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ON THE FREE-ENERGY EXPANSION OF A CLASSICAL COULOMB GAS. I: THE NODAL-RING TERM

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ABSTRACT: The nodal expansion for the free-energy of a classical Coulomb gas, introduced by Abe, Friedman and Meeron, is used to produce results which are hopefully meaningful for intermediate values of the plasma parameter. The results show no divergences and the calculation of the free energy is reduced to a quadrature The connection of this result to the nodal expansion of the pair distribution function is shown explicitly.

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INTRODUCTION

On this paper we consider a classical system of charged point particles in equilibrium, embedded in a fixed uniform background of the opposite charge. According to the basic work of Abe[2], Friedman[3] and Meeron[4], the Helmholtz free energy of the system may be expanded in a series

$$\beta(F-F_0) = -N\left[S_{\text{ring}} + \sum_{j=2}^{\infty} S_j(\Lambda)\right]; \tag{1}$$

where the functions S_j depend on the plasma parameter

$$\Lambda = \beta e^2/\lambda_D \tag{2}$$

and $\lambda_D = (4\pi\beta e^2\rho)^{-1/2}$ is the Debye-Hückel screening length. $S_2(\Lambda)$ was calculated[2-4] as the first correction to the classical Debye-Hückel result, represented in Eq. (1) by S_{ring}. The leading terms of S_3 in a low-coupling expansion, i.e. $\Lambda \ll 1$, are presented in another paper[1], where the terms of S_4 and S_5 are calculated analytically by means of a simple approximation. That approximation amounts to the substitution of the Debye screened potential

$$w_1 \equiv -\beta U_s(x) = -\frac{\Lambda}{x} e^{-x} \quad , \tag{3}$$

where $x = r/\lambda_D$, by a hard-sphere potential in the function

$$W_1 = \exp\left[-\beta U_s\right] - 1 \; .$$

As the function S_j can be written in terms of W_1 and w_1 only, the approximation for W_1 allows the calculation of the terms in a complicated but straightforward manner. Furthermore, it is shown there that starting with S_2, there are terms that diverge if one attempts an expansion in powers of Λ. In this paper we will show how the divergences can be removed by a partial summation involving terms from all S_j; this is done in section I. In section II we will establish the connection between such a summation and similar devices used in the expansion of the correlation function in the theory of dense fluids.

I. NODAL-RING SUMMATION

We now describe how to add up certain classes of free-energy diagrams to produce a result that is the natural extension of the Debye-Hückel S_{ring} term. The details are fully developed in the original articles of Abe, Friedman and Meeron [2-4], here we just give a short description of their results. Nevertheless, in those references the nodal-ring summation is not carried out explicitly, which is one of the purposes of this work. All the diagrams corresponding to the terms in the free-energy expansion can be expreesed by means of the Debye w_1 bond, eq. (3), and the bond

$$W_2 = \exp\left[-\beta U_s\right] - 1 + \beta U_s \; ; \tag{4}$$

We will call w_1 a "chain", and W_2 a "bubble".

Thus, we can look, among all the terms of eq. (1), for all those diagrams that are formed by any number of w_1 and W_2 bonds arranged in a ring. The vertices of such a ring have to be nodes, i.e., a vertix cannot be joined to others by just two w_1 bonds, see Fig. (1). We will call those diagrams "nodal rings". If a given nodal ring is identified by the numbers c of Debye bonds and b of W_2 bonds, its contribution to the free energy is

$$S_{b,c} = -\frac{1}{j!\,\Lambda^{j-1}} \int \frac{d^3x_i}{4\pi} \cdots \frac{d^3x_{j-1}}{4\pi}\, w_1(x_1)\, w_1(x_2 - x_1) \cdots$$

$$w_1(x_c - x_{c-1})\, W_2(x_b - x_c) \cdots W_2(x_{j-1}) \; ; \tag{5}$$

Introducing in eq. (5) the Fourier transforms $\tilde{w}$ and $\tilde{W}$ of $w_1(X)$ and $W_2(X)$, the convolution theorem allows to write simply

$$\beta F_{b,c} = -\frac{1}{j!} \int \frac{\Omega\, d^3k}{(2\pi)^3} \left[N\tilde{w}(k)\right]^c \left[N\tilde{W}\right]^b \tag{6}$$

where the number of nodes is $j = b + c$; $\Omega = V/\lambda_D^3$ and N is the number of particles in the system.

Now we must find the multiplicity of a diagram, i.e., the number of different diagrams that have b W_2's and c w_1's. The multiplicity of a nodal

ring is the number of ways j nodes can be arranged in the ring, $1/2(j-1)!$, times the number of ways c chains can be put in between b W_2's, so that no chains are consecutive. To obtain the latter we realize that the first bubble may be on any of j places, then the first chain has $b-1$ places to fit, the second has $b-2$, and so on. But the final result must be independent of the order in which the chains and bubbles are arranged. Thus the multiplicity is

$$\frac{j(j-1)!(b-1)!}{2(b-c)!\,c!}$$

Now we can add up the contributions from all nodal rings. We get, from Eq. (6),

$$\beta F_1 = -\frac{1}{2}\int \frac{\Omega d^3k}{(2\pi)^3} \sum_{b,c} \frac{(b-1)!}{(b-c)!\,c!} (N\tilde{w})^c (N\tilde{W})^b . \qquad (7)$$

We still have to choose properly the limits of the double summation in Eq. (7). For $b > 3$ the allowed values of c range from 0 to b; but if $b = 2$ then c can only be 1 and 2, corresponding to the diagrams in Fig. (1b). Using these limits, the summation in Eq. (7) can be performed with respect to c to give

$$\beta F_1 = -\frac{1}{2}\int \frac{\Omega d^3k}{(2\pi)^3} \left[N\tilde{w}(N\tilde{W})^2 + \frac{1}{2}(N\tilde{w})^2(N\tilde{W})^2 + \right.$$

$$\left. + \sum_{b=3} \frac{1}{b}(N\tilde{W})^b (1+N\tilde{w})^b \right] . \qquad (8)$$

To get the free energy to this approximation, we have to include the ring term, and Abe's S_2 result,[2]

$$\beta F_{\text{ring}} = -\frac{1}{2}\int \frac{\Omega d^3k}{(2\pi)^3} \left[N\beta\tilde{u}(k) - \log(1 - B\beta\tilde{u}) \right]$$

where $N\beta\tilde{u}(k) = \frac{1}{k^2}$ is the Fourier transform of the Coulomb potential. Therefore the nodal-ring approximation to the excess free energy is

$$\beta(F - F_0) = -\frac{1}{2}\int \frac{\Omega d^3k}{(2\pi)^3}\,[N\beta\tilde{u} - N\tilde{W} + N\tilde{W}_3(k)\,\delta(k) +$$

$$+ N\tilde{w}\,N\tilde{W} - \frac{1}{2}(N\tilde{W})^2 - \log(1 + N\beta\tilde{u} - N\tilde{W})]\ . \qquad (9)$$

The problem of calculating the free energy of the Coulomb gas has been reduced, in our approximation, to a quadrature by Eq. (9). We will turn our attention to the relation between this result for the free energy and the expansion of the pair distribution function for the same system.

III. CONNECTION WITH THE NODAL EXPANSION FOR THE PAIR DISTRIBUTION FUNCTION.

The basic equation relating the excess free energy of the Coulomb system to the radial distribution function arises in the Debye charging process. We may write

$$\beta(F - F_0) = \frac{1}{2}N\rho\int_0^1 \frac{d\alpha}{\alpha}\int d^3r\,\beta u_\alpha(r)\,g_\alpha(r) \qquad (10)$$

Eq. (10) gives the free energy in terms of the radial distribution, and should also hold term by term if one expands both F and $g(r)$. The charging parameter is such that

$$u_\alpha(r) = \frac{\alpha(Ze)^2}{r}\ .$$

Nevertheless, it is simpler if from the free energy we obtain the internal energy

$$\beta E = \lim_{\alpha \to 1} \alpha\,\frac{d}{d\alpha}(\beta F_\alpha) \qquad (11)$$

and write the internal energy in terms of the radial distribution

$$\beta(E - E_0) = \frac{1}{2} N^2 \int \frac{\Omega d^3k}{(2\pi)^3} \beta\tilde{u}(k)\tilde{g}(k) . \qquad (15)$$

Therefore, using Eq. (11) on the nodal-ring result, Eq. (9), we can obtain the internal energy. Comparison with Eq. (12) will give the equivalent result for $g(r)$. To be able to do so we must find the effect of the differentiation with respect to the charging factor, which is actually multiplying the Coulomb potential in all places where the latter appears implicitly in Eq. (9).

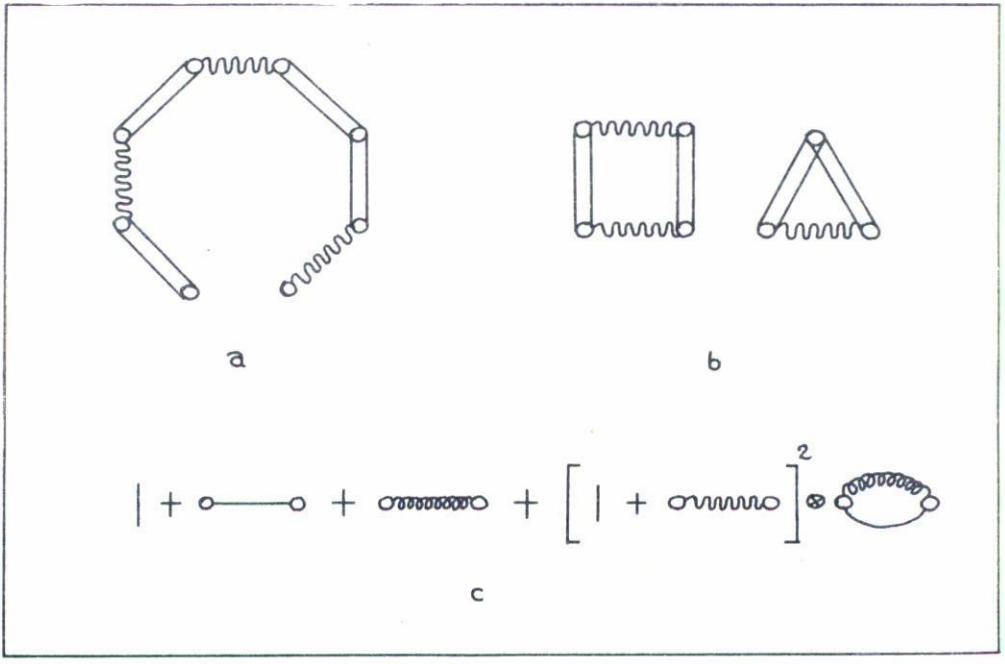

Fig. 1. (a) General form of a term in the nodal-ring summation. The double line represents the W_2-bond and the wavy line the Debye bond.

(b) Special cases in the nodal ring summation.

(c) Representation of the right hand side of Eq. (20). The single solid line is a W_1-bond, the curly line is the first nodal chain h_1.

Diagrammatically, the differentiation with respect to α corresponds to cutting off the free-energy graphs in all possible places. Thus, broadly speaking, a free-energy "ring" diagram corresponds to radial-distribution "chain" graphs. More precisely, we write Eq. (9) in terms of W_1 and of

$$B(x) = -N\beta u(x) + NW_2(x) . \qquad (13)$$

We obtain

$$\beta(F - F_0) = -\frac{1}{2}\int \frac{\Omega d^3k}{(2\pi)^3}\left[\tilde{B}(k)\,\delta(k) - \log(1-\tilde{B}) - \tilde{B}(k) - \frac{1}{2}(N\tilde{W}_1)^2\right],$$

where we have made use of the neutrality condition to cancel one term of the integrand proportional to $\tilde{u}(k)\,\delta(k)$. From Eq. (11)

$$\beta(E - E_0) = -\frac{1}{2}\int \frac{\Omega d^3k}{(2\pi)^3}\left\{\delta(k)\,\frac{d\tilde{B}}{d\alpha} + \frac{\tilde{B}}{1-\tilde{B}}\cdot\frac{d\tilde{B}}{d\alpha} - N\tilde{W}_1\,\frac{d}{d\alpha}N\tilde{W}_1\right\} \tag{14}$$

It is easy to see that

$$\frac{dW_2}{d\alpha} = W_1\,\frac{dw_1}{d\alpha} \tag{15}$$

and that, in momentum space,

$$\frac{d\tilde{w}_1}{d\alpha} = -\beta\tilde{u}(1 + N\tilde{w}_1)^2 . \tag{16}$$

From Eqs. (15) and (16)

$$\frac{d\tilde{W}_1}{d\alpha} = \int \frac{\Omega d^3k''}{(2\pi)^3}(-\beta\tilde{u})(1 + N\tilde{w})^2\left[\delta(k + k'') + \tilde{W}_1(k + k'')\right] \tag{17}$$

and

$$\frac{d\tilde{B}}{d\alpha} = \int \frac{\Omega d^3k''}{(2\pi)^3}(-\beta\tilde{u})\left[\delta(k + k'') + (1 + N\tilde{w})^2\tilde{W}_1(k + k'')\right] \tag{18}$$

Substitution of Eqs. (17) and (18) into (14), and comparing with Eq. (12) we find

$$\tilde{g}(k) = \int \frac{\Omega d^3k''}{(2\pi)^3} [\delta(k+k'') + \tilde{W}_1(k+k'')][\delta(k'') + \tilde{M}(k'')]$$

$$+ \tilde{l}(k) \int \frac{\Omega d^3k''}{(2\pi)^3} \tilde{W}_1(k+k'') \tilde{M}(k'') \qquad (19)$$

where we have defined

$$N\tilde{M}(k) \equiv \tilde{B}(k) - N\tilde{W}_1(k) + \frac{\tilde{B}(k)^2}{1-\tilde{B}(k)}$$

$$\tilde{l}(k) \equiv -2N\tilde{w}_1(k) + (N\tilde{w}_1)^2 .$$

We may now compare the result for g, Eq. (19), with those obtained by the direct expansion using the Mayer-Montroll theorem[5] for the radial distribution. There it is shown that the sum of the Debye result for the potential of average force, h_0, and the first nodal chain, is[6]

$$\tilde{h}_0 + \tilde{h}_1 = \frac{\tilde{W}_2 - \beta\tilde{u}}{1-(N\tilde{W}_2 - N\beta\tilde{u})} - \tilde{W}_2 .$$

From this equation and the definition of $B(x)$, Eq. (13),

$$M(x) = h_1(x) .$$

Therefore we may write Eq. (19) in configuration space as

$$g(x) = e^{h_0}(1+h_1) + \int \frac{d^3x^1}{\Omega} l(x-x^1) W_1(x^1) h_1(x^1) . \qquad (20)$$

Fig. (1c) shows the diagram form of Eq. (20). Nevertheless, in regard to previous results[6], one should notice that Fig. (2), represents an approximation to $g(x)$ but not to the potential of average force.

We have been able to obtain a divergence-free result for the free energy, Eq. (9), and shown its relation to similar expansions for the radial

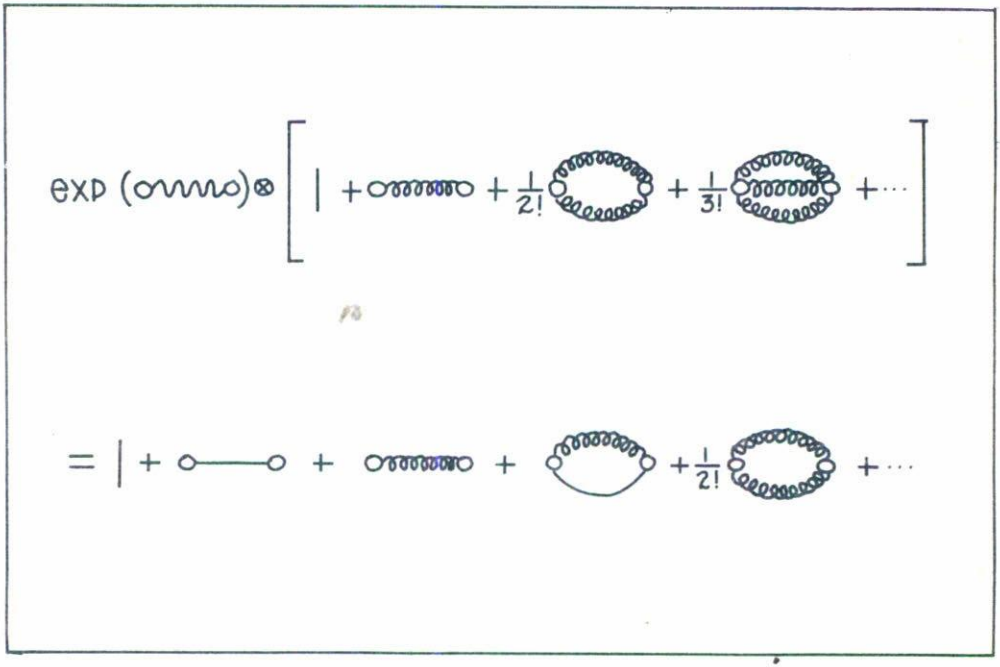

Fig. 2. Diagrammatic representation of the $g(r)$ when the potential of average force is calculated up to the first nodal chain. The terms are to be compared with those of Fig. (1c) showing the first nodal ring result.

distribution. Eqs. (9) and (20) are equivalent to each other. This fact throws light into the summation procedure to obtain the nodal-ring expression, For, the nodal-chain approximation is just one stage in solving the hipernetted-chain equation for the system[7], and as the nodal chain has been shown[8] to give a meaningful approximation in the region $\Lambda < 7$, one can expect the same order of accuracy from the nodal ring result for the free energy. Furthermore, this connection is useful if one thinks of improving the approximation: one only needs to build up nodal rings of greater complexity, in the same manner as the HNC equation is obtained.

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RESUMEN

A partir del desarrollo de Abe, Friedman y Meeron para la energía libre de un gas clásico de Coulomb, se obtienen resultados que deben ser significativos en la región donde el parámetro del plasma toma valores del orden de la unidad. El problema se simplifica hasta una cuadratura y no aparecen divergencias. Se muestra explícitamente la equivalencia entre el método usado y resultados similares que se han obtenido para la distribución binaria en equilibrio.