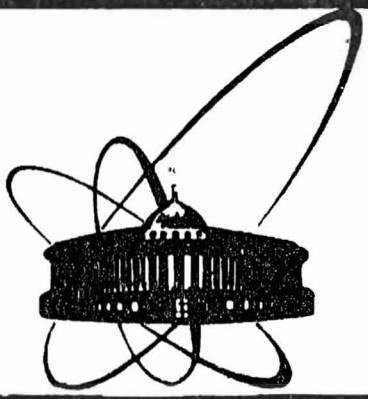

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THE COULOMB LATTICE GAS WITHIN THE MEAN SPHERICAL APPROXIMATION

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1. INTRODUCTION

The three-dimensional Coulomb lattice gas (CLG) is often considered as the simplest nontrivial model of the system of charged point defects in ionic crystals. The model is a lattice version of the restricted primitive model (charged hard spheres) of ionic solution theory and consists of positive and negative charged particles occupying the sites of a regular lattice with the restriction that two particles cannot occupy the same lattice site. However, the importance of the CLG is not restricted to the case of the charged defects. It is a well-known fact that there exist the isomorphisms (with possible short range modifications of the Coulomb interaction) between the CLG and other interesting statistical mechanical models - namely "discrete gaussian" and "harmonic rotator" models [1]. In this paper we will not use the aspects of these isomorphisms.

Some time ago a commonly used approach for studying the CLG and related models was the Debye - Hückel (DH) theory [2-4] or its later modifications [5,6]. It is well known that the DH theory is predictive when the concentration of particles is below ≈ 1% and the coupling constant is not very high. Indeed, in this case it has recently been rigorously proved that the DH results are correct [7]. In fact, there is a large class of materials known as superionic conductors (see, for example, [8]) which appear to have the concentrations of defects higher than is the limit of the validity of the DH theory. Some of the superionic conductors (CaF_2, for example) exhibit a diffusive phase transition when the temperature increases. March et al. [9] have proposed that the transition may be driven by the defect subsystem. These proposals have stimulated a new interest in the study of the CLG.

Recently, the CLG has been investigated by Walker and Gillan [10]. They obtained the free energy of the CLG by the Padé extrapolation of the series expansion of the free energy in powers of $k_D a$ (k_D is the DH screening parameter and a is a lattice constant). They found the phase transition of the vapour-liquid type. There is a clear connection between this

critical point and the critical point found by Stell et al.[11] in the restrictive primitive model (further RPM). Very recently another attempt towards the understanding of the behaviour of the CLG has been made by Harder and Allnatt [12]. They have obtained the thermodynamic quantities and correlation functions from the numerical solution of the hypernetted chain equations. A good agreement with the results of Walker and Gillan was found although they were not able to reach numerically the critical point.

On the other hand, there have appeared renormalisation group treatments of the problem [13, 14]. It is interesting that they led to the contradictory result that the three-dimensional CLG does not exhibit the transition. However, as we shall see, the value of the coupling constant plays a crucial role hare and we leave further discussion of this controversy to the last paragraph.

The aim of this paper is to find the correlation functions of the CLG by a different method from the previously reported ones. In sect. 2 we define the model and use the correlation functions theory in the mean spherical approximation as a method of solution. We shall see that it will be convenient to express the free energy by the Padé extrapolation of Walker and Gillan but the coefficients will be recalculated according to the present results. The comparing with the previous treatments will be given in sect. 3 by the example of the localization of the critical point. The last paragraph is devoted to the brief discussion of the results.

2. THE MODEL AND ITS SOLUTION WITHIN THE MEAN SPHERICAL APPROXIMATION

We consider a neutral system of two kinds of particles with charges $\pm e$. The n particles of each kind occupy a three-dimensional simple cubic lattice with the lattice constant a and the total number of sites N. The particles i and j with the positions $\vec{r}_i$ and $\vec{r}_j$, respectively, interact through the pair potentials

$$\phi(|\vec{r}_i - \vec{r}_j|) = \begin{cases} \infty, & \vec{r}_i = \vec{r}_j \\ \dfrac{e_i e_j}{\epsilon |\vec{r}_i - \vec{r}_j|}, & \vec{r}_i \neq \vec{r}_j \end{cases} \qquad (1)$$

where ϵ is the dielectric constant. The total energy is given by

$$E(\vec{r}_1, \ldots, \vec{r}_{2n}) = \sum_{1 \le i < j \le 2n} \phi(|\vec{r}_i - \vec{r}_j|), \qquad (2)$$

Now we start from the well-known Ornstein – Zernike relation (see, e.g., [15]) between the pair correlation functions $g_{k\ell}(\vec{r}) = h_{k\ell}(\vec{r}) + 1$ and the direct correlation functions $c_{\ell m}(\vec{r})$ written in the lattice form

$$h_{k\ell}(|\vec{r}_i|) = c_{k\ell}(|\vec{r}_i|) + \sum_m \rho_m \sum_j h_{km}(|\vec{r}_j|) c_{m\ell}(|\vec{r}_i - \vec{r}_j|). \quad k, \ell = 1, 2 \qquad (3)$$

Here, we explicitly assumed that the correlations are independent of the direction (k, ℓ, m denote the types of particles, ρ_m is the concentration of particles of the type m). In our case $\rho_1 = \rho_2 = \rho = n/N$ and because of the symmetry of charges we have $h_{11}(|\vec{r}_i|) = h_{22}(|\vec{r}_i|)$, $h_{12}(|\vec{r}_i|) = h_{21}(|\vec{r}_i|)$. It is clear that analogous relations hold for the direct correlation functions. Now only two equations (3) remain instead of four. If we add and subtract them, we obtain

$$H_+(|\vec{r}_i|) = C_+(|\vec{r}_i|) + \rho \sum_j H_+(|\vec{r}_j|) C_+(|\vec{r}_i - \vec{r}_j|), \qquad (4a)$$

$$H_-(|\vec{r}_i|) = C_-(|\vec{r}_i|) + \rho \sum_j H_-(|\vec{r}_j|) C_-(|\vec{r}_i - \vec{r}_j|), \qquad (4b)$$

with

$$\begin{aligned} H_+(|\vec{r}_i|) &= h_{11}(|\vec{r}_i|) + h_{12}(|\vec{r}_i|) \\ H_-(|\vec{r}_i|) &= h_{11}(|\vec{r}_i|) - h_{12}(|\vec{r}_i|) \\ C_+(|\vec{r}_i|) &= c_{11}(|\vec{r}_i|) + c_{12}(|\vec{r}_i|) \\ C_-(|\vec{r}_i|) &= c_{11}(|\vec{r}_i|) - c_{12}(|\vec{r}_i|). \end{aligned} \qquad (4c)$$

Now for the direct correlation functions we assume the mean spherical approximation [16]

$$c_{11}(|\vec{r}_i|) = -\frac{k}{|\vec{n}_i|}, \quad \vec{n}_i \neq 0 \tag{5a}$$

$$c_{12}(|\vec{r}_i|) = -\frac{k}{|\vec{n}_i|}, \quad \vec{n}_i \neq 0 \tag{5b}$$

together with

$$h_{11}(0) = h_{12}(0) = -1 \tag{5c}$$

and the coupling constant K is given by

$$K = \frac{e^2}{\epsilon a k_B T}, \tag{5d}$$

and finally

$$\vec{n}_i = \frac{1}{a}\vec{r}_i. \tag{5e}$$

In the lattice case for the complete solution of equations (4) and (5) only the quantities $C_+(0)$ and $C_-(0)$ are needed. From (4a) with the use of (5) we immediately obtain

$$\rho C_+(0) = -\frac{2\rho}{1-2\rho}. \tag{6}$$

The quantity $C_-(0) = c_{11}(0) - c_{12}(0)$ is more difficult to find. We rewrite (4b) into the reciprocal space and by assuming (5) we obtain the relation

$$\frac{1}{8\pi^3}\int \frac{d^3\vec{g}}{1-\rho C_-(0)+\rho 2K\phi(\vec{g})} = 1, \tag{7}$$

where

$$\phi(\vec{g}) = \sum_{\vec{n}_i \neq 0} \frac{e^{-i\vec{g}\cdot\vec{n}_i}}{|\vec{n}_i|}, \tag{8}$$

and the integration in (7) has to be performed over the first Brillouin zone. Equation (7) in a slightly different form is

$$M(\alpha) = \frac{x^2}{4\pi}, \tag{9}$$

where

$$M(\alpha) = \frac{1}{8\pi^3}\int \frac{d^3\vec{g}}{\alpha^{-1}+\phi(\vec{g})}, \tag{10}$$

where

$$\alpha^{-1} = \frac{1-\rho C_-(0)}{\frac{x^2}{4\pi}} \tag{11}$$

and

$$x^2 = 8\pi\rho K = \frac{8\pi\rho e^2}{k_B T \epsilon a} = k_D^2 a^2. \tag{12}$$

Now we consider the function $M(\alpha)$ defined by (10). $M(\alpha)$ is finite in the interval $0 \leq \alpha \leq \alpha_C \cong 0.572...$ and $M(\alpha_C) \cong 2.86$. The values of $M(\alpha)$ are found numerically by the modified Monte-Carlo method with typical errors ≈ 0.5-3%. (The details of the numerical part of the work will be given elsewhere [17]). The importance of the function $M(\alpha)$ is clear from the fact that the internal energy U of the system may be expressed by

$$\frac{U}{N} = \frac{1}{2}\rho k_B T C_-(0), \tag{13}$$

which follows from (4b) and (5). A convenient representation of $M(\alpha)$ is obtained by using for the internal energy the Padé expression of Walker and Gillan [10]

$$\frac{U}{N} = -\frac{1}{24\pi} k_B T f'(x) x, \tag{14}$$

with

$$f(x) = x^3 \frac{1+p_1 x}{1+g_1 x+g_2 x^2}. \tag{15}$$

Originally the constants p_1, g_1, g_2 were found from the series expansion for the free energy as a function of x up to x^6-order. This procedure gave $p_1 = 0.555$, $g_1 = 1.087$, $g_2 = 0.2396$. However, the series appeared to be an alternating one with a

rather slow convergence. So, we will try to find the constants in such a way as to obtain the best possible approximation of the relation (9). This will be performed in the following manner. Two relations between the coefficients will be the same as in the original

$$p_1 = B_1 + g_1, \tag{16}$$

$$g_2 = - B_2 - B_1 g_1, \tag{17}$$

with $B_1 = - 0.53199$, $B_2 = 0.33869$. The constant g_1 is found from the condition of the best approximation of (9) (in the least squares sense) in the interval $0 \leq \alpha \leq 0.55$. After solving the corresponding nonlinear equation, one obtains

$$p_1 = 0.3295, \quad g_1 = 0.8615, \quad g_2 = 0.1196. \tag{18}$$

The approximation of $M(\alpha)$ in this way is completely within the previously involved numerical accuracy in the considered interval. Now, by integration of the internal energy one obtains the Helmholtz free energy A_{CLG}

$$A_{CLG} = A_{LG} + A_C, \tag{19}$$

where A_{LG} is the lattice gas part

$$\frac{\beta A_{LG}}{N} = 2\rho \ln \rho + (1 - 2\rho) \ln (1 - 2\rho) \tag{20}$$

and A_C is the Coulomb part

$$\frac{\beta A_C}{N} = - \frac{1}{12\pi} f(x), \tag{21}$$

(as usually $\beta = 1/k_B T$).

We have obtained the desired free energy but equations (5), (6) and (13) give also the estimations of the correlation functions. Moreover, because $M(\alpha)$ is divergent for $\alpha \to \alpha_C$, we may express the boundary of the stable solution of equations (4), (5). Assuming $M(\alpha_C) \doteq 2.86$ together with (9) we obtain a stable region

$$x \leq 5.99. \tag{22}$$

For x greater than this value we come to the region of the condensation [16] to the new (ordered) phase. It is rather interesting that very similar values were obtained by Harder and Allnatt (1986) by the numerical solution of the problem in the hypernetted chain approximation. They have assumed that the AgCl system may precipitate into a perfect Suzuki phase [18] . Their estimates of the stability of the disordered phase were

$$x \leq 6.76.$$

for $T = 476\,K$ and

$$x \leq 5.35$$

for $T = 676\,K$, which is in a remarkable agreement with our result.

3. THE VAPOUT-LIQUID CRITICAL POINT

In this part we compare present results of the localization of the critical point with the estimations of Walker and Gillan [10] and also with the classical DH theory so as to see the differences.

The expression for the Coulomb part of the free energy is given by

$$\frac{\beta A_C^{(DH)}}{N} = - \frac{1}{8\pi} (x^2 - 2x + 2 \ln (x + 1)). \tag{23}$$

We shall try to obtain the critical point parameters by its localization on the pressure-density diagram. The pressure is simply

$$p = - \left(\frac{\partial A}{\partial N}\right)_\beta. \tag{24}$$

Both (21) and (23) together with (24) lead to the isotherms that exhibit the typical van der Waals at the sufficiently low temperature. The critical parameters are found by the solution

$$\left(\frac{\partial p}{\partial \rho}\right)_\beta = \left(\frac{\partial^2 p}{\partial \rho^2}\right)_\beta = 0. \tag{25}$$

The critical parameters in the dimensionless units ($T^* = \frac{a \cdot \epsilon \cdot k_B T}{e^2}$, $p^* = \frac{a \cdot \epsilon \cdot p}{e^2}$, $\mu^* = \frac{a \cdot \epsilon}{e^2} \mu$) are listed in the Table:

Theory	DH	WG	Present
ρ_C	0.002	0.009	0.017
T_C^*	0.062	0.095	0.104
$10^4 p_C^*$	0.27	1.62	2.87
μ_C^*	-1.25	-1.65	-1.73
x_C	0.99	1.56	2.03

The Table shows that the DH estimates are considerably lower when comparing with the other theories. It is also clear that the correction of the Pade´ term in the high x region leads to higher values of the critical parameters especially of the density and pressure. It is known that the Pade´ approximation of the series expansion of the RPM has led to the lower values of the critical parameters when comparing with the best estimates as was illustrated by Stell, Wu and Larsen /11/. So, we believe that the increase of the values of the critical parameters when comparing with the "pure" Pade´ extrapolation is correct also for the CLG.

4. DISCUSSION

In this paper we propose a solution of the CLG within the MSA. We have improved the accuracy of the expression for the free energy suggested by Walker and Gillan (1983), further we have obtained the estimations of the correlation functions and finally we have expressed the region of stable solution of the MSA equations. We have also find the vapour-liquid critical point with the critical parameters higher than was reported by Walker and Gillan what is, as we believe, the right tendency.

The critical behaviour of the CLG is in a clear controversy with the results of Kosterlitz /13/ and with very recent results of Kholodenko and Beyerlein /14/. The claiming of Kholodenko and Beyerlein is: "Our results indicate the absence of phase transition in d = 3 for a sufficiently diluted symmetric electrolyte in complete agreement with the results of Kosterlitz". It is clear that this claiming includes also the RPM model. However, as Kholodenko and Beyerlein have claimed, their renormalization group method and also the corresponding method of Kosterlitz are not valid for $\eta^3 > 1$, where η is denoted by them as a nonideality parameter which in our case reads

$$\eta = \frac{e^2 Z_i Z_j}{\epsilon k_B T a}; \qquad (26)$$

where Z_i, Z_j are valencies of the particles (so $Z_i = Z_j = 1$ in our case). However, it is clear that $\eta = T^{*-1} \cong 10$ at the critical point. From this point of view they are right: for $T^* > 1$ there is really no phase transition at the CLG at low densities. However, in the light of present and previous treatments of the CLG (and the RPM), their conclusion that there is no transition at all is not correct, as we believe.

We may try to apply our results to the real problem of the defects in the ionic crystal. Probably, the most convenient will be a CaF_2 which is a representative of the high temperature superionic systems which exhibit the diffusive phase transition (Hayes 1978). The effective role of the chemical potential in that system is played by the energy E_F required for the formation of the vacancy-interstitial Frenkel defect pair. For CaF_2 the ratio $E_F/k_B T_C$ (T_C is the temperature of the superionic transition) is estimated to be ≈ 20 /9/ .Our estimation $\mu_C^* - T_C^{*-1} = 16.6$ is in a qualitative agreement with this value. Our estimation of the critical temperature

$$T_C = T_C^* \frac{e^2}{\epsilon a k_B} \quad (\epsilon \cong 6.5, \ a = 0.28 \text{ nm}) \text{ is } \approx 950\,\text{K}, \text{ which}$$

is again qualitatively right when comparing with the experimental value ≈ 1420 K. The existing discrepancies are completely understandable from the point of view of neglecting all possible short range modifications of the interactions and other factors (many-particle interactions, etc).

Finally, we note that the effect of "condensation" for the thermodynamic region $x \gtrsim 6$, we breifly discussed in the second

part of the paper. The possible appearance of ordering will be a subject of future investigations.

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Миташ Л. E17-87-103

Кулоновский решеточный газ
в рамках среднесферического приближения

Приведено решение кулоновского решеточного газа (d-3) в среднесферическом приближении с использованием результатов Уолкера и Джиллена. Показано, что система происходит через критическую точку типа газ-жидкость при низких концентрациях, и приведены соответствующие критические параметры. Из решения можно дать оценку корреляционным функциям и области стабильных решений с точки зрения появления возможных эффектов упорядочения.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна 1987

Mita'š L. E17-87-103

The Coulomb Lattice Gas within
the Mean Spherical Approximation

The solution of the Coulomb lattice gas (d-3) in the mean spherical approximation by using the results of Walker and Gillan is proposed. It is shown that the system undergoes a vapour-liquid phase transition at low concentrations and the corresponding critical parameters are given. From the solution it is possible to obtain the estimation of the correlation functions and the region of stable solutions with respect so the possible ordering effects is estimated as well.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1987