l = 0$  ( $\Delta_l = w_l \rho_{01}$ ,  $w_l = 0$ ).

The situation changes dramatically at the point  $\rho_{02} = -d$ ;  $\mu^* = 0$ . Here the probabilities are equal:  $w_g = w_l = \frac{1}{2}$ . The system influenced by the outer pressure bears the droplet. At the point  $\rho_{01} = d$  the  $\Delta_l = \frac{1}{2}d$  the droplet of liquid arises, we get the two-phase system vapor + droplet of liquid. The FOPT starts.

We are not able to describe the situation by means of the expression  $Pv = \Theta\mu^*(\Delta)$ , where  $\Delta$  is a function of the mean density, and  $v$  is the mean volume (per one particle). Just now in TL we have the two-phase system,  $N_g$  and  $V_g$  we refer to the vapor and  $N_l$  and  $V_l$  — to the liquid droplet. These quantities change continually, and cannot be fixed. But they are mutually connected  $dN_g = -dN_l$ ,  $n_g dV_g = -dV_l n_l$ ,  $n_g$  and  $n_l$  become constant.

Taking that in mind let us write down the left-hand side of (5.1) for a two-phase system. We start with the initial relation  $PV = P_{\text{exp}}V$ , where  $P_{\text{exp}}$  is the outer pressure,  $PV = P(V_g + V_l \frac{n_l}{n_g})$ , add and subtract  $(P - \frac{\alpha}{R})V_l$ ,  $V_l$  is the droplet volume,  $n_l$  is the density of liquid in the droplet,  $n_g$  is the vapor density,  $V_g$  is the vapor volume. We have in mind that

$$V_l = \frac{4\pi}{3}R_l^3 \text{ and } -\frac{\alpha}{R_l} \frac{4\pi R_l^3}{3} = \frac{2\alpha}{R_l}V_l - \alpha S_l,$$

where  $S_l$  is the droplets surface,  $S_l = 4\pi R_l^2$ ,  $\alpha$  is the surface tension,  $R_l$  is the droplets radius. Then the left-hand side of (5.1) can be written down as

$$PV = P \left[ V_g + V_l \left( \frac{n_l}{n_g} - 1 \right) \right] + \left( P + \frac{2\alpha}{R_l} \right) V_l - \alpha S_l + \frac{\alpha}{R} V_l. \quad (5.4)$$

For the right hand side of (5.1) we shall do the same transformation: we add and subtract the energy of the droplet  $\pm \Theta \frac{3}{2} D d n_l V_l$ . Then the last item in (5.4) can be reduced with the quantity  $\Theta \frac{3}{2} D d n_l V_l$ . In result the equation of state along the line  $\varphi = \frac{\pi}{2}$  is

$$P \left[ V_g + V_l \left( \frac{n_l}{n_g} - 1 \right) \right] + \left( P + \frac{2\alpha}{R} \right) V_l - \alpha S_l = N \Theta \mu(\Delta_g \Delta_l) - \Theta \frac{3}{2} D d N_l. \quad (5.5)$$

Using expressions (5.2) we can describe the process of pressing vapor inside the area  $Q < 0$  in more detail then in (5.5).

In (5.1) and in (5.5) the expression  $\mu^*(\Delta_g \Delta_l)$  is a compound one. It's

equal zero at the points  $\Delta_g = -\frac{1}{2}d$ ,  $\Delta_l = \frac{1}{2}d$ , as well as the expressions

$$\mu^*(\Delta_g, \Delta_l) \Big|_{\substack{\Delta_g = -\frac{1}{2}d \\ \Delta_l = \frac{1}{2}d}} = \mu_l^*(\Delta_g, \Delta_l) \Big|_{\substack{\Delta_g = -\frac{1}{2}d \\ \Delta_l = \frac{1}{2}d}} = 0.$$

According to Section 4, when pressing a vapor in the state  $\mu_g^*(\Delta_g, \Delta_l)$  along the trajectory  $\Delta_g$ , the density fluctuations of the liquid-type arise spontaneously inside the vapor along the relative maxima of the trajectory  $\Delta_l = w_l \rho_{01}$ . The system performs an inner work  $\Theta \mu_l^*(\Delta_l \Delta_g)$  (per one particle). The outer pressure has to compensate this inner work. Therefore an additional work of the outer pressure has to be equal

$$- \Theta N_l \mu_l^*(\Delta_g, \Delta_l). \quad (5.6)$$

At all finite  $N$  the value of  $-\Theta \mu_l(\Delta_g, \Delta_l)$  is different from zero, (only at the point  $\Delta_l = \frac{1}{2}d$ ,  $\Delta_g = -\frac{1}{2}d$  it equals zero). In result inside the rectangular  $Q = 0$  in the process of the pressing of vapor along the trajectory  $\Delta(\varphi) = \Delta_g(\varphi)$ ,  $\frac{\pi}{2} \leq \varphi \leq \pi$  (here  $\rho_{02}$  is the main trajectory, and  $\rho_{01}$  is the relative one) for the equation  $PV/\Theta = N\mu^*(\Delta_g, \Delta_l)$  in the right side of (5.1) instead of  $N\mu^*(\Delta_g, \Delta_l)$  one has to write:

$$\begin{aligned} N\mu^*(\Delta_g, \Delta_l) &= N_g \mu_g^* + N_l (\mu_g^*(\Delta_g \Delta_l) - \mu_l(\Delta_g \Delta_l)), \text{ where} \\ N_l (\mu_g^* - \mu_l^*) &= \\ &= N_l \left[ -2D(\Delta_g - \Delta_l) + 4G(\Delta_g^3 - \Delta_l^3) + 12G(\Delta_g \Delta_l^2 - \Delta_l \Delta_g^2) \right]. \end{aligned} \quad (5.7)$$

It is easy to make sure that at the point of equal probability  $\Delta_g = -\frac{1}{2}d$ ,  $\Delta_l = \frac{1}{2}d$  it is rightly:

$$\begin{aligned} -2D(\Delta_g - \Delta_l) + 4G(\Delta_g^3 - \Delta_l^3) &= \frac{3}{2}Dd, \\ 12G(\Delta_g \Delta_l^2 - \Delta_l \Delta_g^2) &= -\frac{3}{2}dD. \end{aligned}$$

In the right hand side of (5.1) instead of  $N\mu^*(\Delta_g, \Delta_l)$  we can write the expression (5.8). Then reduce in (5.4) and (5.8) from the both sides the following

$$\frac{\alpha}{R} V = N \left[ -2D(\Delta_g - \Delta_l) + 4G(\Delta_g^3 - \Delta_l^3) \right]$$

and get an acceptable form for the two-phase system:

$$\begin{aligned} P \left[ V_g + V_l \left( \frac{n_l}{n_g} - 1 \right) \right] + \left( P + \frac{2\alpha}{R_l} \right) V_l - \alpha S_l &= \\ &= \Theta N_g \mu_g^*(\Delta_g, \Delta_l) + \Theta N_l 12G(\Delta_g \Delta_l^2 - \Delta_l \Delta_g^2). \end{aligned} \quad (5.8)$$

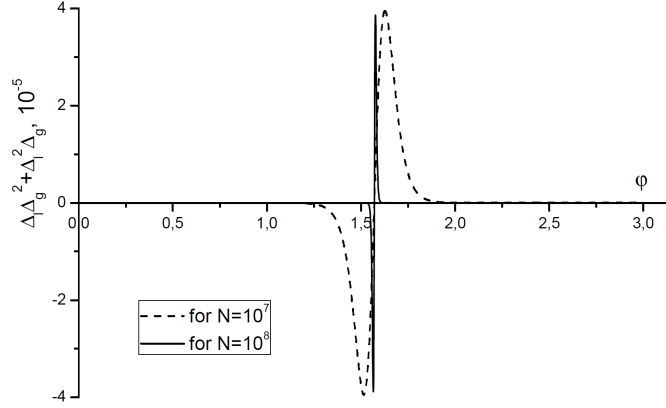


Figure 9. Localization of the mixed products  $12\Delta_g\Delta_l^2$  and  $12\Delta_l\Delta_g^2$  as functions of  $\varphi$  (or  $\mu^*$ ) at the point  $\varphi = \frac{\pi}{2}$ , for  $-d \leq \Delta_g \leq -\frac{d}{2}$ ,  $\frac{d}{2} \leq \Delta_l \leq d$  at different values of  $N$ . Their difference  $12(\Delta_g\Delta_l^2 - \Delta_l\Delta_g^2)$  describes the mantle around the droplet of liquid inside the vapor phase [28–31].

Here the expression

$$\frac{2\alpha}{R_l} - \alpha S_l = \Theta N_l 12G(\Delta_g\Delta_l^2 - \Delta_l\Delta_g^2) = -\frac{3}{2}\Theta N_l Dd \quad (5.9)$$

describes the energy of the droplet.

Now concerning the events on the axis  $\mu^* = 0$ . Here in points  $\Delta_l = -\frac{1}{2}d$ ,  $\Delta_g = \frac{1}{2}d$  all three functions  $\mu$ ,  $\mu_g^*$ ,  $\mu_l^*$  are zero. The latter are the significant points of the system not only in TL but at all finite numbers of  $N$ . Those are the points of equal probability for the system with the arbitrary number of particles to form the agglomerations of the vapor and of the liquid types.

Each one of the curves  $\mu_g^*(\Delta_g, \Delta_l)$  and  $\mu_l^*(\Delta_g, \Delta_l)$  has on the axis  $\mu^* = 0$  two points of intersection. Depending on  $N$  the former are located inside the intervals  $-d < \Delta_g < -\frac{d}{2}$ ,  $\frac{d}{2} < \Delta_l < d$ . The latter points are  $\Delta_g = -\frac{d}{2}$ ,  $\Delta_l = \frac{d}{2}$  with no respect to  $N$ . Likely to the former points the van der Waals points  $\Delta_g = -d$ ,  $\Delta_l = d$  can be reached only in TL.

Equations (5.8) and (5.9) work on the very beginning of the phase-transition process and describes the first stage of FOPT. Now we start to describe the second stage: the jump of densities.

The vapor system experiences the latent work of pressure, let us mark

it  $A_{\text{LW}}$ . Per one particle  $A_{\text{LW}}$  equals:

$$A_{\text{LW}} = P_{\text{LW}}(v_l - v_g) = P_{\text{LW}} \frac{\pi\sigma^3}{6} \frac{1}{\eta_c} \frac{-2d}{1-d^2}, \quad (5.10)$$

where  $v_l$ ,  $v_g$ ,  $v_c$  are (per one particle) volumes of liquid, vapor and a critical one,  $P_{\text{LW}}$  is the pressure of the latent work,

$$v_l = \frac{1}{n_l} = \frac{\pi\sigma^3}{6} \cdot \frac{1}{\eta_l} = \frac{\pi\sigma^3}{6} \frac{1}{\eta_c(1+d)}, \quad v_g = \frac{\pi\sigma^3}{6} \frac{1}{\eta_c(1-d)}. \quad (5.11)$$

The expression (5.10) has to coincide with that of (5.9)

$$A_{\text{LW}} = -\frac{3}{2}\Theta Dd = -v_l \frac{\alpha}{R_l}. \quad (5.12)$$

Then for  $P_{\text{LW}}$  we obtain the value of the pressure, which forms the magnitude of the latent work of pressure in (5.9)

$$P_{\text{LW}} = \frac{1}{2} \frac{v_l}{v_c} \frac{\alpha}{R_l} \frac{1-d^2}{d} \frac{6}{\pi\sigma^3} = \frac{3}{4}\Theta D\eta_c(1-d^2) \frac{6}{\pi\sigma^3}. \quad (5.13)$$

An external pressure in the form of the latent work of pressure continues to influence the system. The transition of particles from the vapor phase to the liquid phase takes place. The volume of the vapor decreases, the volume of the droplet increases. The vapors density remains equal to  $\eta_g = \eta_c(1-d)$ , the density of liquid in the droplet is also fixed,  $\eta_l = \eta_c(1+d)$ . When almost all vapor condenses and transits into a growing volume of liquid, *the vanishing vapor phase transforms into the vapor bubble with the density of the surface energy*

$$\frac{\alpha}{R_g} = n_g \frac{3}{2} Dd\Theta \quad (5.14)$$

inside the liquid phase. It is positive, the analogous energy of droplet (5.10) is negative. The vapor bubble disappears and this means the end of the first-order phase transition process.

In the TL the processes of bubble disappearance, as well as the droplet appearance, passes the line  $\mu^* = 0$ , and are the main parts of the first-order phase transition process. Both phases, the liquid and the vapor one, take place in the process of disappearance of vapor bubble. With respect to the changes of density, this process passes along the horizontal parts of isotherms  $\mu_l^*(\Delta_g, \Delta_l)$  and  $\mu_g^*(\Delta_g, \Delta_l)$  but in the mutually reverse directions: from  $\Delta_l = \frac{1}{2}d$  to  $\Delta_l = d$ , for liquid, and from  $\Delta_g = -\frac{1}{2}d$  to  $\Delta_g = 0$ ,  $\rho_{02} = -d$ ,  $w_g(-d) = 0$  for vapor.

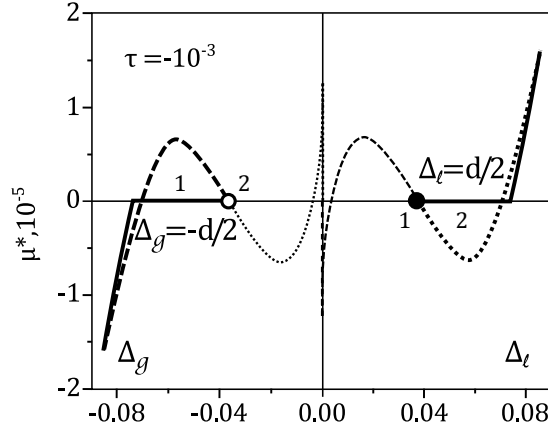


Figure 10. The isotherms of the equation of state, for fixed:  $N = 10^5$  — dashed lines, in TL — solid lines, (1) the start and the passage of the process of FOPT. The black circle depict the droplet of liquid in the vapor phase, (2) the end of the process of the FOPT. The circle depict the bubble of vapor in a liquid phase. The bubble of vapor is all that remains from the maternal phase of vapor after the FOPT. We use here considerations opposite to those given in (4.8). In the end, the bubble disappears. The resulting liquid moves along the trajectory 2 to the point  $d$ . Releasing the energy  $-(4/3\sqrt{3})\theta Dd$  in the reverse direction to (4.9) it reaches the state  $\mu^* = 0$ ,  $\Delta = \Delta_l = b$ .

Now we shall try to single out from formulas (4.11) and (5.16) the expressions, which may be related to the surface tension coefficient, and to the expressions which determine the radii of the nuclei spheres

Let us take the ration of formulas (4.12) and (5.15) and get

$$\frac{R_g}{R_l} = \frac{\eta_l}{\eta_g} = \frac{(1+d)}{(1-d)}. \quad (5.15)$$

Thus, during the process of FOPT the ratio of the last bubble radius to the first droplet radius is the same as the ratio of the droplet density to the bubbles density.

An invariant of these ratios in (4.12) and (5.16) is the  $\alpha$  from the left-hand side and the quantity  $(3/2)Dd\eta_c(6/\pi\sigma^3)$  from the right-hand side. The dimension of  $\alpha$  is  $[\alpha] = \text{Joule/m}^2$ , the dimension of  $R$  is  $[R] = \text{m}$ . Then in expressions (4.12) and (5.16) we set the following value of the surface tension coefficient and its behavior while approaching the

critical point  $\tau = 0$

$$\alpha = \frac{9}{\pi} Dd\Theta \frac{1}{\sigma^2} \sim \tau^{\frac{5\nu}{2}}, \quad (5.16)$$

where  $D = D_{m_\tau}$ ,  $d = \sqrt{D/2G}$ , and  $G = G_{m_\tau}$  according to formula (2.1). Then for  $R_l^{(\min)}$  and  $R_g^{(\min)}$ , i.e., the minimal values of the liquid droplet and vapor bubble radii, we have:

$$R_l^{(\min)} = \frac{\sigma}{\eta_c(1+d)}, \quad R_g^{(\min)} = \frac{\sigma}{\eta_c(1-d)}. \quad (5.17)$$

Here  $\eta_c$  is the universal quantity,  $\eta_c = 0.130443$ . The radii are determined by the value of the hard-sphere diameter  $\sigma$  (which is different for different substances, as can be seen from Table 1) and by the value of the parameter  $d = \sqrt{D/2G}$ .

The FOPT process ends with disappearance of the vapor bubble. The work, necessary for this, equals to the value (5.16) with the opposite sign, multiplied by the volume of the bubble. Let us denote this work by  $A_g$ . Taking into account that  $(\pi\sigma^3/6)n_g = \eta_g$ ,  $\eta_g = \eta_c(1+2\Delta_g) = \eta_c(1-d)$  and (5.12), after some manipulations we get

$$A_g = -\frac{4\pi R_g^3}{3} \frac{\alpha}{R_g} = -\frac{12}{(1-d)^2} \frac{Dd\Theta}{\eta_c^2}. \quad (5.18)$$

The work to create the bubble  $A$  (see Fig 10) occurs in the process, when  $\Delta_l$  varies from  $d$  to  $d/2$ ; the disappearance of the bubble goes in the reverse direction:  $\Delta_l$  varies from  $d/2$  to  $d$ . Therefore we can say that the end of the first-order phase transition occurs in the points  $\Delta_g = -d$  and  $\Delta_l = d$ , similar to the van der Waals theory.

The latent work of pressure is connected to the sum of three works:

1. the work for creation of the liquid droplet in the vapor phase, which is given in formulas (5.6) and (5.10), multiplied by the droplet volume  $4\pi R_l^3/3$  — this is the beginning of the phase transition;
2. the work (5.19) for vanishing the vapor bubble in the completely formed liquid phase — this is the end of the phase transition, thus in total:

$$A_l = 12 \frac{1}{\eta_c^2(1+d)^2} Dd\Theta, \quad A_g = -12 \frac{1}{(1-d)^2} \frac{Dd\Theta}{\eta_c^2}; \quad (5.19)$$

3. and of the work  $A_{ph}$  for transition of all vapor into liquid. The latter one is the main part of the process. The transition occurs

between the points  $\Delta_g = -\frac{1}{2}d \div \Delta_l = \frac{1}{2}d$  along the line  $\mu^* = 0$ :

$$A_{ph} = \Theta(\mu_l^*(\Delta_l) - \mu_g^*(\Delta_g)) = P_l v_l - P_g v_g = -\frac{3}{2}\Theta Dd. \quad (5.20)$$

However, those expressions are not commensurable. Equation (5.20) characterizes the energy of a jump per one particle. Equations (5.19) determine the energies of the liquid droplet and of the vapor bubble. If the quantities given by these formulas recalculate with respect to energy per one particle, we arrive at a “magic” characteristic  $\Theta Dd$ , which enters various quantities with corresponding coefficients. The numbers of particles within the “initial droplet” and within the “last bubble” are equal to their volumes multiplied by the density of the droplet and bubble, respectively. Thus, for the number of particles in the initial droplet and the last bubble we have

$$N_l = n_l \frac{4\pi R_l^3}{3} = \frac{6}{\pi\sigma^3} \eta_c (1+d) \frac{4\pi\sigma^3}{3} \frac{1}{\eta_c^3 (1+d)^3},$$

$$N_l = \frac{8}{\eta_c^2 (1+d)^2}, \quad N_g = \frac{8}{\eta_c^2 (1-d)^2}. \quad (5.21)$$

And the works for creation of the droplet and vanishing of the bubble per one particle according to (5.19) and (5.21) are as follows

$$A_g = -\frac{3}{2}Dd\Theta, \quad A_{dr} = \frac{3}{2}Dd\Theta. \quad (5.22)$$

Their sum equals zero. The latent work is given only by the expression (5.20).

At the final stage we have only a liquid phase. The latent work of pressure is determined by the points of jump  $\Delta_g = -\frac{1}{2}d$  and  $\Delta_l = \frac{1}{2}d$ , by the densities  $\eta_c(1-d)$  and  $\eta_c(1+d)$  accordingly, like from the van der Waals points  $-d$  and  $d$ .

We have completed the whole picture of the FOPT. The investigation of  $\Xi_{\rho_0}$  is the only one that describes the process of the first order phase transition. Merely  $\Xi_{\rho_0}$  inside the full expression (1.3) depends both on  $\mu^*$  and the order parameters  $\Delta_g, \Delta_l$ . The remaining  $\Xi' = \Xi_0 \Xi_{\{\rho_k\}}$  in (1.3) is independent on  $\Delta_g, \Delta_l$  being a function of  $\tau$  and  $\eta$  only. During the FOPT the order parameters  $\Delta_g$  and  $\Delta_l$  are constant:  $\Delta_g = -d/2$ ,  $\Delta_l = d/2$ . Their sum is equal to 0. Therefore during the FOPT,  $\Delta = \Delta_g + \Delta_l = 0$ ,  $\Delta = (\eta - \eta_c)/\eta_c$ , so  $\eta = \eta_c = 0.14033$ . We have to substitute this value of density  $\eta$  in the formula for  $\Xi'$  (1.3). The ultimate expression of the grand partition function takes the form

$$\Xi = \Xi(\Delta_g, \Delta_l) = [\Xi_0 \Xi_{\{\rho_k\}}]_{\eta=\eta_c} \cdot \Xi_{\rho_0}(\Delta_g, \Delta_l) \Big|_{\substack{\Delta_g=-d/2 \\ \Delta_l=d/2}}. \quad (5.23)$$

## 6. The restrictive curves of FOPT [27]

Let us consider a system of restrictive curves which follow from the results obtained above. Recall that the vapor is continuously under the outer pressure.

The bound of the bifurcation area BBA crosses the critical point ( $\tau = 0, \eta = \eta_c$ ) and two points in the vertices of the diagonal of the rectangle  $Q = 0$  (see Fig. 1), the first point,  $\mu^* = -a, \Delta_g = -b$  and the second  $\mu^* = a, \Delta_l = b, a = (2/3)Db \sim \tau^{\frac{5}{2}\nu}, b = \sqrt{(2/3)D/G}$ . They accordingly correspond to the following values of densities and pressures:

$$\eta_g|_{\substack{-a \\ -b}} = \eta_c(1-b), \quad P_g = \Theta \frac{N_g}{V} \mu^*(\Delta_g, \Delta_l) \Big|_{\substack{\Delta_g=-b \\ \Delta_l=0}} = -\Theta \frac{6}{\pi\sigma^3} \eta_g a;$$

$$\eta_l|_a = \eta_c(1+b), \quad P_l = \Theta \frac{6}{\pi\sigma^3} \eta_l a. \quad (6.1)$$

Here  $a = Gb^3, b = \sqrt{(2/3)D/G} \sim \tau^{\nu/2}, \mu_i^*(\Delta_g, \Delta_l) = -2D\Delta_i + 4G\Delta_i^3, \Delta_i = w_i(\eta_i/\eta_c - 1), i = g, l, w_i = 1$ ; at  $\tau = 0$  we have:  $\eta_i = \eta_c, \Delta_g = \Delta_l = 0$ . So the bifurcation curve for the vapor phase  $\eta_g \leq \eta_c$  is:

$$-2D(\eta_g/\eta_c - 1) + 4G(\eta_g/\eta_c - 1)^3 = -\frac{2}{3}Db$$

and for the liquid phase,  $\eta_l \geq \eta_c$

$$-2D(\eta_l/\eta_c - 1) + 4G(\eta_l/\eta_c - 1)^3 = \frac{2}{3}Db. \quad (6.2)$$

**The bounds of the real FOPT.** The restrictive curves surround the area of the entropic processes, connected with the arising of a new phase, in our case arising of the droplet of liquid inside the vapor. The variables here are the chemical potential and the temperature, and new order parameters  $\Delta_g$  and  $\Delta_l$ .

We distinguish two situations. The former is the beginning of the nucleation of a droplet inside the vapor and the emergence of a two-phase system: vapor plus droplet of liquid. We have named that process “nucleation”. The latter situation is the transition of vapor into the droplet until whole vapor disappears. Finally, the new liquid phase locates on the vertex  $\mu^* = a, \Delta_l = b$ . That process is called transition.

The curve surrounding the situation of “nucleation” is going through the critical point and the points of the first zeros of  $\mu_g^*(\Delta_g, \Delta_l)$  and  $\mu_l^*(\Delta_g, \Delta_l)$  (see Fig. 10). In TL that are the points  $\Delta_g = -d, \Delta_l = 0$ ;

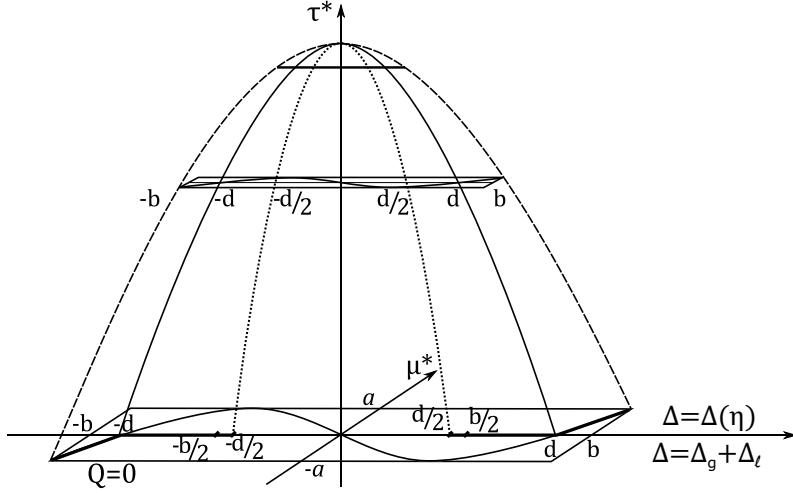


Figure 11. (a) The restrictive curves of FOPT along the formulae (6.1)–(6.5). The bifurcation curve 1: gets through the critical point and the points  $(\mu^* = -a, \Delta = -b)$  and  $(\mu^* = a, \Delta = b)$ ,  $\Delta = \frac{1}{\eta_c}(\eta - \eta_c)$ . The *nucleation* curve in TL is going through the critical points and the points  $\Delta_g = -d, \Delta_l = 0$  (for vapor) and  $\Delta_g = 0, \Delta_l = d$  – for liquid (it coincides with the van der Waals binodal). The transition curve 3: gets through the critical point and the points of the jump  $(\mu^* = \mu_g^* = 0, \Delta_g = -\frac{1}{2}d)$  and  $(\mu^* = \mu_l^* = 0, \Delta_l = \frac{1}{2}d)$ . As functions of densities  $\eta_g = \eta_c(1 - d)$  and  $\eta_l = \eta_c(1 + d)$ . [Likely to the van der Waals theory, the points of the spinodal 4: are  $(\mu^* = a, \Delta = \Delta_g = -b/2)$  and  $(\mu^* = -a, \Delta = \Delta_l = b/2)$  – but those points are unattainable in our theory (see Fig. 7).] (b) The quantity  $\mu^*$  is proportional to  $\tau^{\frac{5}{2}\nu}$ , the density  $\eta \sim \tau^{\nu/2}$ , therefore in the regions very near to the critical point the curves of restrictive curve and binodal turn into lines, the difference between the processes of pressing a vapor (and get droplets of liquid) or stretching a liquid (and have bubbles of vapor) occur with equal probability. We obtain effects described by Bakai in [32]: the interphase system with droplets and bubbles.

$\Delta_g = 0, \Delta_l = d$  (see Fig. 10, formula (3.11), Fig. 3; Fig. 6). Those are the points of van der Waals binodal.

The dependence between  $\Delta_g, \Delta_l$  and  $\eta_g, \eta_l$  is given in (3.13). From that we can write the equations for “nucleation” curves:

- for vapor:  $\Delta_g = -d, \mu_g^* = -2D\Delta_g + 4G\Delta_g^3 = 0|_{\Delta_g=-d},$

$$-d = \frac{1}{\eta_c}(\eta_g - \eta_c), -2D\frac{1}{\eta_c}(\eta_g - \eta_c) + 4G\frac{1}{\eta_c^3}(\eta_g - \eta_c)^3 = 0;$$

- for liquid:  $\Delta_l = d, \mu_l^* = -2D\Delta_l + 4G\Delta_l^3 = 0|_{\Delta_l=d}, d = \frac{1}{\eta_c}(\eta_l - \eta_c),$   
 $-2D\frac{1}{\eta_c}(\eta_l - \eta_c) + 4G\frac{1}{\eta_c^3}(\eta_l - \eta_c)^3 = 0.$

A spinodal curve is a geometric place of the points of a jump like a transition from the host vapor phase into a liquid phase (droplet) while vapor is isothermally compressed. On the plot of probabilities shown on Figs. 5 and 6, the spinodal corresponds to the crossing point for the probabilities  $w_g = w_l = \frac{1}{2}$ . In the thermodynamic limit it corresponds to the point  $\frac{1}{2}$  on the Heaviside curves. The points of a jump have the following coordinates  $\Delta_g = w_g\rho_{02} = -\frac{1}{2}d$  and  $\Delta_l = w_l\rho_{01} = \frac{1}{2}d$  (see Fig. 6). Here the isotherm  $\mu_g^*$  and  $\mu_l^*$  equal zero:

$$\begin{aligned}\mu_g^*(\Delta_g, \Delta_l) &= -2D\Delta_g + 4G\Delta_g^3 + 12G\Delta_g\Delta_l^2 = 0, \\ \mu_l^*(\Delta_g, \Delta_l) &= -2D\Delta_l + 4G\Delta_l^3 + 12G\Delta_l\Delta_g^2 = 0.\end{aligned}\quad (6.3)$$

This equalities may serve as the definitions of the spinodal.

Here  $\Delta_g = -\frac{1}{2}d = -\frac{1}{2}\sqrt{\frac{1}{2}D/G}$ ,  $\Delta_l = \frac{1}{2}d = \frac{1}{2}\sqrt{\frac{1}{2}D/G}$ . Taking into account (from (3.13)) the dependencies of  $\Delta_g$  and  $\Delta_l$  on densities and that  $w_g = w_l = 1/2$ , one may write for both vapor and liquid:

$$\left(\frac{\eta_g}{\eta_c} - 1\right) = -d, \quad \left(\frac{\eta_l}{\eta_c} - 1\right) = d. \quad (6.4)$$

We associate these equalities in one common expression holding some peculiar distinguish of the phenomena. Taking into account explicit forms of the third terms in (6.3) one can rewrite (6.3) for the vapor part of the spinodal and for the liquid part, respectively:

$$\begin{aligned}-D\left(\frac{\eta_g}{\eta_c} - 1\right) + \frac{1}{2}G\left(\frac{\eta_g}{\eta_c} - 1\right)^3 &= \frac{3}{4}Dd, \\ -D\left(\frac{\eta_l}{\eta_c} - 1\right) + \frac{1}{2}G\left(\frac{\eta_l}{\eta_c} - 1\right)^3 &= -\frac{3}{4}Dd.\end{aligned}\quad (6.5)$$

In (6.3)–(6.5) we have got expressions for nucleation and the transition curves of the FOPT in a one-component system.

## 7. Conclusions

After obtaining the restrictive curves, the problem of the first-order phase transition in a simple system on the example of the vapor-liquid system



is completed. Taking the quartic density measure as a basic one, we have finished a long chain of investigations on the single integral of the Landau type. All considerations are made on the first principles. It seems to be topical to make some short overview of the main steps of those interpretations of FOPT that are made from the very beginning to the end.

We start from the potential of interaction between two particles. Usually, the potential consists of two parts: one describes the repulsion, the other one corresponds to attraction. Accordingly to that, the integration of the grand partition function is made in two phase-spaces. The former is the Cartesian phase-space over the coordinates  $r_1, \dots, r_N$  of particles describing the behavior of a system of hard spheres which simulate the mutual impenetrability of the particles. The latter is the phase-space of collective variables  $\{\rho_{\mathbf{k}}\}$  describing the long-range attractive interactions. In both integrations we work in thermodynamical phase-space  $p, \tau, V$ .

To describe the FOPT events, we need to work in the thermodynamical phase-space  $p, T, \mu^*$ , where  $\mu^*$  (as a result of the previous two types of integration) is the generalized chemical potential of the system. Therefore we finish the whole work on the investigation of the single integral of Landau type over the macroscopic variable  $\rho_0$ .

The small parameter  $(N/V)\sigma^3$  inherent to the system of hard spheres (HS) is proportional to the density, or the ratio  $\sigma/\langle r \rangle$ , where  $\sigma$  is the diameter of a hard sphere,  $\langle r \rangle$  is the average distance between particles.

The main characteristic phenomenon of the long-range interactions is screening. The radius of screening  $r_0$  is an effective radius of the long-range interaction (for charged particles  $r_0$  is the Debye radius which is inversely proportional to the square root of density). Because of the negative value of the potential  $\psi(0)$ , the effective attractions either in the vicinity of the critical point or in the vicinity of the FOPT, become as  $1/r$ ,  $r_0 \sim (N/V)^{-1/2}$  and  $r_0/\langle r \rangle \sim (N/V)^{-1/6}$ . The ratio  $r_0/\langle r \rangle$  is inverse to the small parameter of a hard-sphere. In this case the Gaussian density measure cannot be the basic measure [12].

It's useful to mark, that the attraction acts on long distances, that means on small  $k$ ; the repulsion acts on short distances, that is on large  $k$ .

In  $\{\rho_{\mathbf{k}}\}$ -space the attractive part of the potential energy is quadratic with respect to  $\rho_{\mathbf{k}}$ :

$$\sum_{\substack{i,j \\ i \neq j}} \phi(\mathbf{r}_{ij}) \rightarrow \sum_{\mathbf{k}} \tilde{\phi}(k)(\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - 1).$$

On all those reasons we describe the repulsion in the Cartesian phase-

space and the attraction in the collective variable (CV) phase space  $\{\rho_{\mathbf{k}}\}$  [27]. In [33], the first steps of describing both potentials of interaction between particles through functions belonging to space  $L_2$  having the Fourier transform were described. Functions of the grand canonical ensemble were investigated in two phase spaces of different sets of collective variables.

Thanks to the works of Perkus and Jevik, Andersen and Chandler, Week now we have complete results for the thermodynamics of the system of hard spheres [34–38]. In works [9–11, 13, 14, 25–27], the method of CV had also been entirely elaborated.

In the present article both phase spaces are connected by the Jacobian of transition. After integration in the Cartesian phase-space over the coordinates of individual particles, we obtain the initial expression for the partition function in the collective variables phase-space [27]:

$$\Xi = \Xi_0 \Xi_1,$$

where  $\Xi_0$  is the partition function of the system of hard spheres (HS). The HS system is the reference system in the CV phase-space,  $\Xi_1$  is the resulting form for the partition function of the attractive interactions

$$\begin{aligned} \Xi_1 = & \int \exp(h\rho_0 - \frac{1}{2} \sum_{\mathbf{k}} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \\ & + \sum_{n \geq 1} \frac{1}{n!} (-i2\pi)^n \left( \sum_{k_1, \dots, k_n} \mathfrak{M}_n(k_1 \dots k_n) \omega_{k_1} \dots \omega_{k_n} \right) (d\omega)(d\rho), \end{aligned}$$

here the designations are the following;  $h = \mu - \mu_0$ ,  $\mu_0$  is the chemical potential of the HS,  $\alpha(k) = (N/V)\beta\tilde{\phi}(k)$ ,  $\tilde{\phi}(k)$  is the Fourier transform of  $\phi(r)$   $\{\omega_{\mathbf{k}}\}$  is the system of Fourier variables conjugated to the CV,  $\mathfrak{M}_n$  are semiinvariants constructed from the RS-correlation functions. For the first two semiinvariants we have

$$\begin{aligned} \mathfrak{M}_1(k) &= N\delta_{\mathbf{k}}, \\ \mathfrak{M}_2(k_1, k_2) &= (\langle N^2 \rangle - \langle N \rangle^2) \delta_{\mathbf{k}_1} \delta_{\mathbf{k}_2} + \frac{1}{V} N(N-1) \mu_2^N(k) \delta_{k_1+k_2}, \end{aligned}$$

where  $\mu_2(k)$  is the Fourier transform of the binary correlation function of the RS. The explicit formulas of the cumulants  $\mathfrak{M}_n$  are known [39–41]. All  $\mathfrak{M}_n$  are decreasing functions of  $n$ , their limits at  $k_i \rightarrow 0$  possess wide platos, as it is seen from the Figs. 13 and 14 (see Appendix B).

For the potential  $\alpha(k) = (N/V)\beta\tilde{\phi}(k)$  or  $\phi(r)$  which describes the attraction between two particles, we demand its Fourier transform to



be negative at small  $k$ , moreover  $\tilde{\phi}(k)|_{k=0} < 0$  always. The curve of  $\tilde{\phi}(k)$  intersects the axis  $k$  in many points. We mark the first point of intersection by  $B$ ,  $\tilde{\phi}(B) = 0$ . For  $k > B$  the curve  $\tilde{\phi}(k)$  behaves with the periodical character and is rapidly decreasing. So we assume that the main events connected with the attraction are gathered inside the interval  $0 \leq k \leq B$ , and we put  $\tilde{\phi}(k) = 0$  for  $k > B$ .

The curves of cumulants  $\mathfrak{M}_n(k_1, \dots, k_n)$  are changing very slowly at small values of  $k_1, \dots, k_n$  and have wide threshold platos at  $k_i = 0$ , as it is shown in Fig. 14. It's significant that the coordinate of the first zero of  $\tilde{\phi}(k)|_{k=B} = 0$  is located in the middle region of platos of all cumulants. We assume that all important events connected with attraction occur in (7.1) at the platos of  $\mathfrak{M}_n(0, \dots, 0)$  and we put here values of all cumulants at  $k_i = 0$ . *That means the solution of the problem: the great partition function can be calculated.* In the future, it is of the same interest to take into account the terms proportional to  $k^2$  for  $\mu_2(k)$ .

Since  $\alpha(k)|_{k>B} = 0$  for all  $k > B$  we integrate in (7.1) over  $\rho_{\mathbf{k}}$  at  $k > 0$ , get  $\delta(\omega_{\mathbf{k}})$  at  $k > B$ , then integrate over  $\omega_{\mathbf{k}}$  at  $k > B$  and obtain quite suitable form of  $\Xi_1$  for further consideration in the present work:

$$\begin{aligned} \Xi_1 = & \int \exp h\rho_0 - \frac{1}{2} \sum_{k < B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + i2\pi \sum_{k < B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \\ & + \sum_{n \geq 1} \frac{1}{n!} (-i2\pi)^n \sum_{\substack{k_1, \dots, k_n \\ k_i < B}} \mathfrak{M}_n(0, \dots, 0) \omega_{k_1} \dots \omega_{k_n} \delta_{k_1 + \dots + k_n} (d\rho)(d\omega), \end{aligned} \quad (7.1)$$

Here we make some definitions. We say that

$$\begin{aligned} w_n(\rho, \omega) = & h\rho_0 - \frac{1}{2} \sum_{k < B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + i2\pi \sum_{k < B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \\ & + \sum_{m=1}^n \frac{(-i2\pi)^m}{m!} \sum_{\substack{k_1, \dots, k_m \\ k_i < B}} \mathfrak{M}_m(0, \dots, 0) \omega_{k_1} \dots \omega_{k_m}, \end{aligned} \quad (7.2)$$

is the  $n$ -th basic density measure, if all momenta

$$\int w_n(\rho, \omega) \rho_{k_1} \dots \rho_{k_l} (d\rho)(d\omega)$$

are convergent. In [12] it was proved, that in the vicinity of the critical point ( $\tau = 0$ ,  $\eta = \eta_c$ ) the density measure  $w_6(\rho, \omega)$  is a basic one.

Concerning the screening. Integration with the Gaussian density measure as a basic density measure automatically gathers together the polarisation diagrams and convert the attractive potential  $\tilde{\phi}(k)$  into the screened form

$$g(k) \simeq \frac{\alpha(k)}{\kappa^2 + k^2}, \quad \alpha(k) = \frac{N}{V} \beta \tilde{\phi}(k),$$

$\kappa^{-1}$  equals to  $r_D$ , where  $r_D$  is the radius of screening, which tends to infinity at the critical point. That fact cause divergences in some diagrams in the expression of the partition function  $\Xi_1$  and expressions of the distribution functions. Namely, the diagrams for  $\Xi$  in which three lines of  $\tilde{g}(k)$  come out of the vertices are divergent. To avoid divergences we have to change the form of the basic density measure from the Gaussian to the quartic one. "Quartic" means that in the exponent of this form we have a polynomial of degree two, three and four in the indeterminate of  $\rho_{\mathbf{k}}$  (in general from degree two to six). In Fig. 14 and in [13] the quantities  $\mathfrak{M}_n(k, 0, \dots, 0)$  are given. The integrals of all momenta will be convergent when  $\mathfrak{M}_4(0, \dots, 0)$  is negative.

The cumulant  $\mathfrak{M}_5$  has the imaginary number  $i$ , therefore the convergence of all momenta is guaranteed by the term

$$-\frac{(-i2\pi)^4}{4!} \sum_{k_1, \dots, k_4} |\mathfrak{M}_4| \omega_{k_1} \dots \omega_{k_4} \delta_{k_1 + \dots + k_4}.$$

The imaginary term

$$\frac{(-i2\pi)^5}{4} \sum_{k_1, \dots, k_5} \mathfrak{M}_5(0) \omega_{k_1} \dots \omega_{k_5} \delta_{k_1 + \dots + k_5}$$

influences on the form of the rectilinear radius  $\eta = \eta_c$  [42]. In this work we do not deal with the questions about the forms of the rectilinear radius [43] and restrict ourselves to the quartic form  $w_4$ , and take the quartic density measure as a basic one.

In [12], it was proved that the description of different events by using the distribution functions demand to use the sixth degree density measure as a basic one, for example, phase transitions in the region near the three-critical point of one component systems.

We leave the investigation of  $w_5$  or  $w_6$  for the future. Here we have considered only one- and two-phase systems. From [13] and Fig. 14 it is clear, that all cumulants  $\mathfrak{M}_1, \dots, \mathfrak{M}_4$  have a proper mathematical signs. We calculate  $\Xi_1$  only for the basic density measure, assuming  $\Xi_1 = \int w_4(\rho_{\mathbf{k}} \omega_{\mathbf{k}}) (d\rho)(d\omega)$ .

Solving the problem of screening and the basic density measure, we have to describe the situation of the renormalization group symmetry. The latter arises in some part of the space of  $\{\rho_{\mathbf{k}}\}$  for  $B_{n_\tau} \leq k \leq B$ , where  $B_{n_\tau} = B/s^{n_\tau}$ ,  $s$  is the parameter of partition of the space  $\mathbf{k}$ ,  $k \leq B$  into blocks,  $n_\tau$  is the (critical) number of the last block in this partition,  $k_{n_\tau} = B/s^{n_\tau}$  is the limit value of  $k$ . For  $\{\rho_{\mathbf{k}}\}$  with  $k > B/s^{n_\tau}$  we are obliged to take the quartic density measure as a basic one. For  $k \leq B/s^{n_\tau}$  the basic is the Gaussian's density measure. To get that situation explicitly one needs to obtain the Hamiltonian in  $\Xi_1$  in the Ising form. For that reason we have to put the cumulant  $\mathfrak{M}_3(0)$  equal to zero in the Hamiltonian of  $\ln w_4(\rho\omega)$ . In result, for  $\Xi_1$  we obtain the Ising problem in an external field, and specific universal critical value for the critical density

$$\eta_c = \left( \frac{N}{V} \right)_c \frac{\pi\sigma^3}{6} \Big|_c = 0.13044.$$

Substituting the experimental value for the critical density of a particular physical system for  $(N/V)_c$  in the formula of  $\eta_c$ , we obtain the value of the hard core diameter of the particle of that system. In Table 1 such values are illustrated.

Going on with the investigations of  $\Xi_1$ , we obtain very important information: we get the maximal values of  $w_4(\rho_{\mathbf{k}})$  only at  $\rho_{\mathbf{k}} = 0$  for all  $k \neq 0$  and at  $\rho_0 \neq 0$  for  $k = 0$ . That means, that the integrals  $\Xi_1 = \int w_4(\rho_{\mathbf{k}})(d\rho)$  are split on two macroscopic problems: the integral over  $\rho_{\mathbf{k}}$  for  $k \neq 0$  and a single integral over the macroscopic variable  $\rho_0$ :  $\Xi_1 = \Xi_1(\rho_{\mathbf{k}})\Xi_{\rho_0}$ , where  $\Xi_{\rho_0}$  is given in (1.3) and (2.1). It is important that the chemical potential in the whole expression of  $\Xi_1$  is contained only in  $\Xi_{\rho_0}$ . The integrant in (2.1) depends on  $\tau$  and  $\mu^*$ , and at fixed  $\tau$  it is a complete differential of  $\mu^*$  (or of  $\varphi$ ) [44]. This case is considered in the present work.

In our calculations we have neglected the influence of the states with very small probability. For that aim the unstable solution  $\rho_{03}$  in Section 3 is not taken into consideration. Analyzing Figs. 2, 3 and 4 that seems to be right. As a result of this step, we are able to talk about the probabilities. We say that in the system under the continuous action of the outer force the FOPT starts when the probabilities to stay in a vapour or a liquid phase are 1/2. At that moment inside the maternal phase (vapor) the nucleus of the new phase (droplet of liquid) and two new order parameters  $\Delta_g$  and  $\Delta_l$  arise. The characteristic function of that process is  $Pv/\theta$ , where  $v = V/N$  depends on  $\mu^*$  but not on  $V$  at fixed  $T$ . In TL the shifts of the order parameters  $\Delta_g$  from  $-d$  to  $-d/2$ ,

and  $\Delta_l$  from  $d$  to  $d/2$  cannot be explained in the  $P, T, \eta$  theory by the conservations of densities. The most important here are Section 2, where the two trajectories  $\rho_{01}$  and  $\rho_{02}$  of the maximal positive values of the basic density measure are found, and Section 3, where the envelope curve in the form of probabilities of those solutions is obtained.

We didn't take into account the unstable solution  $\rho_{03}$ , the probability of which is small at all  $N$ , and is zero in the thermodynamic limit (TL). It is important to say that only in TL we have the two-phase system. Only in TL the mantle around the droplet does not have any thickness and does not have any particles but is has the surface energy. It was shown that the event of FOPT really occur on the horizontal part of the isotherm. The main part of those processes is the arising of the nuclei — the droplet of liquid inside a vapor system.

The essence in description of the phenomenon of FOPT is that the points  $-d$  and  $d$  (see Fig. 1), the points of the beginning and the end of the horizontal part of the isotherm are not the points of the arising of a new phase (liquid) inside the maternal phase (vapor). The nuclei of a new phase arise at the points  $\Delta_g = -\frac{1}{2}d$  and  $\Delta_l = \frac{1}{2}d$ , where  $\Delta_g$  and  $\Delta_l$  are new order parameters. We are working in the thermodynamic space  $p, \tau, \mu^*$  but not in the space  $p, \tau, V$ , or  $p, \tau, N$ . The densities at the points  $\Delta_g = -\frac{1}{2}d$  and  $\Delta_g = -d$ , at the points  $\Delta_l = \frac{1}{2}d$  and  $\Delta_l = d$  are respectively the same. The values of  $\Delta_g$  and  $\Delta_l$  are different from each other.

The generalized chemical potential  $\mu^*(\Delta_g, \Delta_l)$  of a two-phase system was rigorously divided into the potential of vapor  $\mu_g(\Delta_g, \Delta_l)$  and liquid  $\mu_l(\Delta_g, \Delta_l)$  in Section 5. From that we have obtained the expression for the energy of the droplets mantel. It was shown that the mantel consists of four layers and both neighbour phases — vapor and liquid — take their part in its formation. In experiments of [28–31] the layered structure of the mantel was confirmed.

Note that in our consideration we start from the first principles, repeated and used the works and results of our predecessors and, particularly, the results of van der Waals and Landau, however, here we got the explicit expressions for all coefficients in the Hamiltonians.

In general we have finished the description of the main events occurring during the phenomenon of the FOPT in the simple system. As it is known, in equilibrium, the simple system can exist in three phases: gas, liquid, and solid. It means that there have to be three main trajectories of the thermodynamic development, and two unstable trajectories between them. The sixth order density measure will serve as a basic density measure. There should be the tricritical point. But the problem may

consists of three problems of two-phase systems: gas-liquid, liquid-solid, gas-solid. In each one of them the quartic density measure plays the role of the basic density measure.

All these tasks can be solved after corresponding consideration of each part of solutions given in that work. In the whole work we exploit the fact that at fixed  $\tau$  the expression  $PV = \theta \ln \Xi$  is a complete differential of  $\mu^*$  [44].

In the formulas (1.3) and (5.23) only the integral in  $\Xi_{\rho_0}$  describes the FOPT. The expression  $\Xi_0 \Xi_{\{\rho_k\}}$  is constant, since it should be taken at  $\eta = \eta_c = 0.14033$ . Therefore, in terms of the description of the FOPT, the considerations given in the present paper are complete.

Appendix A and B would be helpful to clear the advantage of the method of steepest descent in solving the problems of FOPT.

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## Appendix A. Direct integration in the GPF

To validate the previous results of the Part 1 we do the direct integration of the Landau-type single integral over the macroscopic variable  $\rho_0$

$$\Xi_{\rho_0} = \int_{-\infty}^{\infty} \exp \left[ \sqrt{N}(\mu^*(\rho_0 + \tilde{\mathfrak{M}}_1) + D\rho_0^2 - \frac{1}{N}G\rho_0^4) \right] d\rho_0, \quad (\text{A.1})$$

where  $\tilde{\mathfrak{M}}_1 = \sqrt{N}(1 - \Delta)$ ,  $N$  is the mean number of particles,  $\Delta$ ,  $\mu^*$ ,  $D$ ,  $G$  are the quantities, given in the first part of the present paper,  $\Delta = (\eta - \eta_c)/\eta_c$  or  $\eta = \eta_c(1 + \Delta)$ ,  $\eta = (N/V)(\pi\sigma^3/6)$  is the density,  $\sigma$  is the diameter of a hard sphere,  $D$  and  $G$  are values of the resulting Hamiltonian, obtained, firstly, after integration in the phase-space of Cartesian coordinates of particles where the short-range interactions between the hard spheres are described, and, secondly, after integration in the phase-space of collective variables  $\{\rho_k\}$ ,  $k \neq 0$  where the long-range interactions are taken into account,  $\mu^*$  is the generalized chemical potential.

We put here  $\rho_0 = \sqrt{N}\rho'_0$ , omit the prime, mark  $N\mu^* = \nu$ , neglect the values of the order  $\ln N$  in the expression for  $\ln \Xi_{\rho_0}$  and write (A.1) in the initial form

$$\begin{aligned} \Xi_{\rho_0} &= \int_{-\infty}^{\infty} \exp \left\{ \nu(1 - \Delta) + \nu\rho_0 + ND\rho_0^2 - NG\rho_0^4 \right\} d\rho_0 \\ &= \exp \left[ \nu(1 - \Delta) + c_0 + \frac{1}{2}c_2\nu^2 + \frac{1}{4!}c_4\nu^4 + \dots \right]. \end{aligned} \quad (\text{A.2})$$

Or

$$\begin{aligned} \Xi_{\rho_0} &= \exp[\nu(1 - \Delta)]J, \\ J &= \int_{-\infty}^{\infty} \exp \left[ \nu\rho_0 + ND\rho_0^2 - NG\rho_0^4 \right] d\rho_0, \\ J &= J_0 \exp \left[ \frac{1}{2}c_2\nu^2 + \frac{1}{4!}c_4\nu^4 + \dots \right]. \end{aligned} \quad (\text{A.3})$$

Here

$$\begin{aligned}
J_0 &= J_{\nu=0} = \exp c_0 = \\
&= \int_{-\infty}^{\infty} \exp(ND\rho_0^2 - NG\rho_0^4) d\rho_0 = 2 \int_0^{\infty} \exp\{ND\rho_0^2 - NG\rho_0^4\} d\rho_0, \\
c_0 &= (\ln J)_{\nu=0}, \\
c_2 &= \frac{1}{J_0} \left( \frac{\partial^2 J}{\partial \nu^2} \right)_{\nu=0} - \left[ \frac{1}{J_0^2} \left( \frac{\partial J}{\partial \nu} \right)^2 \right]_{\nu=0}, \\
c_4 &= \left( \frac{\partial^4 \ln J}{\partial \nu^4} \right)_{\nu=0} = \left[ \frac{1}{J} \frac{\partial^4 J}{\partial \nu^4} - 3 \frac{1}{J^2} \frac{\partial^3 J}{\partial \nu^3} \frac{\partial J}{\partial \nu} - 3 \frac{1}{J^2} \frac{\partial^2 J}{\partial \nu^2} \frac{\partial^2 J}{\partial \nu^2} + \right. \\
&\quad \left. + 6 \frac{1}{J^3} \left( \frac{\partial J}{\partial \nu} \right)^2 \frac{\partial^2 J}{\partial \nu^2} + \right. \\
&\quad \left. + 6 \frac{1}{J^3} \left( \frac{\partial J}{\partial \nu} \right)^2 \frac{\partial^2 J}{\partial \nu^2} - 6 \frac{1}{J^4} \left( \frac{\partial J}{\partial \nu} \right)^4 \right]_{\nu=0} = \\
&= \left( \frac{1}{J} \frac{\partial^4 J}{\partial \nu^4} - 3 \frac{1}{J^2} \frac{\partial^2 J}{\partial \nu^2} \frac{\partial^2 J}{\partial \nu^2} \right)_{\nu=0}. \tag{A.4}
\end{aligned}$$

Odd derivatives are zero. Calculation of  $c_0$  may be fulfilled using parabolic functions: After substitutions

$$\begin{aligned}
NG\rho_0^4 &= \frac{s^2}{2}, \quad \rho_0^4 = \frac{s^2}{2NG}, \quad d\rho_0 = \frac{1}{2\sqrt{s}} \frac{1}{\sqrt[4]{2NG}} ds, \\
ND\rho_0^2 &= \frac{ND}{\sqrt{2NG}} s = zs, \quad z = \frac{ND}{\sqrt{2NG}} \gg 1
\end{aligned}$$

one gets

$$\begin{aligned}
J_0 &= \frac{1}{\sqrt[4]{2NG}} \int_0^{\infty} e^{zs - s^2/2} \frac{1}{\sqrt{s}} ds = \\
&= \frac{1}{\sqrt[4]{2NG}} \Gamma\left(\frac{1}{2}\right) e^{z^4/4} U(0, -z) = \frac{1}{\sqrt[4]{2NG}} \pi e^{z^2/4} V(0, z), \\
V(0, z) &= \sqrt{\frac{2}{\pi}} e^{z^2/4} z^{-1/2} \left\{ 1 + \frac{1 \cdot 3}{2^3 z^2} + O\left(\frac{1}{z^4}\right) \right\}.
\end{aligned}$$

Finally  $J_0$  equals

$$J_0 = \sqrt{2\pi} \frac{1}{\sqrt{ND}} e^{\frac{ND^2}{4G}} \left\{ 1 + \frac{1 \cdot 3}{2^3 z^2} + O\left(\frac{1}{z^4}\right) \right\}, \tag{A.5}$$

and for  $c_0$ , neglecting the term  $\sim \ln N$ , we have

$$c_0 = \frac{ND^2}{4G}. \tag{A.6}$$

The coefficients  $c_2$  and  $c_4$  are as follows

$$c_2 = \frac{\partial \ln J_0}{\partial ND} = \frac{\partial}{\partial (ND)} \frac{ND^2}{4NG}, \quad c_2 = \frac{1}{2} \frac{D}{G} \tag{A.7}$$

and

$$\begin{aligned}
c_4 &= -\frac{\partial}{\partial (NG)} \frac{(ND)^2}{4NG} - 3 \left[ \frac{\partial \left( \frac{(ND)^2}{4NG} \right)}{\partial (ND)} \right]^2 = \frac{1}{4} \frac{D^2}{G^2} - 3 \left( \frac{1}{2} \frac{D}{G} \right)^2, \\
c_4 &= -\frac{1}{2} \frac{D^2}{G^2}. \tag{A.8}
\end{aligned}$$

The same value for  $c_0$  one may get in the method of steepest descend (SDM). Coefficients  $c_2$  and  $c_4$  are connected with averaging over the density. From this moment the differences between these two methods starts.

Taking into account (A.6)–(A.8) rewrite the expression (A.2) for  $\Xi_{\rho_0}$  as

$$\Xi_{\rho_0} = \exp[\nu(1 - \Delta)] \exp \left[ \frac{1}{4} \frac{ND^2}{4G} + \frac{1}{4} \frac{D}{G} \nu^2 - \frac{1}{4!} \frac{1}{2} \frac{D^2}{G^2} \nu^4 + \dots \right]. \tag{A.9}$$

Then write the equation for envelope in the form

$$\frac{\partial \ln \Xi}{\partial \mu} = \frac{\partial \ln \Xi_{\rho_0}}{\partial \mu} = \frac{\partial \ln \Xi_{\rho_0}}{\partial \mu^*} = N \frac{\partial \ln \Xi_{\rho_0}}{\partial \nu} = N. \tag{A.10}$$

After substitution from (A.9), we get

$$\frac{1}{12} \frac{D^2}{G^2} \nu^3 - \frac{1}{2} \frac{D}{G} \nu + \Delta = 0 \tag{A.11}$$

or in a standart form:

$$\nu^3 + p\nu + q = 0, \tag{A.12}$$

where  $p = -6 \frac{G}{D}$ ,  $q = 12 \frac{G^2}{D^2} \Delta$ , with the discriminant  $Q$ :

$$Q = \frac{q^2}{4} + \frac{p^3}{27} = 36 \frac{G^4}{D^4} \Delta^2 - 8 \frac{G^3}{D^3}. \tag{A.13}$$

The value of  $Q$  may be positive, negative and equal to zero. For  $Q > 0$  we have one real root, for  $Q < 0$  there are three real roots, the value  $Q = 0$  means the boundary of bifurcation.

When  $Q > 0$ , from (A.13)

$$\frac{q^2}{4} > \left| \frac{p^3}{27} \right|, \quad |\Delta| > \sqrt{\frac{2D}{9G}} = \frac{1}{\sqrt{3}}b = \frac{2}{3}d, \quad (\text{A.14})$$

and for  $\nu$  we have two values:

$$\begin{aligned} \nu^{(1)} &= \sqrt[3]{-\frac{q}{2} \left\{ \left(1 - \frac{2\sqrt{Q}}{q}\right)^{1/3} + \left(1 - \frac{2\sqrt{Q}}{q}\right)^{1/3} \right\}} \\ &= \sqrt[3]{-6\frac{G^2}{D^2}\Delta \left\{ 2 + \frac{2 \cdot 4}{3 \cdot 3} \frac{Q}{q^2} + \dots \right\}}; \end{aligned} \quad (\text{A.15})$$

$|\Delta| > \frac{2}{3}d$ ,  $\Delta = \Delta_l > \frac{2}{3}d$  for liquid,  $\Delta = \Delta_g < -\frac{2}{3}d$  for vapor.

In the limit  $Q \rightarrow 0$ ,

$$\Delta \rightarrow \pm \frac{2}{3}d = \pm \frac{2}{3}\sqrt{\frac{1D}{2G}}, \quad \nu^{(1)}|_{Q=0} = \pm \frac{2}{d}.$$

Inside the region  $Q < 0$ ,  $\frac{q^2}{4} < \left| \frac{p^3}{27} \right|$ , we have three real roots (Table 5) for the equation (A.12).

$$\nu_1 = 2\sqrt{\left| \frac{p}{3} \right|} \cos \frac{\psi}{3} = \frac{2}{d} \cos \frac{\psi}{3}, \quad \nu_2 = \frac{2}{d} \cos \frac{\psi + 2\pi}{3}, \quad \nu_3 = \frac{2}{d} \cos \frac{\psi + 4\pi}{3}; \quad (\text{A.16})$$

$$\cos \psi = -\frac{q}{2\sqrt{-p^3/27}} = -\frac{\Delta}{(2/3)d}, \quad \Delta = -\frac{2}{3}d \cos \psi. \quad (\text{A.17})$$

The forms of  $\nu_{1,2,3}$  behave slightly reversely to the forms of  $\rho_{01}$ ,  $\rho_{02}$ ,  $\rho_{03}$  in Part 1.

This is a quite new expression in comparison to the equality  $\mu^* = a \cos \varphi$ ,  $a = Gb^3 \sim \tau^{\frac{5}{2}}\nu$ , which we have in the Part 1. That means the solutions  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  are the trajectories of the main density, and we have done some smoothing of the FOPT.

In Table 5 we have given also the values of  $\nu_{1,2,3}$  in nodal points  $\psi = 0, \frac{\pi}{2}, \pi$ .

Comparing with (A.15), we see that  $\nu_1$  continues the positive values of  $\nu^{(1)}$ , and  $\nu_2$  — the negative values of  $\nu^{(1)}$  inside the area  $Q < 0$ .

From (A.16) it is clear that  $\nu_{1,2,3}$  are finite quantities, and therefore in the TL in (A.9) the contribution of  $\nu_{1,2,3}$  tend to zero. This means,

Table 5. The values of  $\nu_{1,2,3} = 2/d \cos(\psi + 2n\pi)/3$  at nodal points of  $\psi$ ,  $\psi = 0, \pi/2, \pi$ .

$\psi$	$\nu_1$	$\nu_2$	$\nu_3$
0	$2/d$	$-\frac{1}{2}(2/d)$	$-\frac{1}{2}(2/d)$
$\pi/2$	$\sqrt{3}/2(2/d)$	$-\sqrt{3}/2(2/d)$	0
$\pi$	$\frac{1}{2}(2/d)$	$-2/d$	$\frac{1}{2}(2/d)$

that there has to be another quantity characterizing the events at  $Q < 0$ . That are  $\Delta_1$ ,  $\Delta_2$ ,  $\Delta_3$  — the mean densities, which correspond to  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ .

After substitution of  $\nu_{1,2,3}$  from (A.16) into (A.12) we obtain three curves for  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$ .

$$\Delta_{1,2,3} = 2d \cos \frac{\psi + 2\pi n}{3} \left( 1 - \frac{4}{3} \cos^2 \frac{\psi + 2\pi n}{3} \right), \quad n = 0, 1, 2. \quad (\text{A.18})$$

$0 \leq \psi \leq \pi$ ,  $n = 0, 1, 2$ ;  $d = \sqrt{(1/2)D/G}$ . Quantities (A.16) for  $\nu_{1,2,3}$  and (A.18) for  $\Delta_{1,2,3}$  have one common discriminant  $Q$ , given in (A.13).

Table 6 shows the values of  $\Delta_{1,2,3}$  at the nodal points of the argument  $\psi = 0, \pi/2, \pi$ ,  $\psi_i = \psi + 2\pi n_i$ ,  $n_i = 0, 1, 2$ .

One can see that the curve  $\Delta_1(\nu_1)$  is an extension of  $\Delta(\nu^{(1)})$  in case  $\nu^{(1)}$  is positive (vapor), and  $\Delta_2(\nu_2)$  is an extension of  $\Delta(\nu^{(1)})$  in case  $\nu^{(1)}$  is negative (liquid) and that  $\Delta_3$  is connected with the (unstable)

Table 6. The values of  $\Delta_{1,2,3} = \Delta_1, \Delta_2, \Delta_3$ , at the nodal points  $\psi_i = \psi + 2n_i\pi$ ,  $\psi = 0, \pi/2, \pi$ .

$\psi$	$\psi_1$	$\Delta_1$	$\frac{d\Delta_1}{d\psi}$	$\psi_2$	$\Delta_2$	$\frac{d\Delta_2}{d\psi}$	$\psi_3$	$\Delta_3$	$\frac{d\Delta_3}{d\psi}$
0	0	$-\frac{2}{3}d$	0	$2\pi$	$-\frac{2}{3}d$	0	$4\pi$	$-\frac{2}{3}d$	0
$\frac{\pi}{2}$	$\frac{\pi}{2}$	0	$\frac{2}{3}d$	$2\pi + \frac{\pi}{2}$	0	$\frac{2}{3}d$	$\frac{\pi}{2} + 4\pi$	0	$\frac{2}{3}d$
$\pi$	$\pi$	$\frac{2}{3}d$	0	$2\pi + \pi$	$\frac{2}{3}d$	0	$5\pi$	$\frac{2}{3}d$	0

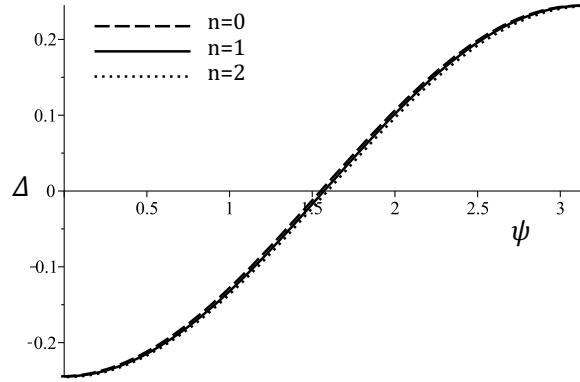


Figure 12. Plot of  $\Delta_{1,2,3} = 2d \cos[(\psi + 2\pi n)/3] \{1 - (4/3) \cos^2[(\psi + 2n\pi)/3]\}$  on the interval  $0 \leq \psi \leq \pi$ , for different  $n = 0, 1, 2$ . At the points  $(2\pi n + \pi/2)/3$ ,  $n = 0, 1, 2$  all three curves  $d\Delta_{1,2,3}/d\psi = (2/3)d$  have the same inclination of the tangents. The same behavior is true for the simplified curve  $\Delta = -(2/3)d \cos \psi$ .

$\nu_3$  states at  $Q < 0$  (only inside the rectangular  $Q = 0$ ). The width of the area  $\Delta$  equals  $(4/3)d$ ; the size of the area of bifurcation  $Q = 0$ , also equals  $(4/3)d$ .

From (A.17), written in the form  $\cos \psi_{1,2,3} = \frac{-\Delta_{1,2,3}}{2\sqrt{3}d}$  follows, that for every  $\Delta_i$ ,  $i = 1, 2, 3$  has its own argument  $\psi_i$ ,  $\psi_1 = \psi$ ,  $\psi_2 = \psi + 2\pi$ ,  $\psi_3 = \psi + 4\pi$ .

For  $\Delta$  we always have  $\Delta = \eta_c \left( \frac{\eta}{\eta_c} - 1 \right)$ ,  $\eta = \eta_c + \Delta$ . Along (A.17) there is a correspondence between  $\psi$  and  $\eta$ . At  $\Delta \leq 0$  for  $\eta \leq \eta_c$  we have a vapor, for  $\eta \geq \eta_c$  and  $\Delta \geq 0$  — a liquid. We regard here the process of the isothermal compression of vapor, therefore we follow the trajectory  $\nu^{(1)} < 0$  from outside the rectangular  $Q = 0$  to the point  $\nu^{(1)} = \nu_1 = 2/d$  and  $\psi = 0$  (see Tables 5 and 6). From the latter point both the bifurcation and the process of the FOPT start. The value of  $\Delta$  here is  $\Delta = \Delta_1(\nu_1) = -\frac{2}{3}d$ ; the density of vapor  $\eta|_{Q=0} = \eta_c \left( 1 - \frac{2}{3}d \right)$ . Further on inside the rectangular  $Q = 0$ , we move along  $\nu_1(\psi)$ . The curves  $\Delta_2$  and  $\Delta_3$  take the same values. Therefore we can say that all curves  $\Delta = \Delta_{1,2,3}$  and  $\Delta = -\frac{2}{3}d \cos \psi$  coincide at  $0 \leq \psi \leq \pi$ . In Table 6 the values of  $\Delta_{1,2,3}$  at nodal points and values of derivatives at those points are given. At the point  $\Delta = \Delta_2(\nu)|_{\nu=\frac{1}{2}d}$  we say that we have a liquid with density  $\eta_l = \eta_c(1 + \frac{2}{3}d)$ . The difference between the density

values at the end-points is  $\Delta(\nu_2)|_{\nu_2=\frac{1}{2}d} - \Delta(\nu_1)|_{\nu_1=-\frac{1}{2}d} = \frac{4}{3}d$ .

So the first order phase transition occurs in a special manner. There is no jump of densities and no two phases. The difference of the density at between the points  $\nu_1 = \frac{2}{d}$ ,  $\Delta_1 = -\frac{2}{3}d$  and  $\nu_2 = -\frac{2}{d}$ ,  $\Delta_2 = \frac{2}{3}d$  equals  $\frac{4}{3}d$ .

**Equation of state.** Let us return to the formula (A.9) and write the equation of state.

$$\frac{PV}{D} = \ln \Xi_{\rho_0} \quad \text{or} \quad \frac{PV}{D} = \nu(1 - \Delta) + \frac{1}{4} \frac{ND^2}{4G} + \frac{1}{4} \frac{D}{G} \nu^2 - \frac{1}{4!} \frac{1}{2} \frac{D^2}{G^2} \nu^4. \quad (\text{A.19})$$

After substituting the values of  $\nu_{1,2,3}$  from (A.16), inside the rectangular  $Q = 0$  we obtain

$$\begin{aligned} \left( \frac{PV}{D} \right)_{1,2,3} &= \nu_{1,2,3}(1 - \Delta_{1,2,3}) + \frac{1}{4} \frac{ND^2}{4G} + \frac{1}{4} \frac{D}{G} (\nu_{1,2,3})^2 - \\ &- \frac{1}{4!} \frac{1}{2} \frac{D^2}{G^2} (\nu_{1,2,3})^4 = \left( \frac{d}{2} \right)^{-1} \cos \frac{\psi + 2n\pi}{3} (1 - \Delta_{1,2,3}) + \frac{1}{16} \frac{ND^2}{G} + \\ &+ \frac{1}{4} \frac{D}{G} \left[ \left( \frac{d}{2} \right)^{-1} \cos \frac{\psi + 2n\pi}{3} \right]^2 - \frac{1}{48} \frac{D^2}{G^2} \left[ \left( \frac{d}{2} \right)^{-1} \cos \frac{\psi + 2n\pi}{3} \right]^4, \end{aligned}$$

for  $d$  we have  $d = \sqrt{\frac{1}{2} \frac{D}{G}}$  and for  $\Delta$  — expression (A.17), then after reducing for  $\frac{PV}{D}$  we shall have

$$\begin{aligned} P &= \Theta \frac{1}{16} \frac{N}{V} \frac{D^2}{G} + \frac{1}{V} \left\{ - \left( \frac{1}{2} \sqrt{\frac{1}{2} \frac{D}{G}} \right)^{-1} \cos \frac{\psi + 2n\pi}{3} (1 - \Delta) + \right. \\ &\left. + 2 \cos^2 \frac{\psi + 2n\pi}{3} + \frac{4}{3} \cos^4 \frac{\psi + 2n\pi}{3} \right\}. \end{aligned} \quad (\text{A.20})$$

In TL the expression in parenthesis may be neglected. So the solutions  $\nu_{1,2,3}$  aren't explicitly represented unlike the mean density  $N/V$ . For  $\frac{N}{V} = \eta \frac{6}{\pi \sigma^3}$ ,  $\eta = \eta_c(1 + \Delta)$ , we have  $\frac{N}{V} = \frac{6}{\pi \sigma^3} \eta_c(1 + \Delta)$ , then

$$P = \frac{1}{16} \Theta \frac{D^2}{G} \eta_c(1 + \Delta) \cdot \frac{6}{\pi \sigma^3}. \quad (\text{A.21})$$

For  $\Delta$  there we have expression (A.17). There are three values of  $\Delta_{1,2,3}$ , accordingly to the values of roots  $\nu_{1,2,3}$ . Outside the rectangular  $Q = 0$  the equation (A.13) has only one root  $\nu^{(1)}$  for vapor and one root  $\nu^{(1)}$  for liquid, expressed in (A.16). At the boundary  $Q = 0$  it tends to the expression (A.15) and along the values in Table 5 for  $\nu_{1,2,3}$  the root  $\nu^{(1)}$  coincide with  $\nu_1$  at  $\psi = 0$  and  $\nu_2$  at  $\psi = \pi$ ,  $\Delta = \frac{1}{\eta_c}(\eta - \eta_c)$ ,  $\eta = \eta_c(1 + \Delta)$ .



But inside the region  $Q < 0$  there are no trajectories of the type  $\rho_{01,2,3}$  from (2.8) (Part 1). We get the three coinciding curves for the mean density  $\Delta$ . They start from the point  $\Delta = \Delta_g = -\frac{2}{3}d$ , that means the density  $\eta = \eta_g = \eta_c - \frac{2}{3}d$  — of a vapor, and terminate at the point  $\Delta = \Delta_l = \frac{2}{3}d$ ,  $\eta = \eta_l = \eta_c + \frac{2}{3}d$ , which means a liquid. Without any dependence on  $N$ . Here the roots  $\nu_1, \nu_2, \nu_3$  are not sufficient.

So using the “direct” integration and substitution  $\mu^*N = V$  at the very beginning in formulas (1.1) and (1.2) we have smoothed the whole picture. We have lost the Fig. 1 (from the Part 1), we have lost the variable  $\mu^*$ , which play the main role in the description of the FOPT.

So, starting from the expression (A.21), and keeping in mind the behavior of  $\nu_{1,2,3}$  and  $\Delta_{1,2,3}$  we would like to describe the process of isothermal pressing the vapor. Our main goal is to obtain the situation of the first order phase transition. Now we want to compare the results we get here by the method of obtaining the main probability trajectories (or mathematically, the method of steepest descent (SDM)) with the results, obtained by “direct” integration of the GPF.

## Appendix B. On the basic density measure

In this article we won't talk about the basic density measure. We start with the GPF in a usual form

$$\Xi = \sum_{N=0}^{\alpha} \frac{e^{\beta\mu N}}{\sqrt{2\pi\hbar m^3 N}} \int \exp -\beta \sum_{1 \leq i < j \leq N} (\varphi(r_{ij}) + \psi(r_{ij})) d\Gamma_N, \quad (\text{B.1})$$

where  $\beta = 1/kT$ ,  $\mu$  is the chemical potential,  $\varphi(r)$  and  $\psi(r)$  potentials of short- and long-range interactions correspondingly. Then introduce the extended phase space consisting of two subspaces. The subspace of Cartesian coordinates  $\{d\Gamma\}$  of particles is for the description of short-range interactions  $\sum \varphi(r_{ij})$ , and the subspace of collective variables  $\{\rho_{\mathbf{k}}\}$  is for the description of long-range interactions. The overfilling of the phase space by introducing the products of the corresponding  $\delta$ -functions is eliminated.

The initial form (B.1) is reduced to the functional integral in the phase space of collective variables  $\{\rho_{\mathbf{k}}\}$ , the system of the short-range interactions become the reference system (RS) of the problem. Then the series of easy operations are realized: writing an explicit form for  $\delta$ -functions we made integration in the Cartesian phase space  $\{d\Gamma\}$ . Now

$\Xi$  is in the form of a functional integral over the set of collective variables:

$$\Xi = \Xi_0 \int \exp \beta h \rho_0 \int \exp \frac{1}{2} \sum_k \frac{\beta \tilde{\psi}(k)}{V} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} J(\rho) (d\rho), \quad (\text{B.2})$$

where  $\Xi_0$  is the partition function of the RS,  $h = \beta(\mu - \mu_0)$ ,  $\mu_0$  is the chemical potential of the RS,  $J(\rho)$  is the Jacobian of transition to the phase space of CV,

$$J(\rho) = \int \exp \left( i2\pi \sum_k \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \sum_{n \geq 1} D_n(\omega) \right) (d\omega), \quad (\text{B.3})$$

$$D_n(\omega) = \frac{(-i2\pi)^n}{n!} \sum_{k_1, \dots, k_n} \mathfrak{M}_n(k_1, \dots, k_n) \omega_{k_1} \dots \omega_{k_n} \quad (\text{B.4})$$

$\dots \omega_{\mathbf{k}} \dots$  is the set of Fourier's variables conjugated to  $\dots \rho_{\mathbf{k}} \dots$ ,  $\mathfrak{M}_n$  is the  $n$ -th cumulant arising as a result of the RS-averaging:

$$\begin{aligned} \exp \sum_{n \geq 1} D_n(\omega) &= \Xi_0^{-1} \sum_N \frac{e^{\beta\mu_0 N}}{N!} \\ &\times \int \exp \left[ -\beta\varphi_N - i2\pi \sum_k \omega_{\mathbf{k}} \left( \frac{1}{\sqrt{N}} \sum_{i=1}^N e^{-i\mathbf{k}r_i} \right) \right] d\Gamma. \end{aligned}$$

Both types of interactions are gathered together: the  $\tilde{\psi}(k)$  from the long-range interactions and semiinvariants  $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$  from the short-range interactions, both as a functions of  $\mathbf{k}$ . But their dependence on  $\mathbf{k}$  is antipodal.

The distinctive features of the long-range interactions  $\psi(r)$  are observed at great distances but in case of Fourier transform  $\tilde{\psi}(k)$  at small values of  $\mathbf{k}$ . The situation is completely inverse for semiinvariants  $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$  since they take main values at small  $\mathbf{r}$  that means at big values of  $\mathbf{k}$ . Fig. 13 and Fig. 14 show the curves of  $\tilde{\psi}(k)$  and  $\mathfrak{M}_n(k, 0 \dots 0)$ .

We suppose that the main events connected with attraction between particles are concentrated inside the interval  $0 \leq k \leq B$  and we put  $\tilde{\psi}(k) = 0$  for  $k \geq B$ . In (B.1)–(B.3) the integration over  $\rho_{\mathbf{k}}$ , for  $\mathbf{k} > 0$ , gives  $\prod_{k > B} \delta(\omega_{\mathbf{k}})$ . Inside the interval  $0 \leq k \leq B$  we take values of the cumulants  $\mathfrak{M}_n(\mathbf{k}_1, \dots, \mathbf{k}_n)$  at  $\mathbf{k}_i = 0$ . In result, the functional integral

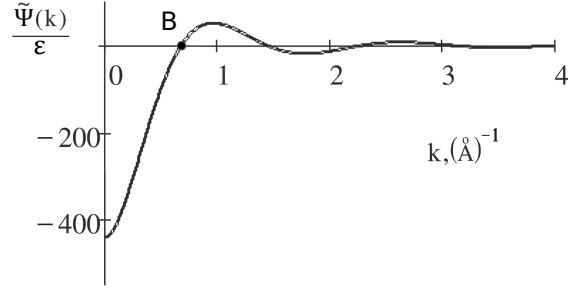


Figure 13. Plot of the Fourier transform of the long-range attractive interactions  $\tilde{\psi}(k)$ .

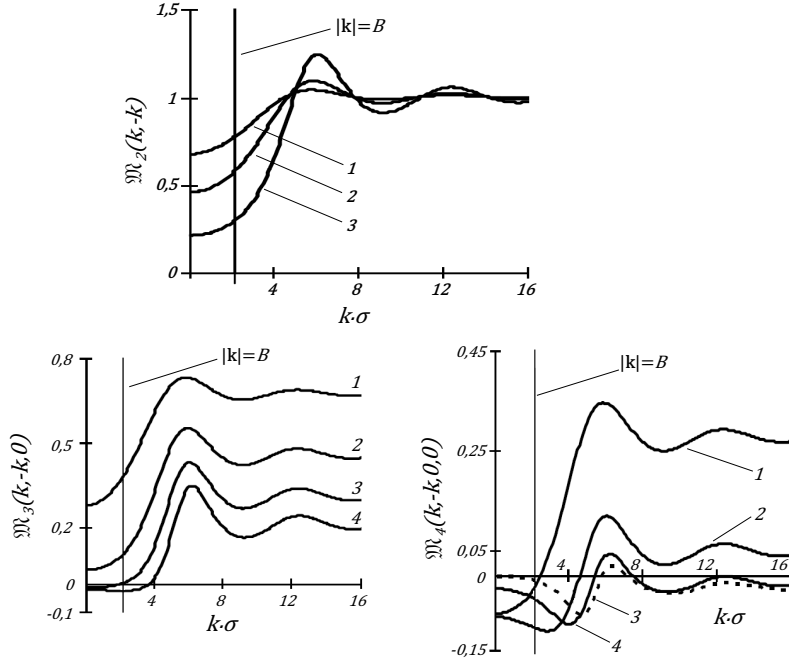


Figure 14. Plot of seminvariants  $\mathfrak{M}_n(\mathbf{k}, 0 \dots 0)$  as functions of  $\mathbf{k}$  at different densities: 1 —  $\eta = 0.05$ ; 2 —  $\eta = 0.1$ ; 3 —  $\eta = 0.2$ ; 4 —  $\eta = 1.5$ . The point B denotes location of the first zero of the Fourier transform  $\tilde{\psi}(k)$  from Fig. 13.

(B.1)–(B.3) for  $\Xi$  can be written in the form:

$$\Xi = \Xi_0 \int \exp(\sqrt{N}\beta h \rho_0) \int \left\{ \exp \left[ \frac{1}{2} \sum_{k \leq B} \frac{\beta \tilde{\phi}(k) N}{V} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \sum_{n < n_0} D_n(\omega) \right] \exp \sum_{n \geq n_0} \hat{D}_n \left( \frac{\partial}{\partial \rho_{\mathbf{k}}} \right) \exp i 2\pi \sum_{k \leq B} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right\} (d\omega)(d\rho), \quad (\text{B.5})$$

where

$$D_n(\omega) = \frac{(-i2\pi)^n}{n!} \mathfrak{M}_n(0, \dots, 0) \sum_k \omega_{k_1} \dots \omega_{k_n} \delta_{k_1 + \dots + k_n},$$

$$\hat{D}_n \left( \frac{\partial}{\partial \rho_{\mathbf{k}}} \right) = \frac{(-1)^n}{n!} \mathfrak{M}_n(0, \dots, 0) \sum_{k \leq B} \frac{\partial}{\partial \rho_{\mathbf{k}_1}} \dots \frac{\partial}{\partial \rho_{\mathbf{k}_n}} \delta_{k_1 + \dots + k_n}.$$

We say that  $w_n(\rho, \rho')$  is the  $n$ -th basic density measure (BDM), if all momenta  $\int w_n(\rho, \rho') \rho'_{\mathbf{k}_1} \dots \rho'_{\mathbf{k}_n} |_{\rho=\rho'} (d\rho)$  are convergent. In expression (B.3) the basic density measure is:

$$w_{n_0}(\rho, \rho') = \exp \sqrt{N}\beta h \rho_0 - \frac{1}{2} \sum_k \frac{\beta \tilde{\phi}(k) N}{V} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \times \int \exp \sum_{n \leq n_0} \left\{ D_n(\omega) \exp i 2\pi \sum_k \omega_{\mathbf{k}} \rho'_{\mathbf{k}} \right\} (d\omega). \quad (\text{B.6})$$

For the whole expression of  $\Xi$  we have:

$$\Xi = \int \left[ \exp \sum_{n \geq n_0} \hat{D}_n \left( \frac{\partial}{\partial \rho_{\mathbf{k}}} \right) w_{n_0}(\rho_1 \rho'_1) \right]_{\rho=\rho'} (d\rho). \quad (\text{B.7})$$

Let us put  $n_0 = 2$ , and get the Gaussian form for BDM

$$w_2(\rho, \rho') = \exp \left\{ \beta h \rho_0 \sqrt{N} - \frac{1}{2} \sum_k \beta \frac{N}{V} \tilde{\phi}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right\} \times \int \exp \left\{ i 2\pi \mathfrak{M}_0 \omega_0 - \frac{(2\pi)^2}{2} \sum_k \mathfrak{M}_2(k) \omega_{\mathbf{k}} \omega_{-\mathbf{k}} + i 2\pi \sum_{k \leq B} \omega_{\mathbf{k}} \rho'_{\mathbf{k}} \right\} (d\omega). \quad (\text{B.8})$$

Then we introduce some new notations,  $\rho = \sqrt{N}\rho'$  for  $\rho_0$  and  $\rho_{\mathbf{k}}$ , omit the prime,  $\beta h + \mathfrak{M}_1(0)/\mathfrak{M}_2(0) = \tilde{\mu}$ ,  $(N/V)\beta \tilde{\phi}(k) = \alpha(k) < 0$ ,

$\mathfrak{M}_2 = N\bar{\mathfrak{M}}_2$ , substitute them into (B.3) and (B.5) and obtain a complete form for the Gaussian BDM

$$w_2(\rho, \rho') = C \exp \left\{ N\tilde{\mu}\rho_0 - N\frac{1}{\mathfrak{M}_2(0)}\rho_0'^2 - N\alpha(0)\rho_0^2 \right\} \times \\ \times \exp \left[ -\frac{N}{2} \sum_{\substack{k \\ k \neq 0}} \frac{1}{\mathfrak{M}_2(k)} \rho'_{\mathbf{k}} \rho'_{-\mathbf{k}} - \frac{N}{2} \sum_{\substack{k \\ k \neq 0}} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right], \quad (\text{B.9})$$

where

$$\sum_{i=0}^m x = \sum_{i=-1}^m x \\ \sum_{i=0}^m x = \sum_{i=-1}^m x \\ C = \exp \left( \frac{N}{\mathfrak{M}_2} \right) \prod_{\substack{k \\ k \neq 0}}' \frac{1}{\mathfrak{M}_2(k)} \times \frac{1}{\sqrt{2\pi\mathfrak{M}_2(0)}}, \quad \max |\alpha(k)| = |\alpha(0)|.$$

We have separated macroscopic variable  $\rho_0$  from the macroscopic set of microscopic variables  $\{\rho_{\mathbf{k}}\}$  but fail to get the Landau form).

In formula (B.6) we now have to split expression  $\exp \sum_{n>2} D_n(\partial/\partial\rho'_{\mathbf{k}})$  into two factors, along (B.3)

$$D_n \left( \frac{\partial}{\partial\rho'_{\mathbf{k}}} \right) = (-1)^n \mathfrak{M}_n(0 \dots 0) \frac{\partial^n}{\partial\rho_0^n} + \\ + \frac{(-1)^n}{n!} \sum_{\substack{k \\ k < B, k \neq 0}} \mathfrak{M}_n(k_1 \dots k_n) \frac{\partial^n}{\partial\rho'_{\mathbf{k}_1} \dots \partial\rho'_{\mathbf{k}_n}}. \quad (\text{B.10})$$

And prepare the formula (B.6) for integration over the set of  $\{\rho_{\mathbf{k}}\}_{k \neq 0}$

$$\Xi = \int \exp \left( \sum_{n \geq 3} (-1)^n \mathfrak{M}_n(0 \dots 0) \frac{\partial^n}{\partial\rho_0^n} \right) \times \\ \times \exp \left( \tilde{\mu}\rho_0 - \frac{1}{\mathfrak{M}_2(0)}(\rho_0')^2 - N\alpha(0)\rho_0^2 \right) \times \\ \times \left\{ 1 + \frac{1}{2} \left( \frac{1}{3!} \sum_{\substack{k_1, \dots, k_3 \\ k_i \leq B}} \mathfrak{M}_3(0 \dots 0) \mathfrak{M}_3(0 \dots 0) \delta_{k_1+k_2+k_3} \times \right. \right. \\ \times \frac{\partial^2}{\partial\rho'_{\mathbf{k}_1} \partial\rho'_{-\mathbf{k}_1}} \dots \frac{\partial^2}{\partial\rho'_{\mathbf{k}_3} \partial\rho'_{-\mathbf{k}_3}} + \dots + \\ \left. + \frac{1}{n!} \mathfrak{M}_n(0 \dots 0) \mathfrak{M}_n(0 \dots 0) \sum_{\substack{k_1, \dots, k_n \\ k_i \leq B}} \delta_{k_1+\dots+k_n} \times \right. \\ \left. \times \frac{\partial^2}{\partial\rho'_{\mathbf{k}_1} \partial\rho'_{-\mathbf{k}_1}} \dots \frac{\partial^2}{\partial\rho'_{\mathbf{k}_n} \partial\rho'_{-\mathbf{k}_n}} + \dots \right) + \dots + \\ \left. + \frac{1}{3!}(\dots) + \dots \right\} \times \\ \times \exp \left( -\frac{1}{2} \sum_{\substack{k \leq B \\ k \neq 0}} \frac{1}{\mathfrak{M}_2(k)} \rho'_{\mathbf{k}} \rho'_{-\mathbf{k}} - \frac{1}{2} \sum_{\substack{k \leq B \\ k \neq 0}} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right) \Big|_{\rho_{\mathbf{k}} = \rho'_{\mathbf{k}}} \{d\rho_{\mathbf{k}}\}. \quad (\text{B.11})$$

So we have explicitly written the third items in expansion of the operator  $\exp \sum_{n \geq 3} (\partial/\partial\rho'_k)$ . Only pair derivatives give a non-zero result. Therefore, we obtain

$$-\frac{1}{\mathfrak{M}_2(k_1)} + \frac{1}{\mathfrak{M}_2^2} \rho'_{\mathbf{k}_1} \rho'_{-\mathbf{k}_1} \quad \text{for each} \quad \frac{\partial^2}{\partial\rho_{k_i} \partial\rho_{-k_i}}.$$

Now we may put  $\rho'_{\mathbf{k}_1} \rho'_{-\mathbf{k}_1} = \rho_{\mathbf{k}_1} \rho_{-\mathbf{k}_1}$  and substitute

$$\rho_{\mathbf{k}_1} \rho_{-\mathbf{k}_1} = -\frac{\partial}{\partial\alpha(k_1)} \quad \text{for} \quad \exp -\frac{1}{2} \sum_{k < B} \alpha(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}.$$

The final form of  $\Xi$  is:

$$\begin{aligned} \Xi = & \int \left[ \sum_{n \geq 3} (-1)^n \mathfrak{M}_n \frac{\partial^n}{\partial \rho_0^n} \right] \exp \left[ \tilde{\mu} \rho_0 - \frac{1}{\mathfrak{M}_2(0)} (\rho'_0)^2 - \alpha(0) \rho_0^2 \right] \times \\ & \times \left\{ 1 + \frac{1}{2} \frac{1}{3!} \sum_{\substack{k_1, k_2, k_3 \\ k \leq B}} \mathfrak{M}_3(0 \dots 0) \mathfrak{M}_3(0 \dots 0) \delta_{k_1+k_2+k_3} \times \right. \\ & \times \left( -\frac{1}{\mathfrak{M}_2(k_1)} - \frac{1}{(\mathfrak{M}_2(k_1))^2} \frac{\partial}{\partial \alpha(k_1)} \right) \times \\ & \times \left( -\frac{1}{\mathfrak{M}_2(k_2)} - \frac{1}{(\mathfrak{M}_2(k_2))^2} \frac{\partial}{\partial \alpha(k_2)} \right) \times \\ & \times \left. \left( -\frac{1}{\mathfrak{M}_2(k_3)} - \frac{1}{(\mathfrak{M}_2(k_3))^2} \frac{\partial}{\partial \alpha(k_3)} \right) + \dots \right\} \times \\ & \times \exp \left[ -\frac{1}{2} \sum_{\substack{k \neq 0 \\ k \leq B}} \left( \frac{1}{\mathfrak{M}_2(k)} + \alpha(k) \right) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right] (d\rho), \end{aligned}$$

the integration over  $(d\rho_{\mathbf{k}})_{k \neq 0}$  is going only along the sample:

$$\begin{aligned} \int \exp \left[ -\frac{1}{2} \sum_{k \neq 0} \left( \frac{1}{\mathfrak{M}_2(k)} + \alpha(k) \right) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right] (d\rho_{\mathbf{k}})_{k \neq 0} = \\ = \exp \left[ -\frac{1}{2} \sum_{\substack{k \\ k_i < B}} \ln \left( \frac{1}{\mathfrak{M}_2(k)} + \alpha(k) \right) \right]. \end{aligned}$$

In the braces we get

$$\left\{ 1 + \frac{1}{2} \frac{1}{3!} \sum_{k_1 k_2 k_3} \mathfrak{M}_3(0 \dots 0) \mathfrak{M}_3(0 \dots 0) \tilde{g}(k_1) \tilde{g}(k_2) \tilde{g}(k_3) + \dots \right\}, \quad (\text{B.12})$$

where  $\tilde{g}(k)$  is the Fourier transform of the screened potential

$$\tilde{g}(k) = \frac{\alpha(k)}{1 + \mathfrak{M}_2(k) \alpha(k)}. \quad (\text{B.13})$$

We have not written the explicit forms for cumulants  $\mathfrak{M}_3(k_1 k_2 k_3)$ . It's enough to say that all  $\tilde{g}(r)$  are zero for  $r < \sigma$ .

The total expression for  $\Xi$  in braces may be written in the form:

$$\begin{aligned} \Xi = & \Xi_{\rho_0} \prod_k \frac{1 + \mathfrak{M}_2(k) \alpha(k)}{\mathfrak{M}_2(k)} \times \\ & \times \left\{ 1 + \text{const} \frac{N(N-1)}{2V} \int_{\sigma}^{\infty} \left( \frac{g^3(r)}{3!} + \frac{g^4(r)}{4!} + \dots \right) dr + \dots \right\}. \quad (\text{B.14}) \end{aligned}$$

The expression in braces is the second virial coefficient in which the integrands are formed on the screened potentials  $g(r)$

$$g(r) = \int \tilde{g}(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}} d\mathbf{k}.$$

We are interested in behavior of integrals over great values of  $\mathbf{r}$  (small values of  $\mathbf{k}$  for  $\tilde{g}(k)$ ). Therefore we use for  $\tilde{\psi}(k)$  a parabolic approximation

$$\tilde{\psi}(k) = \tilde{\psi}(0) \left( 1 - \frac{k^2}{B^2} \right), \quad \tilde{\psi}(0) < 0. \quad (\text{B.15})$$

For  $g(k)$  it is:

$$\tilde{g}(k) = \frac{N}{V} \beta \frac{\tilde{\psi}(0) B^2}{\kappa^2 + k^2}, \quad (\text{B.16})$$

where

$$\kappa = B \sqrt{\left( 1 - \mathfrak{M}_2(0) \frac{N}{V} \beta |\tilde{\phi}(0)| \right)} \quad (\text{B.17})$$

is the inverse radius of screening; and  $g(r) = C(e^{-\kappa r}/r)$ ,  $C$  is the intensity of interactions. There are the temperature  $T_c$  and the density  $(N/V)_c$ , where  $\kappa = 0$  for which  $g(r) \sim 1/r$ , and in (B.12) the integral

$$\int_{\sigma}^{\infty} g^3(r) dr \simeq \int_{\sigma}^{\infty} \frac{1}{r^3} r^2 dr = \ln r \Big|_{\sigma}^{\infty}$$

is divergent.

The second virial coefficient as well as the higher virial coefficients will also diverge, highly diverge. It is explained in more details in [12]. The integral

$$\int_{\sigma}^{\infty} g^4(r) dr \sim \int_{\sigma}^{\infty} \frac{dr}{r^2} = \frac{1}{r} \Big|_{\sigma}^{\infty}$$

is convergent.

Therefore, instead of (B.7) the initial form of the BDM should be:

$$\begin{aligned}
 w_4(\rho, \rho', \omega) = & \exp\left(\beta h \rho_0 - \frac{1}{2} \sum_{k < B} \frac{\beta \tilde{\phi}(k)}{V} \rho_{\mathbf{k}} \rho_{-\mathbf{k}}\right) \times \\
 & \times \int \exp\left[-i 2\pi \mathfrak{M}_1(0) \omega_0 - \frac{(2\pi)^2}{2} \sum_k \mathfrak{M}_2(k) \omega_{\mathbf{k}} \omega_{-\mathbf{k}} + \right. \\
 & + \frac{(i 2\pi)^3}{3!} \sum_{k_1, k_2, k_3} \mathfrak{M}_3(k_1, k_2, k_3) \omega_{\mathbf{k}_1} \omega_{\mathbf{k}_2} \omega_{\mathbf{k}_3} + \\
 & + \frac{(i 2\pi)^4}{4!} \sum_{k_1, \dots, k_4} \mathfrak{M}_4(k_1, \dots, k_4) \omega_{\mathbf{k}_1} \omega_{\mathbf{k}_2} \omega_{\mathbf{k}_3} \omega_{\mathbf{k}_4} + \\
 & \left. + i 2\pi \sum_k \omega_{\mathbf{k}} \rho'_{\mathbf{k}}\right] (d\omega). \quad (\text{B.18})
 \end{aligned}$$

The latter expression is quite enough for describing the events of the first order phase transition, in particular, for the arising and disappearing of two phases inside the maternal phase and other events described in the first part of the present paper. This means that we cannot assume  $n_0 = 2$  in formula (B.8) which cause the momenta of operator  $\exp D_3(\partial/\partial \rho_{\mathbf{k}})$  in (B.7) to diverge. The operator  $D_3$  is proportional to  $i$ , so  $D_3 + D_4$  should be left in the formula of the basic density measure. Consideration of phase transitions in one-component systems in case of the FOPT in a two-phase system includes two main thermodynamic trajectories  $\rho_{01}$  and  $\rho_{02}$ . The unstable state trajectory  $\rho_{03}$  is not realized. The equation of  $\max E(\rho_0)$  is the the first order equation and  $E(\rho_0)$  is itself a polynomial function of degree four in the indeterminate  $\rho_0$ , according to the initial formula (2.1). For more details about the basic density measure refer to [12].

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