

PROPERTIES OF TWO-DIMENSIONAL COULOMB GAS IN THE REGION IN WHICH QUADRUPOLE CLUSTERS ARE DOMINATING

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The liquid-vapor coexistence curve of a two-dimensional Coulomb gas was found to belong – in the phase diagram of the system – to the region in which the ensemble of quadrupole clusters is diluted by a small amount of dipole pairs. The results of computer experiments for the critical temperature and density are well consistent with their analytical dependences. The destruction of quadrupole clusters owing to their thermal excitation and the electrostatic interaction between them has been considered at a qualitative level. The location of the insulator–conductor transition curve in the phase diagram has been analyzed.

1. Introduction

Systems in liquid and vapor-like states with Coulomb interaction between particles comprise important objects of studying in the molecular physics and the physics of liquids. Among such systems, a distinguished place is occupied by a two-dimensional Coulomb gas formed by oppositely charged disks. Despite an extreme simplicity of this system, its thermodynamic and dielectric properties, as well as its conductivity, remain insufficiently studied to date. This circumstance is a consequence of the fact that the zeroth-order approximation, in which the forces of Coulomb interaction are taken into account in a way [1–4] that is standard for plasma researches, is not effective enough. Such an approach to the description of Coulomb gas properties can be considered substantiated enough only for a high-temperature conducting phase of the system. At temperatures corresponding to a liquid dielectric phase, its application is not justified, because, in this case, it is electrically neutral clusters that govern properties of the system.

Really, owing to the Coulomb interaction, disks with opposite charges should attract one another and form electrically neutral dipole pairs. Then, the dipole-dipole interaction and collisions between dipole pairs give rise to their association in quadrupole and hexapolar clusters; and the lower are the temperature and the density of the system, the more stable are those

clusters. One should expect that the thermodynamic and electrophysical properties of the gas in the vicinity of the liquid-vapor coexistence curve in the phase diagram of the system would be of a cluster origin.

The binodal position can be described most naturally by specifying a position of the liquid-vapor critical point. In works [5–7], it was shown that, in the systems formed by dipole pairs D and quadrupole clusters Q , the coordinates of the liquid-vapor critical point are determined by the relations

$$t_c = \begin{cases} \frac{1}{6\sqrt{3}} \approx 0.1, & D, \\ \frac{2\sqrt{2}}{3(1+\sqrt{2})^3} \frac{1}{(1.5+\sqrt{2})^{1/2}} \approx 0.039, & Q, \end{cases} \quad (1)$$

$$n_*^{(c)} = \begin{cases} 1/3\pi \approx 0.106, & D, \\ 4/3(3/2 + \sqrt{2})\pi \approx 0.146, & Q. \end{cases} \quad (2)$$

One can see that the values $t_c^{(1)} = 0.056$ and $t_c^{(2)} = 0.085$ for the critical temperature obtained in computer experiments in works [8] and [9], respectively, fall within the interval from $t_c^{(D)}$ and $t_c^{(Q)}$. On the other hand, a comparison of Eq. (2) with the results $n_c^{(1)} = 0.21$ and $n_c^{(2)} = 0.16$ given in work [8] and [9], respectively, demonstrates that the agreement between analytical and numerical values for the critical density is much better in the case of the system composed of quadrupole clusters.

In this work, we are going (i) to prove that the liquid-vapor coexistence curve for the system under investigation is located in the region in which quadrupole clusters are diluted by a small amount of dipole pairs, (ii) to determine the stability limit for quadrupole pairs, and (iii) to construct the insulator-conductor transition curve at a qualitative level.

2. Clusterization in Coulomb Gas

The most stable among clusters that are formed in a Coulomb gas are dipole pairs and quadrupole clusters. The values of their equilibrium concentrations can be calculated making use of the chemical kinetics methods

[10–12]. To simplify calculations, we take advantage of an additional assumption that dipole pairs and quadrupole clusters are in their ground energy states. As to the interaction between clusters, it will be considered in the same approximation, as the van der Waals equation for a dipole-quadrupole mixture is derived.

The equation of “chemical” equilibrium among dipole pairs and quadrupole clusters reads

$$\frac{(1-c)(2-c)}{c^2} = 0,1 \times 2^{T_*/T} n_* \left(\frac{T_0}{T} \right)^{1/2} \exp \left(\frac{2\mu_d^{(\text{ex})} - \mu_Q^{(\text{ex})}}{T} \right), \quad (3)$$

where $c = n_d/(n_d + n_Q)$ is the relative concentration of dipole pairs; n_d and n_Q are the concentrations of dipole pairs and quadrupole clusters, respectively; $T_* = q^2$ is the characteristic dissociation temperature of isolated dipole pairs, T_0 is the temperature of quantum-mechanical degeneration for the system of hard disks; and $n_* = 2n_+ \sigma^2$ ($n_+ = n_-$) is the dimensionless density of a system of disks, whose diameters are equal to σ . The total concentration $n = n_d + n_Q$, which is connected with the dimensionless density of ions n_* by the relation

$$n = \frac{1}{2(2-c)} \frac{n_*}{\sigma^2}, \quad (4)$$

is also taken into account. The quantities $\mu_d^{(\text{ex})}$ and $\mu_Q^{(\text{ex})}$ are contributions to the chemical potentials of components due to the cluster–cluster interaction (these are the so-called excess values of chemical potentials with respect to those in a perfect mixture). It can be demonstrated (see works [7, 10]) that those quantities are determined by the formulas

$$\mu_d^{(\text{ex})} = v(P - P_{\text{id}}) - T \ln(1 - nv_0(c)) - c \frac{a_{dd}}{v} - \frac{1}{2}(1-c) \frac{a_{dQ}}{v}, \quad (5)$$

$$\mu_Q^{(\text{ex})} = v(P - P_{\text{id}}) - T \ln(1 - nv_0(c)) - (1-c) \frac{a_{QQ}}{v} - \frac{1}{2}c \frac{a_{dQ}}{v}. \quad (6)$$

Here, P is the pressure in the mixture of interacting dipole pairs and quadrupole clusters, $P_{\text{id}} = nT$ is the

pressure in the same mixture but in the ideal-gas approximation, and $v = 1/n$ is the specific volume (the Boltzmann constant was put equal to unity). By its sense, the quantity

$$v_0(c) = v_d c + v_Q (1 - c)$$

has the meaning of the average characteristic volume (characteristic area, in the two-dimensional geometry) of particles in the mixture, while the quantities $v_d = 2\pi r_d^2$ and $v_Q = 2\pi r_Q^2$ are the doubled areas of disks that are formed by dipole pairs and quadrupole clusters as a result of their rotation. It is easy to see that the radii of those disks are equal to $r_d = \sigma$ and $r_Q = \frac{\sigma}{2}(1 + \sqrt{2})$, respectively. The coefficients a_{ij} ($i, j = d, Q$) are defined by the formula

$$a_{ij} = \pi \int_{(r_i+r_j)}^{\infty} |U_{ij}(r)| r dr,$$

where $U_{ij}(r)$ are the potentials of the interaction between dipole pairs and quadrupole clusters averaged over their orientations (see works [5–7]), $r_d + r_d = 2\sigma$, $r_d + r_Q = \frac{\sigma}{2}(3 + \sqrt{2})$, and $r_Q + r_Q = \sigma(1 + \sqrt{2})$. In the van der Waals approximation,

$$P = \frac{nT}{1 - nv_0(c)} - a(c)n^2, \quad (7)$$

where

$$a(c) = a_{dd}c^2 + a_{QQ}(1-c)^2 + 2a_{dQ}c(1-c)$$

is the effective constant of interaction.

The applicability region of formula (3) coincides with that of the van der Waals equation and, as a consequence, is confined by the density

$$n_* < 1/\pi. \quad (8)$$

The distribution of the dipole pair concentration in the plane of Coulomb gas states (n_*, t) is naturally described making use of isoconcentration curves which are defined by the equations $c(n_*, t) = c_0$ for various c_0 -values ($0 < c_0 < 1$). The separatrices, which were calculated in such a way by Eq. (3), are presented in Fig. 1. Their sections beyond the region $(n_* < 1/\pi, t < t_c = 0.25)$ are depicted by dotted curves. It was done because, owing to the excitation of internal vibrations [13] and the electrostatic interaction between particles, the existence of quadrupole clusters beyond the specified region in the phase diagram becomes impossible. One can see that the critical points (D and Q) calculated

in works [5–7] in the framework of the dipole pair and quadrupole cluster approximations are located in the ensemble of quadrupole clusters diluted by a small amount of dipole pairs ($c < 0.1$).

We may assert that the branches of the liquid-vapor coexistence curve are also related to a weak solution of dipole pairs and hexagonal clusters in the quadrupole phase of the system. The same conclusion can be drawn as well by analyzing the data obtained in molecular dynamic experiments [8, 9]. A natural way to construct the binodal and the spinodal of such a system is the thermodynamic perturbation theory.

3. Spinodal and Binodal Positions for a Mixture of Quadrupole Clusters and Dipole Pairs

For the determination of the liquid-vapor coexistence curve position, let us take advantage of the Gibbs equation

$$\mu_Q^{(l)}(t, n_l, c_l) = \mu_Q^{(v)}(t, n_v, c_v) \quad (9)$$

for the chemical potentials of quadrupole clusters in the liquid and vapor phases ($i = l, v$), as well as the equality between pressures which are determined by the van der Waals equation,

$$P^{(l)}(t, n_l, c_l) = P^{(v)}(t, n_v, c_v). \quad (10)$$

Here, we take into account that $\mu_Q = \mu_Q^{(id)} + \mu_Q^{(ex)}$, where $\mu_Q^{(id)}$ is the chemical potential of clusters in the ideal-gas approximation. Note that the equality between the chemical potentials of dipole pairs, $\mu_d^{(l)}(t, n_l, c_l) = \mu_d^{(v)}(t, n_v, c_v)$, is a consequence of Eq. (9), because the condition of chemical equilibrium between them and quadrupole clusters yields $\mu_Q = 2\mu_d$.

The equation of chemical equilibrium (3), which is used to determine the concentrations c_l and c_v in the liquid and vapor phases, respectively, at small total concentrations looks like

$$c^2 = \frac{20}{n_*} \left(1 - \frac{\pi n_*}{4} (1.5 + \sqrt{2}) \right) 2^{-1/t} (10t)^{1/2} \times \exp(- (Z_1 + Z_2)), \quad (11)$$

where

$$Z_1 = nv_0 \left(\frac{1}{1 - nv_0} - \frac{a}{Tv_0} \right),$$

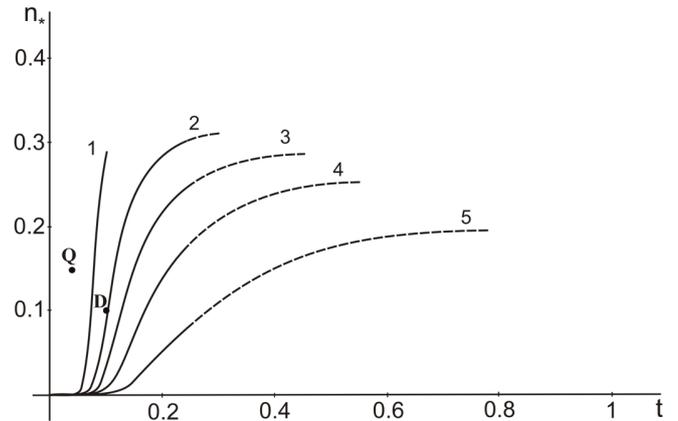


Fig. 1. Family of separatrices $c(n_*, t) = c_0$ corresponding to formula (8) at $T_0 = 0.1T_*$. Curves 1 to 5 correspond to $c_0 = 0.1, 0.3, 0.5, 0.7, \text{ and } 0.9$, respectively

$$nv_0 = \frac{\pi n_*}{4} (1.5 + \sqrt{2}), \quad \frac{a}{Tv_0} = \frac{3}{(1 + \sqrt{2})^6} \frac{1}{1.5 + \sqrt{2}} \frac{1}{t^2},$$

$$Z_2 = -\frac{\pi}{4} \left(\frac{16}{(3 + \sqrt{2})^4} - \frac{3}{(1 + \sqrt{2})^6} \right) \frac{n_*}{t^2}.$$

In the zeroth-order approximation with respect to the concentration c , the binodal of the mixture coincides with that of the quadrupole phase. In the latter, the density values n_v and n_l for the vapor and liquid, respectively, branches of the binodal are determined by the equation

$$\int_{n_v}^{n_l} \left(\frac{t}{(1 - nv_0)^2} - 2an \right) \frac{dn}{n} = 0,$$

which is related to Eq. (7) by means of the Maxwell rule.

In contrast to the binodal position, that of the spinodal is determined in a much easier way. The stability of the system in either the liquid or gaseous state becomes broken at points which satisfy the equation $(\partial P / \partial n)_t = 0$. Taking the dependence of the pressure on the dipole pair concentration into account, this equation transforms into the following one:

$$\frac{\partial P}{\partial n} \Big|_{t,c} + \frac{\partial P}{\partial c} \Big|_t \frac{\partial c}{\partial n} \Big|_t = 0. \quad (12)$$

A comparative behavior of spinodals for the system of quadrupole clusters and for the mixture of quadrupole clusters and dipole pairs is presented in Fig. 2. The critical point for the mixture can be found as a point,

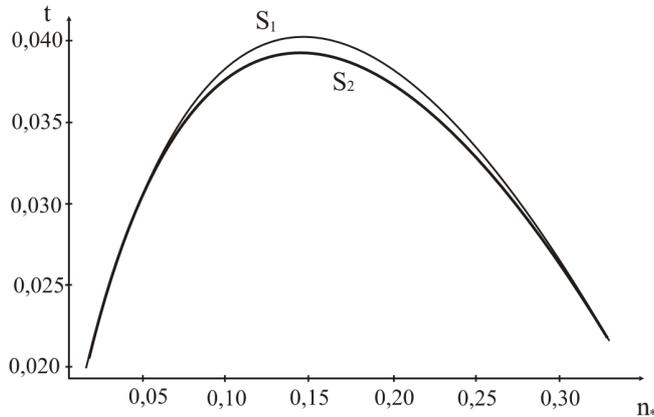


Fig. 2. Comparative behavior of spinodals for the mixture of quadrupole clusters and dipole pairs (S_1) and the system of quadrupole clusters (S_2)

where the left and right branches of the spinodal merge together. In such a way, we find that

$$t_c \approx 0.04, \quad n_c \approx 0.148, \quad c_c \approx 0.01.$$

Hence, taking dipole pairs into account brings about a certain growth of critical parameters. Note that the largest discrepancy between the spinodal branches is observed in the vicinity of the critical point – in a total agreement with the arrangement of isoconcentration curves in the phase diagram (Fig. 1).

Binodal branches become shifted in a similar manner.

4. Destruction of Quadrupole Clusters as a Result of the Electrostatic Interaction Between Them

Quadrupole clusters are not rigid particles and can be destroyed as a result of collisions between them. Cluster collisions also excite internal degrees of freedom inside clusters. The distribution of isoconcentration curves in Fig. 1 corresponds to the simplest case, where all quadrupole clusters are in the ground vibrational state only. The account of the excited vibrational states should be accompanied by a reduction of the quadrupole cluster existence region in the plane of states (n_*, t) . However, of five vibrational degrees of freedom, two have essentially nonlinear character [13], which makes the corresponding calculations more complicated. Therefore, we confine ourselves to the qualitative analysis of the influence of thermal excitations and the electrostatic particle-particle interaction on the cluster integrity.

Owing to the interaction with neighbor clusters, the vibrational energy levels of a quadrupole cluster become

broadened. In the zeroth-order approximation, the level width can be estimated as (see work [14])

$$|\Delta E| \sim \sqrt{\langle U_{QQ}^2 \rangle},$$

where U_{QQ} is the energy of the quadrupole-quadrupole interaction of the cluster with all its near and far neighbors. According to the results of work [7], the square of the pair interaction energy between clusters averaged over all their possible orientations is equal to

$$U_{QQ}^2(r) = 18T_*^2 \left(\frac{\sigma}{r}\right)^8.$$

Summation over all the neighbors in the formula $\langle U_{QQ}^2 \rangle = \sum_{Q'} U_{QQ'}^2(r)$ can be replaced by integration:

$$\langle U_{QQ}^2 \rangle = 2\pi n_Q \int_{R_m}^{\infty} \langle U_{QQ}^2(r) \rangle g(r) r dr,$$

where the lower limit of integration $R_m = 2(\pi n_Q)^{-1/2}$ is identified with the average distance between quadrupole clusters, and n_Q is their density. Since the Coulomb gas is rarefied enough in the vicinity of the liquid-vapor critical point, the binary correlation function $g(r)$ can be admitted equal to unity. In such a way, we obtain that

$$\langle U_{QQ}^2 \rangle = \frac{3\pi^4}{2 \times 4^4} n_*^4 T_*^2,$$

where $n_* = 4n_Q\sigma^2$ is the dimensionless density of ionic system (the ions are supposed to be located at their equilibrium positions). Therefore,

$$|\Delta E| \sim \left(\frac{3}{2}\right)^{1.2} \frac{\pi^2}{16} n_*^2 T_*.$$

The quadrupole cluster becomes unstable, if the sum of its vibrational energy E_v and the level width is of the same order as the energy of the cluster in the ground state $E_Q^{(0)} = -T_* \ln 2$:

$$E_v + |\Delta E| \sim E_Q^{(0)}. \quad (13)$$

In work [7], it was shown that the vibrational energy of a cluster is approximately equal to $E_v \approx 2.75T_*t$. Therefore, it follows from Eq. (13) that the quadrupole cluster destruction temperature t_d is equal to

$$t_d^{(1)}(n_*) \approx 0.25 - \left(\frac{3}{2}\right)^{1/2} \frac{\pi^2}{16} n_*^2. \quad (14)$$

However, it is more reasonable that the lower limit of integration in Eq. (4) should be taken smaller, which is caused by significant fluctuations of the distance between the nearest neighbors. If R_m is identified with half of the distance between clusters, we obtain

$$t_d^{(2)}(n_*) \approx 0.25 - \left(\frac{3}{2}\right)^{1/2} \frac{\pi^2}{2} n_*^2. \quad (15)$$

5. Discussion of the Results Obtained

The most important result of this work is the proof of the fact that, in the case of a two-dimensional Coulomb gas, the liquid-vapor coexistence curve is located in that region of the phase diagram in which properties of a Coulomb gas are determined by quadrupole clusters diluted by a small amount of dipole pairs.

The values obtained for the critical temperature and the density are in good agreement with the results of computer experiments.

We have also considered, at a qualitative level, the influence of thermal excitations of quadrupole clusters and the electrostatic interaction between them on their existence as integral objects. The destruction of clusters is associated with the formation of a plasma-like state of the system, i.e. with the transition of the insulator-conductor type in it. Formulas (14) and (15) can therefore be regarded as the equation for the insulator-conductor transition curve on the phase plane. They quite correctly reproduce the dependence of the transition temperature on the density. It is easy to make sure that formula (15) rather successfully describes the transition curve that was obtained in the computer experiment [8]. One may hope for that a more exact calculation of R_m and the account of fluctuation dipole moments of quadrupole clusters will allow the insulator-conductor transition curve to be reproduced not only qualitatively, but quantitatively as well.

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ВЛАСТИВОСТІ ДВОВИМІРНОГО КУЛОНІВСЬКОГО ГАЗУ В ОБЛАСТІ ДОМІНУВАННЯ КВАДРУПОЛЬНИХ КЛАСТЕРІВ

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Резюме

Доведено, що крива співіснування рідина-пара у двовимірному кулонівському газі розташована в області, в якій квадрупольні кластери розбавлені невеликою кількістю дипольних пар. Значення критичних температури і густини добре узгоджуються з результатами комп'ютерних експериментів. Якісно розглянуто вплив теплових збуджень квадрупольних кластерів і електростатичної взаємодії між ними на їх існування як цілісних об'єктів. Обговорюється положення кривої діелектрик-провідник.