The Coulomb gas partition sum is written in terms of the path integrals formalism. It is shown that perturbation theories based on the Mayer expansion and on the path integrals method lead to the identical results. The well known Debye-Hukkel result for the case of 3D Coulomb plasma is completely rederived. An analogous result is obtained for the case of the Coulomb gas with dipoles. This result can be considered as a generalization of the Debye-Hukkel approximation. Other possible generalizations including the range of interaction potentials for which the Debye-Hukkel approximation can be applied are discussed.

I. INTRODUCTION

The problem of calculating the Gibbs partition sum is well known since the pioneering works in classical satatistical mechanics. The simplest example of precise calculation of the Gibbs free energy is the classical ideal gas. The more general problem of classical statistical mechanics is the evaluation of partition sum for a nonideal system. The main difficulty is the calculation of the configuration integral

\[ Q = \int dr_1 \ldots dr_N e^{-\beta U(r_1 \ldots r_N)}. \]

This problem has no explicit solution. There are several approaches to analyse the thermodynamics of non-ideal systems with short range interactions: Mayer’s method, correlation function method, integral equation method, renormalization group method e.t.c. [1]
Some additional difficulties appear while analysing Coulomb-like systems because of the long range type of the interaction. Since the pioneering work of Debye, the standard solution of this problem is the Debye-Hukkel (DH) mean field approximation [1,2] where the Debye-Hukkel screened interaction appears instead of Coulomb one. This method is widely used in different fields of physics to analyze 3D plasma-like systems.

However, the extension of DH theory to the case of more complex systems is still a challenge to the statistical mechanics. On our opinion, the main reason for this is the absence of the consistent point of view on DH approximation. Really, a number of ways to obtain DH result are known. First of all this is the linearization of the mean field equations which is the simplest and well known way to obtain DH screening. Another way to obtain the DH result is a cycle approximation [1] applied to the Mayer’s diagrams. However, like other chain approximations in statistical mechanics, this method leaves open the question how to choose the relevant chain class. We will discuss another method based on the special property of the configuration integral and the analogy with multiple Gaussian integrals. [3]

Despite the fact that the first attempt to apply method discussed below to continuous systems was undertaken in 1959 [3], to our knowledge this approach has never been used as a regular method to analyse classical systems. At the same time some exotic relations between different correlation functions were obtained by using this approach (See for example [4]). The analogous method has been used to prove the equivalence of a 2D Coulomb gas model to the Euclidean Sine-Gordon model [5]. This equivalence was considered as a tool allowing to obtain some new results in quantum field theory from thermodynamics properties of the 2D Coulomb gas.

There exists some papers in statistical mechanics [1], where authors try to obtain some new results for Coulomb systems by using the Sine-Gordon analogy and the technique of the quantum field theory. But due to some difficulties some well known results for the 3D plasma were not completely rederived in these papers.

Some purely mathematical papers published in 80-th should be specially mentioned [1]. In these papers the 3D Coulomb system has been analysed on the base of its equivalence to
the 3D Sine-Gordon model. A strict mathematical theory was developed for this case. As it was shown, the Debye-Hukkel (DH) result can be easily reproduced in the lowest order of this approach. This is the simplest and the most consistent method to obtain the well known DH result.

In those papers, however, the emphasis was made on the mathematical problems, and it is difficult to see the physical sense of the transformations. Also there are no discussions on possible extension of this method to the case of more complex non-Coulombic systems. The present paper is an attempt to overcome some of these difficulties and to present the application of Gaussian integral method to continuous systems.

In the section II the basis of the Gaussian integral formalism applied to the models of classical statistical mechanics is described. Section III is dedicated to the perturbation theory, that is fully analogous to the usual quantum field theory’s one. The correspondence of this theory to the usual Mayer’s expansion in powers of the activity $z$ is analysed in detail. Some mathematical restrictions caused by the features of our method are also considered. As it is shown, these restrictions are strong enough. This explains, why the DH-like mean field theory can not be applied in the case of non-Coulomb systems.

In the section IV the expansion in powers of density is presented. It is shown that the lowest order of this expansion gives precisely the DH approximation. The exact reproduction of this well known result permits us to expect that the method used in this paper can lead us to some new results in the case of more complexes systems. One such example is given in section V. The results of the present paper are summarized in VI. Some advantages and defects of the method are reviewed in the conclusion.

II. GAUSSIAN FORMALISM FOR THE CONTINUUM CASE

Let us consider the functional:

$$\frac{1}{N} \int D\chi(r) \exp \left\{ -\frac{\beta}{2} \int \chi(r)drH(r-r')dr'\chi(r') + i\beta \int \rho(r)\chi(r)dr \right\} = I[\rho],$$

(1)
where:
\[
\mathcal{N} = \int D\chi(r) \exp \left\{ -\frac{\beta}{2} \int \chi(r) dr H(r - r') dr' \chi(r') \right\}
\]

– is a normalizing factor. \(H(r)\) is a kernel of some linear operator. \(D\chi(r)\) is a mesure on the space of real functions. In other words, in Eq.(1) we integrate over all pathes \(\chi(r)\) as one usually do in quantum field theory [8] and quantum mechanics.

Now we can introduce a function \(V(r)\) satisfying the condition:
\[
\int V(r - r') dr' H(r' - r'') = \delta(r - r'').
\]

This condition means that \(V\) is the inverse operator relative to \(H\). (Here and later in this paper we suppose \(H\) and \(V\) to be translationally invariant)

With the help of \(V(r - r')\) we can transform (1) to the form:
\[
\exp \left\{ -\beta/2 \int \rho(r) dr V(r - r') dr' \rho(r') \right\} = I[\rho(r)] = \int \frac{D\chi}{\mathcal{N}} \exp \left\{ \beta/2 \int \chi(r) dr H(r - r') dr' \chi(r') + i\beta \int \rho(r) \chi(r) dr \right\}.
\]

Later we shall examine the conditions under which the above transformation is valid.

The main aim of this section is to associate Eq.(3) with the statistical mechanics of a classical system. For this purpose we consider a system consisting of \(N = N_+ + N_-\) charged point-like particles. The microscopic charge density of the system can be written as:
\[
\rho_q(r) = \sum_{i=1}^{N_+} \delta(r - r_i) + \sum_{j=1}^{N_-} (-1) \delta(r - r_j).
\]

We also suppose that the interparticle interaction is central – \(s_i s_j V(r_{ij})\) (where \(s_i, s_j\) are the charges of particles), so that we get for the full energy:
\[
U(r_1 \ldots r_N) = \frac{1}{2} \sum_{i \neq j}^{N_+} V(r_i - r_j) + \frac{1}{2} \sum_{i \neq j}^{N_-} V(r_i - r_j) - \sum_{i=1}^{N_+} \sum_{j=1}^{N_-} V(r_i - r_j) = \int \rho_q(r) V(r - r') \rho_q(r') dr dr' - (N_+ + N_-) V(0)
\]
\[ -\frac{\beta}{2} \left( \sum_{i \neq j = 1}^{N_N} V(r_i - r_j) + \sum_{i \neq j = 1}^{N_N} V(r_i - r_j) - 2 \sum_{i=1}^{N_N} \sum_{j=1}^{N_N} V(r_i - r_j) \right) = e^{\frac{N\beta V(0)}{2}} \int \frac{D\chi}{N} e^{-\beta/2(\chi,H,\chi)} + i\beta(\rho_q \chi). \]  

(6)

Here we denoted for simplicity:

\[ \langle \chi, H, \chi \rangle = \int \chi(r) dr H(r - r') dr' \chi(r'), \]
\[ \langle \chi, \rho_q \rangle = \int \chi(r) \rho_q (r) dr. \]

Equation (6) will be the main for our later examinations in this paper. Applying analytical techniques of path integrals calculations to the Eq. (6), we hope to receive \textit{mathematically based} results for thermodynamics of the system in question. Talking about \textit{mathematically based results} we mean the results received directly from the basic physical formulas, using usual mathematical ideas \textit{without} additional physical supposition. Our purpose is to demonstrate the main way to obtain physical results, while the details of a mathematical consideration is the topic of interest for mathematicians.

Let us note the following:

\textbf{a}) Interparticle potentials \( V(r) \) ordinary contain sigularities at \( r \to 0 \). Moreover, there is a large and very important class of potentials weakly decreasing at \( r \to \infty \). (Coulomb potential in \( d = 2, 3 \) is the simplest example) Due to these effects divergences can appear in \( H(r) \) and its integrals. (See Eq. (6)) This may cause each component in the right hand side of Eq.(6) to be infinite. On this stage of consideration we shall ignore this fact by using for our purposes the most general notation. For mathematical completeness we can suppose all divergences caused by the form of \( V(r) \) to be somehow regularized. The regularization parameters should be taken equal to 0 at the final stage of calculations after taking the usual limit \( N \to \infty, \Omega \to \infty, \rho = \text{const} \). We suppose that the final result does not depend on the type of regularization.

\textbf{b}) Let us consider the range of the applicability of Eq. (6). Despite a seeming generality, this formula has some very important restrictions. To understand them we can write the discrete matrix analogue of Eq. (3):
\[
ed \left( \sum_{ij} \xi_i A^{-1}_{ij} \xi_j \right) = \int dx_1 \ldots dx_N e^{\sum_{ij} x_i A_{ij} x_j + i \sum_k \xi_k x_k} \div \int dx_1 \ldots dx_N e^{\sum_{ij} x_i A_{ij} x_j}. \tag{7}
\]

It is well known that this equation is correct only if \( ||A_{ij}|| \) is a positively definite form. Otherwise integrals in the numerator and the denominator of Eq. (7) are diverging. Therefore Eq. (7) is correct only for positively definite operators \( H(r - r') \). Due to the translational invariance of \( H \), we can write this condition with the help of Fourier transforms as:

\[
\hat{H}(q) = \int dxe^{iqr} H(r) > 0; \\
\hat{V}(q) = \frac{1}{\hat{H}(q)} > 0. \tag{8}
\]

We suppose here that the interparticle interaction \( V(r - r') = V(|r - r'|) \) is central, so that \( \hat{V}(q) = \hat{V}(-q) = \hat{V}^\ast(q) \).

Coulomb potential is the simplest example satisfying (8):

\[
\hat{V}(q) = \frac{e^2}{q^2}, \quad d = 2, 3; \tag{9}
\]

Yukav (screened Coulomb) potential is the second example:

\[
\hat{V}(q) = \frac{e^2}{q^2 + \lambda^2}, \quad d = 2, 3; \tag{10}
\]

Another (slightly exotic) example is the intervortex interaction in a thin superconducting film [9]:

\[
\hat{V}(q) = \frac{\phi_0^2}{2\pi\Lambda} \frac{1}{q(q + 1/\Lambda)}, \quad d = 2 \tag{11}
\]

Here \( \phi_0 = \hbar c/2e \) is the flux quantum, \( \Lambda \) is a penetration depth in two dimensions. Statistical mechanics of vortices interacting via this potential is analysed in [10, 12].

c) One should pay the attention to the factor \( e^{N\beta V(0)} \) in Eq. (3). As far as we know, the most authors [3, 4, 6] ignore this factor. To exclude it the potential

\[
\tilde{V}(r) = \begin{cases} 
1/r, & r > \sigma \\
0, & r < \sigma
\end{cases} \tag{12}
\]
was used by Edwards [3] instead of Coulomb potential \((d = 3)\). It is easy to show that Fourier transform of Eq. (12) is not positively definite, so that the correctness of (6) is doubtful.

The most strict method is proposed in mathematical papers (see for example [7]), where the interaction:

\[
V_R(r) = \frac{1}{r} - \varepsilon \frac{e^{-r/\varepsilon}}{r}
\]

(13)
is used, instead of Coulomb potential. The final result should be received after taking the limit \(\varepsilon \to 0\). This provides \(V(q)\) to be positive, and \(V(r)\) equal to zero as \(r \to 0\), so that our factor \(\sim e^{V_r(0)}\) is equal to 1.

It is easy to see that Eq. (13) is no more than one of different ways to regularize \(V(r)\). We can consider a more general method to smooth singularities in \(V(r)\):

\[
V_R(r_1 - r_2) = \int dr' dr'' n(r_1 - r') V(r' - r'') n(r'' - r_2),
\]

with \(V_R(0) \neq 0\), so that the factor \(e^{N\beta V(0)/2}\) cannot be omitted. We shall see later that this coefficient is very important in the mean field and perturbation theories, based on Eq. (3).

### III. DIAGRAMMATIC EXPANSIONS

To apply the Gauss-analogy (3) to the problems of statistical mechanics let us consider a system consisting of ”positively and negatively charged” particles, having absolute activities \(z_+\) and \(z_-\). The term ”charged particles” is employed here in unusual sense: The interparticle interaction may be not Coulomb, but it depends on some special charge-like characteristics of particles. For example the interaction between two vortices in a supercondoctor depends on mutual direction of their magnetic fields.

The grand partition function for such a ”plasma” at a temperature \(1/\beta\) can be written as:

\[
\zeta = \sum_{N_+,N_-=0}^{\infty} \frac{z_+^{N_+} z_-^{N_-}}{N_+! N_-!} \int \{dr^{(+)}\}^{N_+} \{dr^{(-)}\}^{N_-} \exp \left\{ \frac{\beta}{2} \sum_{i \neq j} s_i s_j V(r_{ij}) \right\}. \tag{14}\]
Using Eq. (3) (or Eq. (6)) we can rewrite the above equation:

\[ \zeta = \sum_{N_+, N_-}^{\infty} \frac{z_+^{N_+} z_-^{N_-}}{N_+! N_-!} \int \{dr^{(+)}\}_{N_+} \{dr^{(-)}\}_{N_-} e^{\beta N V(0)/2} \int \frac{D\chi}{N} e^{-\beta/2 (\chi, H, \chi)} e^{i\beta \int \rho_q(r) \chi(r) dr} \]  

(15)

We will suppose our system to be "neutral", so that \( z_+ = z_- = z \). Keeping in mind Eq. (4) we get:

\[ \zeta = \int \frac{D\chi}{N} \exp \left( -\beta/2 (\chi, H, \chi) + 2\bar{z} \int \cos \beta \chi(r) dr \right), \]  

(16)

where \( \bar{z} = ze^{\beta V(0)/2} \). For the case of Coulomb gas, where \( V(q) \sim \frac{1}{q^2} \), and \( H(r - r') \sim \delta(r - r') \nabla^2 \) the equation (14) becomes similar to the Euclidean Sine-Gordon theory. This equivalence is a well known fact for more than two decades [5, 4]. To calculate approximately \( \zeta \) we can use a perturbation theory in the spirit of quantum field theory [8]. For this purpose we need to consider again:

\[ Z[J] = \int \frac{D\chi}{N} e^{-\beta/2 (\chi, H, \chi)} e^{\int J \chi dr} = \exp \left( \frac{1}{2\beta} \int J(r) V(r - r') J(r') dr dr' \right), \]  

(17)

and to define:

\[ < f(\chi(r)) >_H = \int \frac{D\chi}{N} f(\chi(r)) e^{-\beta/2 (\chi, H, \chi)} \cdot f(\frac{\delta}{\delta J(r)}) Z[J] \bigg|_{J=0}. \]  

(18)

In this case we obtain for \( \zeta \):

\[ \zeta = \left\langle \exp \left( 2\bar{z} \int \cos \beta \chi(r) dr \right) \right\rangle_H = \sum_{n=1}^{\infty} \frac{1}{n!} \left[ 2\bar{z} \int \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k)!} \left( \frac{\beta}{\delta J(r)} \right)^{2k} dr \right]^n Z[J] \bigg|_{J=0}. \]  

(19)

Following methods widely used in quantum field theory, we represent each term of the sum in (19) as a diagram with \( n \) vertex connected by \( k \) lines. It is easy to show that an even number of lines are closed in each vertex. Each vertex \( (i) \) contributes an integration over \( dr_i \), the factor \(-\beta V(r_{ij})\) corresponds to each line connecting vertices \( i \) and \( j \).

Quantum field theorists know that \( \zeta \) (Eq. (19)) is infinite in the limit \( \Omega \to \infty \). The infiniteness of \( \zeta \) (Eq. (14)) is also known from statistical physics. To our good both cases need only the value of \( \ln \zeta/\Omega \). This permits us to exclude all disconnected diagrams, like one usually acts in quantum field theory.
Now it's time to examine diagrams, containing tadpoles. Tadpole is a line \(-\beta V(r_{ui})\) which begins and ends at the same vertex, so that the resulting multiplying factor is proportional to \(V(0)\). The term ”tadpole” is well known by field theorists, but is used very seldom in classical statistical mechanics.

Let us consider a vertex with \(l\) tadpoles and \(j\) non-tadpoles lines outgoing from it (external lines with respect to vertex). The combinatorial prefactor in the integral, corresponding to the diagram with such a tadpole is:

\[
\frac{(2k)!}{l!j!2^k},
\]

where \(2k = 2l + j\) is a full number of lines outgoing from the vertex. (note that \(j\) must be even)

Summing by a number of tadpoles \(l\) of the vertex with fixed number \(j\) of external lines, we can prove, that all tadpoles of the vertex can be absorbed into a factor \(e^{-\beta V(0)}\) bound to this vertex. This is equivalent to the renormalization of \(\tilde{z}\) to its original value:

\[
\tilde{z} = e^{\beta V(0)/2} z \mapsto e^{-\beta V(0)/2} \tilde{z} = z.
\]

Now the role of the factor \(e^{N\beta V(0)}\) in Eq. (6) becomes clear. The existence of this factor enables us to compensate the singular contributions of tadpoles in diagrams. To compensate these tadpoles in quantum field theory the normal ordering of the initial Gamiltonian is usually used (see for example [11]). In the case of statistical mechanics we have no base neither to use normal ordering, nor to suppose our initial parameters to be infinite, so that the singular factor appearing in Eq. (6) is the only mathematically correct way to avoid singularities bound with tadpoles.

At the same time it is important to note that such a re-renormalization (20) takes place
only if we consider the full interaction \( \cos \beta \varphi. \)

In the case of substitution:

\[
\cos \beta \varphi = 1 - \frac{(\beta \varphi)^2}{2} + \frac{(\beta \varphi)^4}{4!},
\]

the maximum number of lines in the vertex becomes equal to 4, and the maximum number of tadpoles is limited, so that the factor \( e^{\beta V(0)} \) can not be fully compensated by them.

After the discussion of tadpole-compensating it is not difficult to show by analogy, that summing of multiple lines, connecting two vertexes allows us to change each set of diagrams with multiple lines by one diagram with ”bold” line, where bold lines are associated with Mayer’s function \( f_{ij} = e^{-\beta V(r_{ij})} - 1. \) Here we shall not concentrate on the proof of this fact.

The analogous result is described in [1].

The main conclusion from the above consideration is that the perturbation theory derived from the path integral representation of the Grand partition sum (see Eq. (16)) – path integral perturbation theory, is equivalent to the Mayer’s series derived directly from Eq. (14), and can be written through the same parameters: \( z, f_{ij}. \)

At the same time, despite the similarity of these two evaluation, there are a difference between them: really, Mayer’s diagrammatic expansion of (14) contains two kind of vertices, corresponding to both (positive and negative) kinds of particles. Factors \( z_+ \) and \( z_- \) correspond to these vertices. Each pair of vertices can be connected by two kind of lines, depending on their multiple charges: \( e^{-\beta V_+} \) and \( e^{-\beta V_{\pm}} \). To understand why \( f_{+\pm} \)-type lines do not appear in the path integral perturbation theory, we can expand Mayer’s function \( f_{ij} = e^{-\beta V_{ij}} - 1, \) in powers of \( V_{ij}. \) The difference between \( f_{++} \) and \( f_{+-} \) will be seen only in diagrams, containing one or more vertices with even number of lines (even vertices). For each diagram containing even vertex we can find another graph, differ only in a ”sign” of this even vertex. Due to the neutrality of our system (\( z_+ = z_- \) – see above) these diagrams will compensate with each other, giving no contribution to the final free energy. Thus we

\[^1\text{Here the quantum field theory terminology is used: } (\chi, H, \chi) \text{ is a Hamiltonian’s kinetic term, while } (\cos(\beta \varphi)) \text{ is the interaction.}\]
have shown that for Mayer’s development of the grand partition sum, after representation of $f_{ij}$ as series (see for example [1]) diagrams with even vertices do not contribute to a final result. Summing the rest of diagrams we get the result identical to the one obtained from the path integral perturbation theory.

In this section we have shown schematically the similarity and moreover, the equivalence of both perturbation theories. This result gives us no new methods to calculate thermodynamic properties of the system, but is important for understanding different approximations obtained from Eq. (16) or directly from Eq. (14). This is not a purpose of this section to perform a full consideration of different perturbation theories connected with Mayer’s series. Here we consider only those results that can by obtained from the path integral representation of the partition sum.

IV. THE EXPANSION IN POWERS OF DENSITY

To obtain the expansion in powers of density, it is convenient to consider the partition sum instead of the grand partition sum, used in the previous section. For the system of two sorts of particles with densities $\rho_+$ and $\rho_-$ the partition sum can be written as:

$$Z = \frac{\lambda_+^{N_+}}{N_+!} \frac{\lambda_-^{N_-}}{N_-!} \int \{dr\} \exp \left\{ -\frac{\beta}{2} \sum_{ij} V_{ij}(r_{ij}) \right\}. \tag{21}$$

Here $\{dr\}$ denote the integration over all $N_+ + N_-$ particle positions in $d$-dimensions, $\lambda = \left( \frac{k_B T m}{2 \pi \hbar} \right)^{1/2}$ is a Boltzmann wavelength. We obtain the free energy $F$:

$$-\beta F = \ln Z = N_+ \left[ \ln \left( \frac{\lambda_+}{\rho_+} \right) + 1 \right] + N_- \left[ \ln \left( \frac{\lambda_-}{\rho_-} \right) + 1 \right] + \ln Q,$$

where $\ln Q$ is the nonideal part of the free energy:

$$\ln Q(N_+, N_-, \beta, \Omega) = \ln \int \frac{dr_1}{\Omega} \cdots \frac{dr_N}{\Omega} e^{-\beta U}, \tag{22}$$

$\Omega$ is the $d$-dimensional volume of the system.

Now we rewrite $\exp(-\beta U)$ using Eq. (3):
\[ Q = \exp\left(\frac{N\beta}{2} V(0) \right) \int \frac{D\chi}{N} \exp\{-\beta/2(\chi, H\chi)\} e^{S_1}, \]  

(23)

\[ S_1 = N_+ \ln \int \frac{dr_+}{\Omega} e^{i\chi(r_+)} + N_- \ln \int \frac{dr_-}{\Omega} e^{-i\chi(r_-)} \]

To calculate the path integral \( D\chi \) we need to diagonalize the quadratic form in the exponent of Eqs. (23),(25). For this purpose it is convenient to use Fourier transform as a change of variables in path integrals [14]

\[ \chi(r) = \int \frac{dq}{(2\pi)^d} \hat{\chi}_q e^{-iqr}, \quad \hat{\chi}_q = \int dr \chi(r) e^{iqr}. \]  

(24)

\( \chi(r) \) is real function, its Fourier transform satisfies the requirements \( \hat{\chi}_q^* = \hat{\chi}_{-q} \).

For our further consideration we suppose \( \chi \) to oscillate around \( \chi \equiv 0 \), so that \( S_1 \) can be expanded just to the second order in \( \chi \). In the case of neutrality \( (\rho_+ = \rho_-) \) we get:

\[ S_1 = \frac{\rho_+ + \rho_-}{\Omega} |\hat{\chi}_0|^2 - \frac{\rho_+ + \rho_-}{2} \int \frac{dq}{(2\pi)^d} |\hat{\chi}_q|^2. \]  

(25)

Path integration over \( D\chi(r) \) should be replaced by:

\[ D\hat{\chi}_q \equiv d\hat{\chi}_0 \prod_{q>0} d\text{Re}\hat{\chi}_q d\text{Im}\hat{\chi}_q, \]

where \( q > 0 \) denotes the production through a "half"-space of \( q \). Here it is important to remind the mathematical definition of the path integral as a limit of multiple integral over function values on the discret set of points. Keeping in mind the simmetry of \( V(r) \) and \( H(r) \) we can write:

\[ \int \chi(r) dr H(r - r') dr' \chi(r') = \int \frac{dq}{(2\pi)^d} |\chi_q|^2 \hat{H}(q). \]  

(26)

In this case for the exponent in Eq.(25) we get:

\[ -\beta/2 \sum_{q>0} \frac{2}{\Omega} (\xi_q^2 + \tilde{\xi}_q^2) \hat{H}(q) - \beta^2 \frac{\rho_+ + \rho_-}{2} \sum_{q>0} \frac{2}{\Omega} (\xi_q^2 + \tilde{\xi}_q^2) - \beta/2 \frac{1}{\Omega} \hat{H}(0) \hat{\chi}_0^2. \]  

(27)

Here we use the summation instead of the integration over \( q \)-space following the rule:

\[ \int \frac{dq}{(2\pi)^d} = \frac{1}{\Omega} \sum_q. \]
The notation $\sum_{q>0}$ means a summation over "half"-space $D$ of the $q$-space, so that for each $q$ in $D$, $-q$ is not in $D$. Considering this sum we specially marked a point $q = 0$. We also introduced for convenience:

$$\xi_q = \text{Re}\chi_q \equiv \text{Re}\chi_{-q}; \quad \tilde{\xi}_q = \text{Im}\chi_q \equiv -\text{Im}\chi_{-q}; \quad \chi_0 = \chi_0^*.$$  \hspace{1cm} (28)

Now we can represent the configuration integral $Q$ using the above formulas:

$$Q = \exp \left( \frac{N\beta}{2} V(0) \right) \frac{1}{N} \int \prod_{q>0} d\xi_q d\tilde{\xi}_q d\chi_0 \times$$
$$\times \exp \left[ \frac{1}{\Omega} \sum_{q>0} \left( \beta \hat{H}(q) - \beta^2 (\rho_+ + \rho_-) \right) (\xi_q^2 + \tilde{\xi}_q^2) - \left( \frac{\beta}{2\Omega} \hat{H}(0) \chi_0^2 \right) \right].$$  \hspace{1cm} (29)

Analogously, the normalizing factor $N$ can be written as:

$$N = \int \prod_{q>0} d\xi_q d\tilde{\xi}_q d\chi_0 \times$$
$$\times \exp \left[ \frac{1}{\Omega} \sum_{q>0} \left( \beta \hat{H}(q) (\xi_q^2 + \tilde{\xi}_q^2) \right) - \frac{\beta}{2\Omega} \hat{H}(0) \right].$$  \hspace{1cm} (30)

After simple calculations, we obtain for $\ln Q$:

$$\ln Q = \frac{N\beta}{2} V(0) + \sum_{q>0} \ln \frac{\beta \hat{H}(q)}{\beta \hat{H}(q) + \beta^2 (\rho_+ + \rho_-)}.$$  \hspace{1cm} (31)

At the final stage the sums should be replaced back by the integrals:

$$\ln Q = -\frac{\Omega}{2} \int \frac{dq}{(2\pi)^d} \ln (1 + \beta (\rho_+ + \rho_-) \hat{V}(q)) + \frac{(\rho_+ + \rho_-)\beta\Omega}{2} \int \frac{dq}{(2\pi)^d} \hat{V}(q).$$  \hspace{1cm} (32)

The last term in Eq. (32) reflects the fact that:

$$V(0) = \int \frac{dq}{(2\pi)^d} \hat{V}(q).$$

Finally, for the nonideal part of the free energy we obtain:

$$\frac{\beta \Delta F}{\Omega} = \frac{1}{2} \int \frac{dq}{(2\pi)^d} \left\{ \ln (1 + \beta (\rho_+ + \rho_-) \hat{V}(q)) - \beta (\rho_+ + \rho_-) \hat{V}(q) \right\}. $$  \hspace{1cm} (33)

For the case of the neutral 3D plasma (9), this equation is known as a Debye-Hukkel approximation [1] for the free energy. The way, presented above ia a new method to obtain the well known result directly from the Gibbs partition sum without special physical suppositions.
The fact that Eq.(33) is identical to the result of the summation of cycles diagrams can be simply explained. Really, the expansion of $S_1$ in (23) just to the second order of $\chi$ corresponds to the retaining for later summation only those diagrams which have no more than two lines in each vertex. The vertices without lines appears in disconnected diagrams only, graphs with one line vertexes compensate themselves if the system is neutral. The only diagrams leaving for the summation are cycles, and their summation leads to Eq. (33).

At the same time, the path integral method described above explains us, why the result (33) cannot be applied to the non-Coulomb like systems. For the Van-der-Vaals interparticle interaction $V(r)$, the Fourier transform $V_q$ is usually not positively defined (see section I). Due to this fact we cannot apply all the above considerations to the non-Coulomb-like systems. To obtain the analogue of Eq. (33) in a general case, we need to invent the analogue of the Gauss representation (7) with a sign-alternating quadratic form $A_{ij}$ and to extend it to the continuous case. The aim of this paper is not to realize this plan, but to show some features of the path integral method in statistical mechanics, and to obtain some new results for the simple case of Coulomb gas.

V. SYSTEM WITH DIPOLAR PAIRS

The interesting chance appears while using the path integral representation of the Gibbs partition sum: we can include clusters of particles in our consideration. For simplicity let us consider a system, consisting of $N_+^F$ positively charged and $N_-^F$ negatively charged particles. A part of these particles is organized in clusters of known form. The intercluster interaction and their self energy can be calculated by summing "each with each" interparticles interactions. This fact can be easily used to include clusters of particles in Eq.(6).

As a simple example we consider a system of $N_+ + N_-$ positive and negative free particles. We will suppose also that there are $N_D$ dipoles. Here a dipole is considered as a pair of particles $(+, -)$ with distance between them to be fixed and equal to $a$. Such a dipol has $2d - 1$ degrees of freedom. We can write the microscopic charge density $\rho_q$ of the system as:
\[ \rho_q = \sum_{i=1}^{N_+} \delta(r - r_+^i) - \sum_{j=1}^{N_-} \delta(r - r_-^j) + \sum_{k=1}^{N_D} (\delta(r - r_D^+ - r_D^-)) \],

where \( r_+ \) and \( r_- \) are positions of the free particles and \( r_D^\pm = r^D \pm a/2 \) are positions of positive and negative charges of the dipole.

Gibbs partition sum for the system is:
\[ Z_3 = \frac{z^{N_+} z^{N_-} z^{N_D} D}{N_! N_-! N_D!} \Omega^{N_+ + N_- + N_D} \int \left\{ \frac{dr^+}{\Omega} \right\}_{N_+} \left\{ \frac{dr^-}{\Omega} \right\}_{N_-} \left\{ \frac{dr_D \, d\omega}{\Omega \, \omega_0} \right\}_{N_D} \exp \{-\beta U\}. \quad (35) \]

Here \( z_\pm \) are activities of free particles and \( z_D \) — activity of dipoles. We integrate in (35) over positions of all free particles \( (dr^\pm) \), and over positions of dipol’s centers \( (dr^D) \). In addition in Eq. (35) the integration over all orientations of dipoles \( (d\omega/\omega_0) \) where \( \omega_0 \) is a normalizing factor is performed. For the case \( d = 2 \) we have \( d\omega/\omega_0 = 2\pi, \) for \( d = 3 \) \( d\omega/\omega_0 = \sin \theta \theta_0/4\pi. \)

Taking into account the ”each-with-each” interaction of particles, we write for \( U \):
\[ U = \sum_{i \neq j}^{N_+ + N_- + 2N_D} s_i s_j V(r_{ij}), \]

so that \( U \) includes not only ions-dipoles and dipoles-dipoles interactions, but interaction of particles inside the dipoles. This fact is important when we define the activity of the dipoles.

Due to Eq. (3) we represent \( Z_3 \) through the path integral:
\[ Z_3 = \exp \left\{ \frac{N \beta V(0)}{2} \right\} \int \frac{D\chi}{N} \exp(-\beta/2(\chi, H\chi) + S_2) \frac{z^{N_-} z^{N_D} D}{N_-! N_D!} \Omega^{N}. \quad (37) \]

Where \( N = N_+ + N_- + 2N_D \), and
\[ S_2 = N_+ \ln \int \frac{dr}{\Omega} e^{i\beta \chi(r)} + N_- \ln \int \frac{dr}{\Omega} e^{-i\beta \chi(r)} + N_D \ln \int \frac{dr \, d\omega}{\Omega \, \omega_0} e^{i\beta(\chi(r_D + a/2) - \chi(r_D - a/2))} \quad (38) \]

Now we expand \( S_2 \) just to the second order of \( \chi \), as done in section [IV]. For convinience we use the Fourier transform of \( \chi(r) \). Using:
\[ \chi(r_D + a/2) - \chi(r_D - a/2) = -2i \int \frac{dq}{(2\pi)^d} \tilde{\chi}(q) e^{-iqr_D} \sin(qa/2), \]

\[ ^2\text{Here we consider dipoles as the third kind of particles} \]
we get for $S_2$:

$$S_2 \approx \frac{\rho_+ + \rho_-}{2} \left[ \hat{\chi}^2 \beta^2 \frac{\Omega}{\hat{\chi}^2} - \beta^2 \int \frac{dq}{(2\pi)^d} |\hat{\chi}|^2 \right] - 2 \rho_D \beta^2 \int \frac{dq}{(2\pi)^d} |\hat{\chi}|^2 \Gamma(q),$$  \quad (39)

where a function:

$$\Gamma(q) = \int \frac{d\omega}{\omega_0} \sin^2 \left( \frac{qa}{2} \right)$$  \quad (40)

is used. In Eq. (40) the integration is over all directions $\omega$ of vector $a$.

Using the same notations as in section IV we can perform the same sequence of calculations and for the exponent (similar to Eq. (27)) we can write:

$$- \frac{\beta}{2} \sum_{q>0} \frac{2}{\Omega} \left( \xi_q^2 + \tilde{\xi}_q^2 \right) \hat{H}(q) - \beta^2 \frac{\rho_+ + \rho_-}{2} \sum_{q>0} \frac{2}{\Omega} \left( \xi_q^2 + \tilde{\xi}_q^2 \right) - 4 \beta^2 \rho_D \frac{1}{\Omega} \sum_{q>0} \left( \xi_q^2 + \tilde{\xi}_q^2 \right) \Gamma(q) -$$

$$\frac{\beta}{2} \hat{H}(0) \hat{\chi}^2_0 - 2 \beta^2 \rho_D \frac{1}{\Omega} \Gamma(0) \hat{\chi}^2_0.$$  \quad (41)

The configuration integral can be written as:

$$Q = \exp \left( \frac{N\beta}{2} V(0) \right) \frac{1}{\mathcal{N}} \prod_{q>0} d\xi_q d\tilde{\xi}_q d\hat{\chi}_0 \exp \left\{ \frac{1}{\Omega} \sum_{q>0} \left[ - \beta H_q - \beta^2 (\rho_+ + \rho_-) - 4 \beta^2 \rho_D \Gamma(q) \left( \xi_q^2 + \tilde{\xi}_q^2 \right) + \chi_0^2 \left( - \frac{\beta}{2\Omega} H(0) - \frac{2\beta^2 \rho_D \Gamma(0)}{\Omega} \right) \right] \right\}.$$  \quad (42)

Here $\mathcal{N}$ is the same normalizing factor as in section II. Finally we obtain for $\ln Q$:

$$- \beta F_d = \ln Q = - \frac{1}{2} \ln \left( 1 + 4 \beta \rho_D \Gamma(0) V(0) \right) -$$

$$\Omega \frac{1}{2} \int \frac{dq}{(2\pi)^d} \left\{ \ln \left( 1 + \beta (\rho_+ + \rho_-) V_q + 4 \beta \rho_D \Gamma(q) \right) - (\rho_+ + \rho_- + 2 \rho_D) \Omega V_q / 2 \right\},$$

where the first term can be neglected as it remains finite in the limit $\Omega \to \infty$.

Now we can review additional suppositions introduced in this section while obtaining Eq. (43). The only special supposition in comparison with section IV is the definition of dipoles and their including in the partition sum (35). Other derivations, mathematically are fully equivalent to ones made in section IV. Moreover, it is obvious that in the limit $\rho_D \to 0$ Eq. (43) reduces to the nonideal part of the free energy of pure two-components.
plasma Eq.(33). This fact makes us to hope that the result (43) can be considered as a
generalization of the Debye-Hukkel result for a two component plasma with dipoles.

The including of dipole pairs is not the only way to get some new analytical results using
the path integral formulation in statistical mechanics. For example to describe a hexatic
phase it may be useful to introduce hexagonal clusters, so that the charge density becomes:

$$\rho(r) = \sum_{i=1}^{N_x} \delta(r - r_i^+) - \sum_{j=1}^{N_x} \delta(r - r_j^-) + \sum_{k=1}^{N_H} \rho_{ah}(r - r_k),$$  \hspace{1cm} (44)

Where $\rho_{ah}$ – is a local charge density of the hexagonal cluster of size $a$:

$$\rho_{ah}(r - r_k) = s_0 \delta(r - r_k) + \sum_{n=1}^{6} s_n \delta(r - r_k + a_n).$$

$(s_i)$ are charges of particles of clusters considered.

In this case we shall get a function $\Gamma(q)$ that is different from Eq.(40). This function will
be closely related to the symmetric properties of clusters.

Analogously we can introduce a partition sum including many different types of clusters.
The resulting free energy can be considered as a function of their densities. We may hope
to obtain the physical properties of our system by minimizing this free energy. For example,
the free energy $F_d$ (Eq. (33)) can be considered as a function of free particles ($\rho_+ \sim \rho_-$) and
dipoles ($\rho_D$) densities. If the minimum of such an energy is placed in the region ($\rho_D \gg \rho_+$),
we can conclude that under these conditions free particles couple into dipole pairs.

VI. CONCLUSION

In the present paper a new point of view on the classical Gibbs partition sum is pre-
sented. This method is based on the representation of the configuration integral through the
Gaussian path integration. Obtained results precisely reproduce the Debye-Hukkel result
for the symmetric 3D Coulomb plasma. As it is shown, this method and its extensions
can be applied to the case of Coulomb and quasi-Coulomb systems. Presented method is
applied to the very interesting case of symmetric Coulomb plasma with dipoles [15] and the
generalization of DH result was obtained.
Presented point of view on the statistical mechanics has some advantages and defects. The main defect of this point of view is a formality of computations. Really, all transformations presented above are simple extensions of the well known techniques of multiple Gaussian integrals computation. By the way we were forced to omit the analysis of some questions concerning the divergence of intermediate results.

Talking about the advantages of the described method, it should be mentioned that we got a method allowing us to find the range of the applicability of the DH result (see section II). Also we can see possibles systematic ways to obtain higher order correction to the known results. For example it is obvious that the next order of the DH result is the well known corrections to the Gaussian approximations of the integral: techniques of calculation of these corrections is well developped, and we can try to generalize it to the continuum case. Analogously, we can extend DH (or DH-like) result for the case of more complex systems with Coulomb interparticle interaction, as is done in sec. V.

Method presented in this paper should be extended and analyzed from differents points of view: First of all it should be interesting to obtain numerical results using new formulas derived above and to compare these calculations with others approximations. We hope to get new results by applying the path integral representation to Coulomb systems with differents types of clusters, as it is done with dipols in section V. As it was pointed above, the generalization of the Gaussian path integration to the case of non positively defined Fourier transforms is needed to widely test the presented method. Another topic of interest is the connection of the path integral representation with the renormgroup approach and critical phenomena. There is a good chance that the presented non-trivial representation of the Gibbs partition sum can give us new approaches and methods to physics of critical phenomena.
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