

# PHASE DIAGRAM OF TWO-DIMENSIONAL COULOMBIC GAS

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UDC 532  
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The phase diagram of a 2D-Coulombic gas is investigated. The equation of state is modeled with the help of the van der Waals equation for the system of soft dipole pairs. The positions of a binodal and a spinodal are determined. Dielectric permittivity of such a system is studied with the help of the canonical formalism. The relative position of the insulator–conductor transition line on the phase diagram is discussed.

## 1. Introduction

The 2D Coulombic systems are the object of consideration in many theoretical works, in particular, those involving the computer simulation (see [1–7]). However, even the construction of a general structure of their phase diagrams is very difficult problem. First of all, this is connected with the necessity to take the many-particle interactions in such systems into account.

The space dimensionality of these systems is also of great importance. To illustrate this, let us compare the behavior of the three- and two-dimensional systems. In a three-dimensional space, the interparticle potential weakens when the distance between ions increases, so anions and cations can move independently and form the so-called Coulombic gas. In a two-dimensional space, the interparticle potential between an anion and a cation grows by the logarithmic law. Due to this fact, the existence of free cations and anions appears to be impossible. In such systems, the separation of positive and negative ions is also possible, but it takes place only at enough large values of density when the interaction energy between electrically neutral pairs appears to be comparable with that inside a pair. Additionally, in two-dimensional systems, it is natural to expect the essential association: Coulombic pairs can form quadropole molecules and even associates of greater order [4]. The association influences the values of parameters of the effective interparticle potential and changes the physical properties of systems.

The first attempts to describe the phase diagram of the 2D Coulombic gas were made in [1–4]. In [1], the insulator–conductor transition is treated as the line of

peculiarities for the dielectric permittivity of a system. Unfortunately, it is not clear within this approach, in which phase state of the system, liquid or gas, the insulator–conductor line is situated. Using the RPM (the restricted primitive model) of the Coulombic gas, this problem is investigated in [2]. Analyzing the position of the gas–liquid coexistence curve, it was concluded in [2, 3] that the association degree near a binodal is close to unity. This means that the application of perturbation theory to reproduce the binodal is not quite adequate.

To overcome this difficulty, the equation of state for a not too dense 2D Coulombic gas was described in [8] under the assumption that all anions and cations in the system are joined in dipole pairs. The last are considered as soft particles for which the distance between a cation and an anion is a function of density and temperature. It was shown that the density dependence of the anion-cation spacing arises due to the dipole-dipole interaction between different dipole pairs. In [8], it was established that taking the softness of dipole pairs into account leads to the essential shift of the critical point.

In this paper, we study the relative disposition of the gas–liquid coexistence curve and the insulator–conductor transition line for the 2D Coulombic gas. The positions of a binodal and a spinodal are constructed with the help of the van der Waals equation proposed in [8]. The insulator–conductor transition line is considered as the set of points for which the dielectric permittivity tends to infinity. For this purpose, the properties of dielectric permittivity are analyzed within the canonical formalism [9]. The insulator–conductor transition is also considered as a line of instability of dipole pairs. The self-consistency of such approaches is discussed.

## 2. Dielectric Permittivity of 2D Coulombic Gas

To determine the microscopic expression for the dielectric permittivity of a 2D-gas of dipole pairs, we proceed from its general definition

$$\vec{D} = \varepsilon \vec{E},$$

where  $\vec{D}$  is the electric induction, and  $\vec{E}$  is the Maxwell electric field strength (entering the Maxwell equation). Taking into account that, for the 2D system,

$$\vec{D} = \vec{E} + 2\pi\vec{P},$$

we get

$$\varepsilon - 1 = 2\pi \frac{P}{E}, \quad (1)$$

where  $\vec{P}$  and  $\vec{E}$  are supposed to be equally directed. To exclude the influence of boundary effects, let us consider the dielectric permittivity of an extremely long cylinder, whose symmetry axis is normal to the strength  $\vec{E}_0$  of the external electrical field. In this case, the interrelation between  $\vec{E}$  and  $\vec{E}_0$  is determined from the corresponding boundary-value problem and given by the equation

$$\vec{E} = \frac{2}{\varepsilon + 1} \vec{E}_0. \quad (2)$$

So, (1) and (2) yield

$$\frac{\varepsilon - 1}{\varepsilon + 1} = \pi \frac{P}{E_0}. \quad (3)$$

For comparison, the dielectric permittivity of a 3D system is equal to (see [9])

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \frac{P}{E_0}.$$

The polarization vector  $\vec{P}$  is connected with the average value of the dipole moment  $\vec{D}_N$  of the system in the standard way as

$$\vec{P} = \frac{\langle \vec{D}_N \rangle}{V},$$

where

$$\langle \vec{D}_N \rangle = \frac{\int \vec{D}_N \exp \left[ \beta \left( -H_0 + \vec{D}_N \vec{E}_0 \right) \right] d\Gamma_N}{\int \exp \left[ \beta \left( -H_0 + \vec{D}_N \vec{E}_0 \right) \right] d\Gamma_N},$$

$H_0$  is the Hamiltonian of the system at  $\vec{E}_0$ , and  $d\Gamma_N$  is the phase volume element of the system. In the approximation linear with respect to  $\vec{E}_0$ , the dipole moment  $\vec{D}_N$  is the sum of two contributions,

$$\vec{D}_N = \vec{\alpha}_N \cdot \vec{E}_0 + \vec{D}_N^{(0)} + \dots,$$

where the former is proportional to the polarizability and the latter is the fluctuation dipole moment of the system. In the same approximation, we have

$$\langle \vec{D}_N \rangle = \langle \vec{\alpha}_N \rangle_0 \cdot \vec{E}_0 + \beta \langle \vec{D}_N^{(0)} \left( \vec{D}_N^{(0)} \cdot \vec{E}_0 \right) \rangle_0 + \dots$$

Here,  $\langle \rangle_0$  denotes the averaging operation with the unperturbed Hamiltonian  $H_0$ . Since

$$\langle (\vec{D}_N^{(0)})_\alpha (\vec{D}_N^{(0)})_\beta \rangle = \frac{1}{2} \delta_{\alpha\beta} \langle (\vec{D}_N^{(0)})^2 \rangle, \quad \alpha, \beta = 1, 2,$$

we get

$$\langle \vec{D}_N \rangle = \left[ \langle \vec{\alpha}_N \rangle_0 + \frac{1}{2} \beta \langle (\vec{D}_N^{(0)})^2 \rangle \right] \cdot \vec{E}_0. \quad (4)$$

In general case (see [9, 10]),  $\vec{\alpha}_N$  is the sum of one-particle, two-particle, etc. contributions:

$$\vec{\alpha}_N = \sum_{i=1}^N \alpha_1(\gamma_i) + \sum_{i,j=1}^N \vec{\alpha}_2(\gamma_i, \gamma_j) + \dots,$$

where  $\gamma_i$  is the totality of coordinates setting the state of the  $i$ -th particle. Analogously,

$$\vec{D}_N^{(0)} = \sum_{i=1}^N \vec{d}_1(\gamma_i) + \sum_{i,j=1}^N \vec{d}_2(\gamma_i, \gamma_j) + \dots$$

Later on, we will ignore the contributions of two-particle polarizabilities and ones of higher orders. Considering only symmetric ions, in particular those of the shape of hard disks, we can put  $\vec{\alpha}_1 \Rightarrow \alpha_\pm \delta_{\alpha\beta}$ . The one-particle contributions  $\vec{d}_1(\gamma_i)$  to the dipole moment  $\vec{D}_N^{(0)}$  of the system are formed by dipole pairs. Therefore, we can write  $\vec{d}_1^{(i)} = q\vec{r}^{(i)}$ , where  $\vec{r}^{(i)}$  is the vector connecting the centers of ions inside the  $i$ -th dipole pair. Moreover, for a rarefied gas, one can neglect by correlations of dipole moments for different dipole pairs. In this approximation, formula (4) for the polarizability vector  $\vec{P}$  transforms to

$$\vec{P} = n \left[ \alpha_+ + \alpha_- + \frac{1}{2} \beta \langle \vec{d}_2^2(r_{12}) \rangle_0 \right] \cdot \vec{E}_0 + \dots, \quad (5)$$

where  $n$  is the density of dipole pairs and  $r_{12} = |\vec{r}_2 - \vec{r}_1|$ . It follows from (3) and (4) that, in the two-particle approximation, the dielectric permittivity of the 2D Coulombic gas in its non-conducting phase is described by the formula

$$\frac{\varepsilon - 1}{\varepsilon + 1} = \pi n \left[ \alpha_+ + \alpha_- + \frac{1}{2} \beta \langle \vec{d}_2^2(r_{12}) \rangle_0 \right]. \quad (6)$$

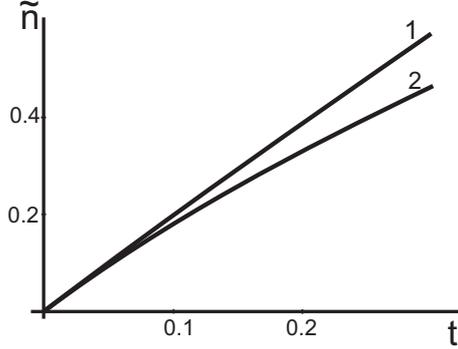


Fig. 1.  $D - C$  transition line according to (13) ( $m = 2$ )

The averaged value of the square of the dipole moment for a dipole pair can be approximated by the formula

$$\langle \vec{d}_2^2(r_{12}) \rangle_0 \approx T_s r_0^2 \tilde{r}^2,$$

where  $T_s = q^2$ ,  $\tilde{r} = \frac{r}{r_0}$ ,  $r_0$  and  $r$  are, respectively, the equilibrium distances between a cation and an anion of some dipole pair in vacuum and the medium with density  $n$ . If ions have the shape of hard disks with the same diameter,  $T_s$  has meaning of the characteristic temperature at which hard disks begin to separate from each other. Due to strong dipole-dipole interactions, the difference between  $r$  and  $r_0$  in a dense system becomes very essential. In [8], it was shown that

$$\tilde{r} = 1 + \gamma_1 \tilde{n} + \gamma_2 \tilde{n}^2 + \dots, \quad (7)$$

where

$$\gamma_1 = \frac{\gamma_1^{(0)}}{t}, \quad \gamma_1^{(0)} = \frac{3}{4m} \lambda, \quad (8)$$

and

$$\gamma_2 = \frac{\gamma_2^{(0)}}{t^2}, \quad \gamma_2^{(0)} = \frac{3(20 + 3m)}{32m^2} \lambda^2. \quad (9)$$

Other designations are:  $\tilde{n} = \frac{n}{n_M}$ , where  $n_M = \frac{1}{\pi r_0^2}$  is the maximal density in the system,  $t = \frac{T}{T_s}$ ,  $m$  is steepness exponent for the repulsive potential between a cation and an anion ( $U_r(r) \sim \frac{1}{r^m}$ ). If  $m \rightarrow \infty$ , ions can be considered as charged hard disks of radius  $\frac{r_0}{2}$ . The coefficient  $\lambda = \frac{1}{2\chi^2}$ , where  $\chi$  is the dielectric permittivity at rotational frequencies, describes the screening effects in a polarizable gas of dipole pairs.

Note that the values of  $\gamma_1$  and  $\gamma_2$  given by (8) and (9) were obtained from the equation

$$-\frac{1}{\tilde{r}^{m+1}} + \frac{1}{\tilde{r}} - \frac{2\lambda\tilde{n}}{t} \tilde{r}^3 \frac{(2 + \tilde{r})}{(1 + \tilde{r})^3} = 0 \quad (10)$$

for the minimum of the internal energy for a dipole pair interacting with its environment.

Rigorously speaking, the parameter  $\chi$  is also a function of density and temperature. However, while getting (7)–(9), we ignored this circumstance and put  $\chi = 1$ .

As a result, Eq. (6) for dielectric permittivity transforms to

$$\frac{\varepsilon - 1}{\varepsilon + 1} = \tilde{n} \left[ \tilde{\alpha}_+ + \tilde{\alpha}_- + \frac{\tilde{r}^2(\tilde{n})}{2t} \right], \quad (11)$$

where  $\tilde{\alpha}_i = \pi n_M \alpha_i$ ,  $i = +, -$ . For the set of points  $(\tilde{n}, t)$  satisfying the equation

$$\tilde{n} \left[ \tilde{\alpha}_+ + \tilde{\alpha}_- + \frac{\tilde{r}^2(\tilde{n})}{2t} \right] = 1, \quad (12)$$

the dielectric permittivity tends to the infinity and the dielectric phase of the Coulombic gas becomes unstable. In other words, (12) is the equation for the dielectric-conductor ( $D - C$ ) transition line.

Since the electronic contributions to the effective polarizability  $\tilde{\alpha}_{eff}(\tilde{n}, t) = \tilde{\alpha}_+ + \tilde{\alpha}_- + \frac{\tilde{r}^2(\tilde{n})}{2t}$  are negligibly small, formula (7) reduces to

$$\tilde{n} \tilde{r}^2(\tilde{n}) \approx 2t. \quad (13)$$

In the variables  $(\tilde{n}, t)$ , the  $D - C$  line is presented in Fig. 1. It is evident that the non-conducting phase of the 2D Coulombic gas exists in the region for which  $\tilde{n} \tilde{r}^2(\tilde{n}) \leq 2t$ . It is necessary to note that only those values of  $\tilde{n}$  and  $t$  are permissible which correspond to stable states of the system, i.e. they are above its spinodal (see below).

Moreover, the permissible values of  $(\tilde{n}, t)$  should satisfy the inequality

$$\tilde{n} \tilde{r}^2(\tilde{n}) < (\ll) 6t, \quad (14)$$

reflecting the smallness of the dipole-dipole interaction energy for two dipole pairs in comparison with their energy of thermal motion ( $|\langle U_{dd}(r_{12}) \rangle| < (\ll) T$ , where  $\langle U_{dd}(r_{12}) \rangle = -\frac{1}{2T} \frac{d^4(r)}{\langle r_{12} \rangle^4}$ ,  $\langle r_{12} \rangle$  is the average distance between dipole pairs). Comparing (13) and (14), we see that Eq. (13) is within the applicability region of the dipole approximation.

In the framework of the microscopic picture, the disintegration of dipole pairs into ions is the necessary condition for the transition to the conductive phase. In the next section, this question will be studied, and it will be shown that (12) and the equation describing the instability of dipole pairs are consistent.

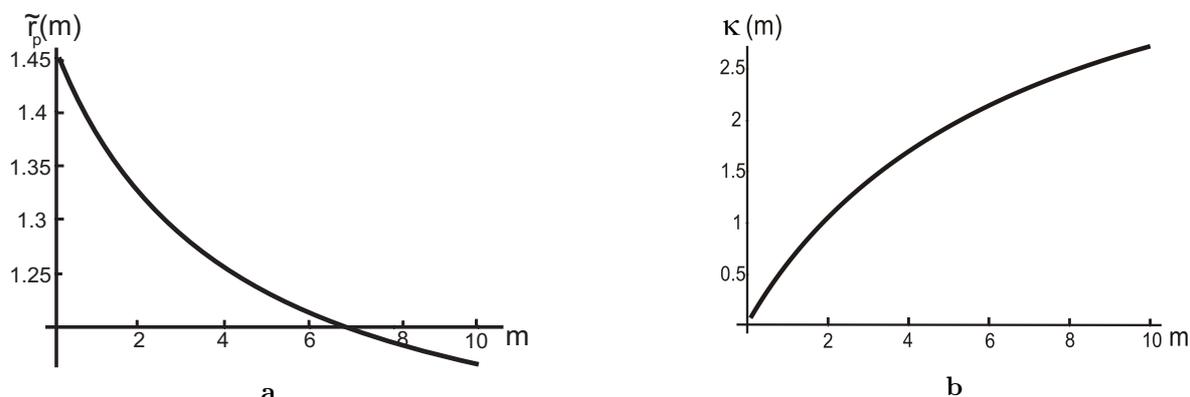


Fig. 2. Quantities  $\tilde{r}_p(m)$  (a) and  $\kappa(m)$  (b) versus the steepness exponent  $m$

### 3. Instability of Dipole Pairs

According to [8], the internal energy of a dipole pair interacting with all dipole pairs from its environment is equal to

$$\tilde{U}(\tilde{r}) = \frac{1}{m\tilde{r}^m} + \ln \tilde{r} - \frac{\lambda}{t} \frac{\tilde{r}^4}{(1+\tilde{r})^2} \tilde{n}. \quad (15)$$

The function has minimum and maximum only at definite values of density and temperature. To find them, let us to complement (10) by the equation

$$\frac{m+1}{\tilde{r}^{m+2}} - \frac{1}{\tilde{r}^2} - \frac{2\lambda\tilde{n}}{t} \tilde{r}^2 \frac{(6+4\tilde{r}+\tilde{r}^2)}{(1+\tilde{r})^4} = 0, \quad (16)$$

that is the second derivative of the potential energy with respect to  $\tilde{r}$ . Equations (10) and (16) determine the position of the point of inflection, at which the maximum and minimum of the function  $\tilde{U}(\tilde{r})$  coincide with each other.

To find this point, let us exclude the parameter  $\frac{2\lambda\tilde{n}}{t}$  from Eqs. (10) and (16). In such a way, we get

$$\frac{m+1}{\tilde{r}^m} - 1 - \left(1 - \frac{1}{\tilde{r}^m}\right) \frac{(6+4\tilde{r}+\tilde{r}^2)}{(2+\tilde{r})(1+\tilde{r})} = 0. \quad (17)$$

Let  $\tilde{r}_P(m)$  be the solution of (17). Then, from Eq. (10), we obtain the linear set of temperatures and densities corresponding to the point of inflection for  $\tilde{U}(\tilde{r})$ ,

$$\tilde{n} = \kappa(m)t, \quad (18)$$

where

$$\kappa(m) = \frac{1}{2\lambda} \frac{(1+\tilde{r}_P(m))^3}{\tilde{r}_P^4(m)(2+\tilde{r}_P(m))} \left(1 - \frac{1}{\tilde{r}_P^m(m)}\right). \quad (19)$$

Dipole pairs remain to be stable in the region

$$\tilde{n} \leq \kappa(m)t.$$

Comparing it with (14), we conclude that our approach will be non-contradictory while the density of the system is limited by the implicit inequality

$$\tilde{r}^2(\tilde{n}, m) < \frac{6}{\kappa(m)}. \quad (20)$$

As follows from Fig. 2, the root of Eq. (17) at  $m = 2$  takes value  $\tilde{r}_P(2) = 1.320$ , which leads to  $\kappa(2) = \frac{0.264}{\lambda}$ . For a rarefied gas of dipole pairs ( $\tilde{n} \ll 1$ ),  $\lambda$  tends to its maximum value 0.5. Therefore, in this region of states, the proportionality coefficient  $\kappa(2)$  tends to its minimal value of 0.52. If the system becomes denser, in particular while approaching the critical point, the parameter  $\lambda = \frac{1}{2\chi^2}$  diminishes. Omitting the detailed analysis of the density and temperature dependences of  $\chi$ , we put  $\chi^2 = 2$ . In this case,  $\kappa(2) \rightarrow 1$  (Fig. 2), so all estimates are within the applicability region (20) of our approach.

Note that the independence of  $\tilde{r}_P(m)$  on density is related to a not quite satisfactory description of the contribution of dipole-dipole interactions to the internal energy (15) of a dipole pair in the medium. More definitely, taking the screening effects into account is relevant only for remote neighbors. This circumstance is essential at both low and great enough densities. This problem will be considered separately, since it should be completed by the consideration of association effects in the system.

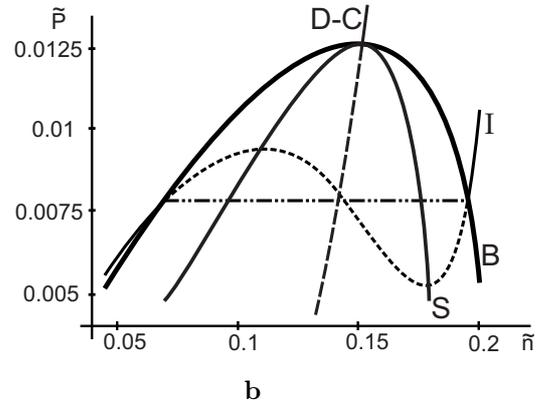
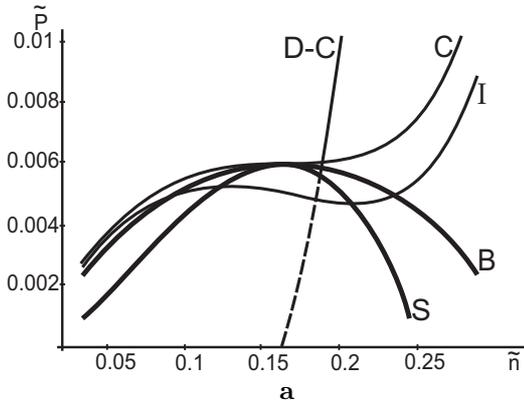


Fig. 3. Phase diagram of the Coulombic gas: *a* – corresponds to the van der Waals equation of state with  $a = \frac{\lambda}{8t}$  and  $b = 2$  at  $\lambda = \frac{1}{2}$ ;  $b - a = \frac{\lambda}{2t} \frac{\tilde{r}^4}{(1+\tilde{r})^2}$  and  $b = \frac{1}{2}(1 + \tilde{r})^2$  at  $\lambda = \frac{1}{2}$  and  $m = 2$  [see (21) and (7)–(9)]. Designations: *B* – binodal, *S* – spinodal, *I* – arbitrary isotherm, *C* – the critical isotherm. The *D* – *C* line is constructed according to (13)

**4. Relative Dispositions of the *D* – *C* Transition Line and a Binodal and a Spinodal for the 2D Dipole Fluid**

The simplest form of the equation of state (EOS), allowing to qualitatively describe the behavior of the 2D dipole fluid is the van der Waals equation. In [8], it was shown that the corresponding EOS for the rarefied 2D gas consisting of soft dipole pairs takes the form

$$\tilde{p} = \frac{\tilde{n}t}{1 - b(\tilde{n}, t)\tilde{n}} - a(\tilde{n}, t)\tilde{n}^2, \tag{21}$$

where

$$\tilde{p} = \frac{p}{n_M T_s}, \quad b(\tilde{n}, t) = \frac{1}{2}(1 + \tilde{r})^2, \quad a(\tilde{n}, t) = \frac{\lambda}{2t} \frac{\tilde{r}^4}{(1 + \tilde{r})^2}. \tag{22}$$

The liquid ( $n_b^{(l)}$ ) and gas ( $n_b^{(g)}$ ) branches of the binodal are determined with the help of the Maxwell rule

$$\int_{\tilde{n}_b^{(g)}}^{\tilde{n}_b^{(l)}} \tilde{p} d\tilde{n} = 0. \tag{23}$$

The position of the spinodal is given by the equation

$$\left. \frac{\partial \tilde{p}}{\partial \tilde{n}} \right|_t = 0. \tag{24}$$

These curves are presented in Fig. 3. They show that the applicability region of the van der Waals equation of state for soft dipole pairs is restricted by the density interval  $0.04 < \tilde{n} < 0.2$ . In addition, by comparing

Fig. 3,*a* and Fig. 3,*b*, we obtain that the asymmetry of a binodal and a spinodal is strongly dependent on the softness of the repulsive potential. Note that the special attention is paid to the case  $m = 2$  which corresponds to the consideration of centrifugal forces as repulsive ones (see [9]).

In [8], it was shown that the coordinates of the critical point, following to Eq. (20), are:

$$t_c = \frac{1}{6\sqrt{3}} + \frac{19}{72}\gamma_1^{(0)} \approx \frac{1}{6\sqrt{3}} \left( 1 + \frac{19\sqrt{3}}{32m} \right), \tag{25}$$

$$\tilde{n}_c = \frac{1}{6} + \frac{4}{9\sqrt{3}}\gamma_1^{(0)} \approx \frac{1}{6} \left( 1 + \frac{1}{\sqrt{3}m} \right).$$

The first terms in them correspond to hard dipole pairs with the equilibrium ion-ion distance  $r_0$ .

Here, it is appropriate to compare the results of the hard-dipole approximation ( $t_c \approx 0.096$ ,  $n_c \approx 0.167$ ) with those obtained in [8] with the help of computer experiments:

$$t_c \approx 0.056, \quad n_c \approx 0.21. \tag{26}$$

It follows from (25) that the critical density approaches its computer value if  $m$  diminishes. At the same time, the difference between the values of  $t_c$  increases. There are several causes for such a discrepancy between theoretical and “experimental” results. The association in the system seems to be most important among them: besides dipole pairs, the formation of quadrupoles, hexapoles, and multimers of higher orders is possible in the system. Indeed, putting the energy of a dipole pair with radius

$r_0$  ( $\tilde{r} = 1$ ) to be equal to zero ( $E_2 = 0$ ), we find that the energy of a regular quadrupole having minimal radius is

$$E_4 = -\ln 2 \cdot T_s.$$

Thus, the formation of quadrupole clusters is paying. This question will be below discussed in more details.

Another cause is connected with the instability of dipole pairs near the critical point. Indeed, as we see in Fig. 3, the  $D - C$  line conjugates with the binodal of the system in an intermediate vicinity of the critical point. For soft dipole pairs ( $m = 2$ ), this effect is especially well-marked. Unfortunately, in the van der Waals equation of state (21) which is the base for estimates (25), the disintegration of dipole pairs is not taken into account. In connection with this, it is necessary to note that the position of the binodal lying on the right of the  $D - C$  line should be define more exactly.

### 5. Hard-Quadrupole Approximation

As noted above, the formation of quadrupoles and electroneutral clusters of higher order is energetically paying. In this section, we consider the van der Waals equation of state in the hard-quadrupole approximation in more details. The simplest stable quadrupole is shown in Fig. 4, *a*. Assuming that the energy of a dipole having minimal radius equals  $E_2 = 0$ , the energies of two configurations of four charges presented in Fig. 4 are as follows:

$$E_4^{(a)} = -q^2 \ln 2, \quad E_4^{(b)} = q^2 \ln 2.$$

As seen, the barrier  $E_4^{(b)} - E_4^{(a)} = (2 \ln 2)T_s$  separating these configurations is essentially higher than the critical temperature  $T_c^{(d)}$  in the hard-dipole approximation. The quadrupole moment for the stable configuration equals

$$Q_{\alpha\beta}^{(a)} = Q(e_\alpha^{(1)}e_\beta^{(1)} + e_\alpha^{(2)}e_\beta^{(2)}), \quad Q = q\sigma^2, \quad (27)$$

where  $\vec{e}^{(1)}$  and  $\vec{e}^{(2)}$  are the unit vectors directed along the axes  $x$  and  $y$ , correspondingly (eigen vectors of the quadrupole matrix).

The interaction energy of two quadrupoles separated by a distance  $r$  is

$$W_{Q_{\alpha\beta}^{(1)}Q_{\gamma\lambda}^{(2)}} = -\frac{1}{2r^4}Q_{\alpha\beta}^{(1)}Q_{\gamma\lambda}^{(2)} \times \left\{ \frac{24}{r^4}x_\alpha x_\beta x_\gamma x_\lambda + [\delta_{\alpha\beta}\delta_{\gamma\lambda} + \delta_{\alpha\gamma}\delta_{\beta\lambda} + \delta_{\alpha\lambda}\delta_{\beta\gamma}] - \right.$$

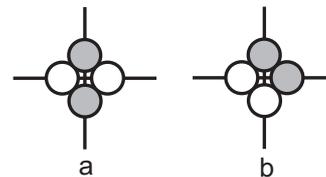


Fig. 4. Simplest quadrupoles

$$-\frac{4}{r^2} \left[ \delta_{\alpha\beta}x_\gamma x_\lambda + \delta_{\alpha\gamma}x_\beta x_\lambda + \delta_{\alpha\lambda}x_\beta x_\gamma + \delta_{\beta\gamma}x_\alpha x_\lambda + \delta_{\beta\lambda}x_\alpha x_\gamma + \delta_{\gamma\lambda}x_\alpha x_\beta \right] \}. \quad (28)$$

To average  $W_{Q_{\alpha\beta}^{(1)}Q_{\gamma\lambda}^{(2)}}$  over the orientations of quadrupoles, we use the approximate expression

$$g(1, 2) = 1 - \beta W_{Q_{\alpha\beta}^{(1)}Q_{\gamma\lambda}^{(2)}} + \dots, \quad (29)$$

for the angular part of the binary correlation function. Combining (27)–(29), we get the average value of the quadrupole interaction energy:

$$\langle W_{Q_{\alpha\beta}^{(1)}Q_{\gamma\lambda}^{(2)}}(r) \rangle = -18 \frac{\beta}{r^8} Q^4.$$

As a result, the attractive part of the interparticle potential defined as  $U_a(r) = \langle W_{Q_{\alpha\beta}^{(1)}Q_{\gamma\lambda}^{(2)}}(r) \rangle$  takes the form

$$U_a(r) = -\frac{\lambda_Q}{t} \left( \frac{R_0}{r} \right)^8, \quad \lambda_Q = 18T_s, \quad (30)$$

where  $R_0 = (1 + \sqrt{2})r_0$  is the effective radius of a rotating quadrupole.

To find the coefficients  $a$  and  $b$  of the van der Waals equation of state we use the standard formulas [11]

$$a = -\pi \int_{2R_0}^{\infty} U_Q(r) r dr, \quad b = 2\pi R_0^2. \quad (31)$$

It is not difficult to see that

$$a(t) \approx 0.06 \frac{\pi T_s R_0^2}{t}. \quad (32)$$

The critical temperature and density are determined by the equations

$$t_c = \frac{8}{27} \frac{a(t_c)}{b}, \quad n_c = \frac{1}{3b},$$

which leads to

$$t_c \approx \frac{1}{24} \approx 0.04, \quad \tilde{n}_c = \frac{1}{6} \approx 0.167. \quad (33)$$

Hence, in the quadrupole fluid approximation, the critical density remains the same as in the dipole fluid approximation, whereas the critical temperature diminishes practically by five times. This fact suggests us that the 2D Coulombic gas for  $\tilde{n} \leq \tilde{n}_c$  can be considered as a solution of the quadrupole component in a dipole fluid. By the order of magnitude, the concentration of the quadrupole component should not exceed  $0.2 \div 0.3$ . At  $\tilde{n} > \tilde{n}_c$ , the formation of larger associates is also probable. To describe the associate composition of the 2D Coulombic gas with varying temperature and density, one can apply the methods of chemical kinetics [11]. This question will be investigated in details in the following paper.

## 6. Conclusion

In the present paper, it is shown that the dipole fluid is a quite good initial approximation for the 2D Coulombic gas. The comparison with the results of computer simulations [4] shows that this approach allows one to satisfactorily describe both 1) the position of a binodal and a spinodal and 2) the dielectric-conductor phase transition. The first problem is solved with the help of the van der Waals equation of state, the second – on the base of the canonical formalism for the dielectric permittivity of the system. It is shown that the  $D - C$  line terminates on the binodal near the critical point. This fact correlates with computer experimental data [4].

Dipole pairs are considered as soft particles, properties of which are described in the classical approximation. We have investigated the instability of dipole pairs. In particular, it was established that, on the  $D - C$  line defined as the set of points in which the dielectric permittivity tends to infinity, dipole pairs become instable. The influence of the repulsive potential between the anion and the cation inside a dipole pair on the properties of the system has been studied.

Analyzing the position of the vapor-liquid critical point, it was concluded that, besides dipole pairs, the noticeable role in the system is played by quadrupoles and associates of higher order. This problem is also important for the  $XY$ -model [11] in view of the similarity in its behavior and that of the 2D Coulombic gas [7].

At the same time, the following problems need to be investigated in more details: 1) the association-dissociation processes in the system; 2) their influence on the character of the van der Waals equation of state and the behavior of the dielectric permittivity, in particular, on the position of the  $D - C$  line; 3) the more exact description of the dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, and so on interactions, as well as the instability of dipole pairs; 4) the disintegration of dipole pairs and the influence of free anions and cations on the thermodynamic properties of the system and its transition to the conducting phase.

I would like to express my cordial gratitude to Professor L.A. Bulavin for advices and the discussion of the results obtained.

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Received 14.03.07

## ФАЗОВА ДІАГРАМА ДВОВИМІРНОГО КУЛОНІВСЬКОГО ГАЗУ

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Резюме

Досліджується відносно положення кривих співіснування пара-рідина, спінодалі системи та переходу з діелектричного у провідний стан. Враховано, що в широкій області значень температури та густини катіони та аніони об'єднуються в дипольні пари. Термодинамічні властивості кулонівського газу знаходяться за допомогою рівняння стану Ван-дер-Ваальса, засто-

сованого до системи м'яких дипольних пар. Розглянуто вплив різних факторів на положення критичної точки системи. Отримано канонічний вираз для діелектричної проникності. Лінія

переходу діелектрик–провідник визначається з умови прямування діелектричної проникності до нескінченності. Показано, що саме ця лінія є межею стійкості дипольних пар в системі.