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Particle Correlations in a Classical One-Component Plasma

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The effect of particle correlations in a classical system of charged particles moving in a static uniform background is investigated by means of a dielectric theory developed by Singwi *et al.* for a completely degenerate electron gas. In this theory, the short-range correlations arising from the Coulomb interaction is taken into account through a local-field correction depending on the pair correlation function. In a first approximation (I), the pair correlation function is chosen to be time independent. The extension of allowing also the pair correlation function to adjust itself to the external field results in a screening of the Coulomb potential entering the local field. The effect of this screening has been investigated for the cases of a static random-phase-approximation (RPA) dielectric function (II) and a static fully self-consistent dielectric function (III). Numerical self-consistent calculations have been carried out for the cases I–III in order to determine the static structure factor $S(\vec{q})$. From $S(\vec{q})$ thus obtained, the Helmholtz free energy, the correlation energy, the pair correlation functions, and the isothermal compressibility have been calculated numerically, The plasma dispersion and the compressibility sum rule have also been investigated. The present method can be regarded as a rather natural extension of the RPA. Considerable improvement upon the simple Debye-Hückel (or, equivalently, classical RPA) is also found. The results of the present calculations are also compared with the results of other elaborate methods.

I. INTRODUCTION

The purpose of this work[1] is to study the equilibrium state of a classical system of equally charged particles imbedded in a static uniform background of the opposite charge. Such a simplified model exhibits many of the important characteristics of more complicated Coulomb systems as plasmas, electrolytes, etc., and has consequently been subject to a large number of investigations. Debye and Hückel[2] thus developed the first successful theory, strictly valid for weakly interacting systems. Specifically, their theory predicts a simple static pair correlation function

$$g_{\mathrm{DH}}(r) = 1 - \beta(Ze)^2 \exp(-\kappa r)/r \quad , \tag{1}$$

where $\kappa = (4\pi n Z^2 e^2 \beta)^{1/2}$ is the inverse Debye-Hückel radius, n the number density, Ze the charge of the particles, and, as usual, $\beta = 1/kT$. Equation (1) is meaningful only for large distances between the particles $r > \beta(Ze)^2$. At small distances the static pair correlation function (1) results in absurd negative probabilities. Nevertheless, in spite of this difficulty for small r, the Debye-Hückel result is useful since it describes the screening out of particle correlation at distances such that $r \sim 1/\kappa$. Also, Eq. (1) may be used to obtain the correct leading-order result for the Coulombic interaction energy at high temperatures and low densities, i.e., when $\beta(Ze)^2\kappa < 1$.

Since the early work of Debye and Hückel, considerable efforts have been spent on improving the theory in order to make it applicable to systems of higher densities and lower temperatures.[3–5] As a result of these studies, we have a fairly reliable description available for our model system. In the present work, we will investigate an approach which was designed originally by Singwi *et al.*[6–8] for a completely degenerate electron gas. In the present context this approach differs from most of the earlier developments[3–5] in the sense that it is a dynamic one.

Treated in the random-phase approximation (RPA) the degenerate electron gas exhibits, like the Debye-Hückel approximation (or, equivalently classical RPA), large negative probabilities at small interparticle separations. This situation persists over the whole range of metallic densities. By making a particular decoupling of the two-particle distribution function, namely, the product of two one-particle functions and a pair correlation function, Singwi *et al.* were able to derive in the linear response approximation an expression for the density-density response function $\chi(\vec{q}, \omega)$ of the system. The function $\chi(\vec{q}, \omega)$, where $\vec{q}$ is the momentum and ω the frequency, turns out to be a functional of the static form factor $S(\vec{q})$, which is simply related to the static pair correlation function $g(\vec{r})$ as

$$S(\vec{q}) = 1 + n \int d\vec{r}\,[g(\vec{r}) - 1]\, e^{i\vec{q}\cdot\vec{r}} \quad . \tag{2}$$

In order to determine $S(\vec{q})$ [and $g(\vec{r})$] the dissipation-fluctuation theorem[9]

$$nS(\vec{q}) = -\hbar \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi}\, \mathrm{Im}\ \chi(\vec{q}, \omega) \coth \tfrac{1}{2}\hbar\beta\omega \quad , \tag{3}$$

with $\beta \to \infty$ was then superimposed on the approximate theory. It is noteworthy that the relation (3) is exact. With $\chi(\vec{q}, \omega)$ as a functional of $S(\vec{q})$, the fluctuation-dissipation theorem (3) thus provides us with a self-consistency requirement on $S(\vec{q})$. The results of the iterative numerical solutions of Eq. (3) in the case of a degenerate electron gas are reported in Refs. 7 and 8. The behavior at metallic densities of the calculated pair correlation function is most pleasing and shows a marked improvement upon the RPA treatment. The fact that the calculated $g(r)$ may still be negative for small r is less troublesome. In all cases, the values of $g(0)$ are so small that for practical purposes one can consider them to be zero.

With the promising results of Singwi *et al.* in mind we will now turn our attention to the classical plasma. In Sec. II, some basic formulas will be given. Since Refs. 7 and 8 contain a detailed formal framework we feel that these formulas can be given without a derivation. In Sec. III, the thermodynamic quantities are stated. The plasma dispersion is derived in Sec. IV, and the compressibility and the compressibility sum rule in Sec. V. In Sec. VI, the results of numerical calculations are presented and compared with other calculations. Section VII, finally, contains a summary.

II. SOME BASIC FORMULAS

If the infinite hierarchy of equations for the classical distribution functions $f_N(\vec{r}_1, \vec{p}_1; \vec{r}_2, \vec{p}_2; \ldots; \vec{r}_N, \vec{p}_N | t)$ in phase space is terminated, as was done in Refs. 6 and 7 by the decoupling of the two-particle function as

$$f_2(\vec{r}, \vec{p}; \vec{r}', \vec{p}' | t) = f_1(\vec{r}, \vec{p} | t) \times f_1(\vec{r}', \vec{p}' | t) g(\vec{r} - \vec{r}') \ , \qquad (4)$$

a linear response analysis gives the density-density response function for the interacting system

$$\chi(\vec{q}, \omega) = \chi_0(\vec{q}, \omega) / [1 - \psi(\vec{q}) \chi_0(\vec{q}, \omega)] \ . \qquad (5)$$

In Eq. (5), $\chi_0(\vec{q}, \omega)$ is the density-density response function for a classical system of noninteracting particles with a Maxwellian distribution of momenta. For real values of ω, the function $\chi_0(\vec{q}, \omega)$ can be separated into its real and imaginary parts as

$$\chi_0(\vec{q}, \omega) = \chi_0'(\vec{q}, \omega) + i \chi_0''(\vec{q}, \omega) \ , \qquad (6)$$

where[10]

$$\chi_0'(\vec{q}, \omega) = -n\beta[1 - 2yF(y)] \ , \qquad \chi_0''(\vec{q}, \omega) = -n\beta\sqrt{\pi}\, y e^{-y^2} \ , \qquad (7)$$

with $y = \omega(\beta m/2)^{1/2}/q \ (m = mass)$,

and $$F(y) = e^{-y^2} \int_0^y dt\, e^{t^2} \ . \qquad (8)$$

$F(y)$ is sometimes referred to as Dawson's integral. The symbol $\psi(\vec{q})$ in Eq. (5) stands for

$$\psi(\vec{q}) = \Phi(\vec{q})[1 - G(\vec{q})] \ , \qquad (9)$$

where $\Phi(\vec{q})$ is the bare Coulomb interaction $4\pi(Ze)^2/q^2$, and

$$G(\vec{q}) = -\frac{1}{n} \int \frac{\vec{q} \cdot \vec{p}}{p^2} [S(\vec{q} - \vec{p}) - 1] \frac{d\vec{p}}{(2\pi)^3} \ . \qquad (10)$$

Equation (5) has the same structure as the RPA result, except that $\Phi(\vec{q})$ has been replaced by $\psi(\vec{q})$.

In the classical region $\hbar \to 0$ and $\beta \to 0$, the self-consistency condition (3) takes a particularly simple form.[1,11] By means of the Kramers-Kronig relation, the integral in Eq. (3) can be expressed in terms of the static value $\chi(\vec{q}, 0)$, so that

$$S(\vec{q}) = [1 + n\beta\psi(\vec{q})]^{-1} \ . \qquad (11)$$

Equation (11) may also be written $\psi(\vec{q}) = -c(\vec{k})/\beta$, where $c(\vec{k})$ is the Fourier transform of the direct correlation function of Ornstein and Zernike. As pointed out,[1,11] this fact makes a nice connection with Nelkin and Ranganathan's[12] treatment of collisionless sound in classical liquids.

In the decoupling (4), the function g is chosen as the static pair correlation function. Consequently, $g(r)$ cannot respond to the weak outer field which is exerted on the system in a linear response analysis. In Ref. 8, Singwi *et al.* have relaxed this restraint so that the adjustment of the pair correlation function to the external disturbance is taken into account in an approximate way. The only changes which result from this extension is that the function (10) will now contain a dynamic screening $\epsilon(\vec{q}, \omega)$ and a dynamic factor $S(\vec{q}, \omega)$ (the Fourier transform of the time-ordered density correlation function[8]), such that

$$G(\vec{q}, \omega) = -\frac{1}{n} \int \frac{d\vec{p}\, d\omega'}{(2\pi)^4} \frac{\vec{q} \cdot \vec{p}}{p^2} \frac{1}{\epsilon(\vec{p}, \omega')} S(\vec{q} - \vec{p}, \omega - \omega') \ . \qquad (12)$$

In the limit of static screening, one obtains[8]

$$G(\vec{q}) = -\frac{1}{n} \int \frac{\vec{q} \cdot \vec{p}}{p^2 \epsilon(\vec{p})} [S(\vec{q} - \vec{p}) - 1] \frac{d\vec{p}}{(2\pi)^3} \ , \qquad (13)$$

where ϵ is the static dielectric function. The value for $\epsilon(\vec{q})$ is

$$\epsilon(\vec{q}) = 1 + \frac{\kappa^2}{q^2 - \kappa^2 G(\vec{q})} \ . \qquad (14)$$

Concluding this section, we note that the Debye-Hückel approximation (or classical RPA) is obtained by putting $g(\vec{r} - \vec{r}') = 1$ in Eq. (4) and $G(\vec{q}) = 0$ in the expression (9) for $\psi(\vec{q})$. From Eq. (11), we then have the well-known result

$$S_{\mathrm{DH}}(\vec{q}) = 1 - \kappa^2/(q^2 + \kappa^2) \ , \qquad (15)$$

which converted to configurational space gives the Debye-Hückel pair correlation function (1).

III. THERMODYNAMIC PROPERTIES

The classical static pair distribution function enables us to calculate average values from functions which depend on the coordinates and momenta of the particles of the system. For the Coulomb interaction energy, one has (see, e.g., Ref. 3)

$$\bar{U} = N 2\pi n \int_0^\infty \Phi(r)[g(r)-1]r^2 dr \quad . \tag{16}$$

The -1 in $[g-1]$ in Eq. (16) comes from the uniform background and N is the total number of particles. Expression (16) may alternatively be written

$$\bar{U} = N \frac{(Ze)^2}{\pi} \int_0^\infty dk\,[S(k)-1] \quad . \tag{17}$$

The average value of the total energy of the system is

$$\bar{E} = \tfrac{3}{2}NkT + \bar{U} \quad . \tag{18}$$

For Coulomb interactions, the total pressure takes the particularly simple form

$$PV = NkT + \tfrac{1}{3}\bar{U} \quad , \tag{19}$$

where V is the total volume. The Helmholtz free energy is, according to Ref. 3,

$$(F - F_0) = \int_0^\Gamma d\Gamma' \,\bar{U}/\Gamma' \quad , \tag{20}$$

where F_0 is the free energy of a perfect gas. The quantity Γ is the dimensionless Brush-Sahlin-Teller parameter,[3] defined as

$$\Gamma = (Ze)^2\beta/r_s \quad , \tag{21}$$

where r_s is the radius of a sphere containing one particle.

In the limit of weak coupling ($\Gamma \ll 1$) the Debye-Hückel approximation should be reliable. In this limit, one has

$$\bar{U}/NkT = -\tfrac{1}{2}\sqrt{3}\,\Gamma^{3/2} \quad , \tag{22}$$

and $$(F - F_0)/NkT = -\Gamma^{3/2}/\sqrt{3} \quad . \tag{23}$$

IV. PLASMA DISPERSION

The plasma dispersion $\omega(\vec{q})$ is determined by the poles in the response function $\chi(\vec{q},\omega)$. For small values of $|\vec{q}|$ and finite ω, the imaginary part of the denominator in Eq. (5) may be neglected to a first approximation. For small arguments, the function $G(\vec{q})$ can further be written

$$G(\vec{q}) = G''(0)q^2 \quad , \tag{24}$$

where[7] $$G''(0) = -\frac{1}{3\pi^2 n}\int_0^\infty dk\,[S(k)-1] \quad , \tag{25}$$

in the case of the decoupling (4), and[8b]

$$G''(0) = -\frac{1}{3\pi^2 n}\int_0^\infty dk\,\frac{S(k)-1}{\epsilon(k)}\left(1-\frac{d\ln\epsilon(k)}{d\ln k}\right) , \tag{26}$$

in the case when the pair correlation function is allowed to adjust itself to the outer perturbing field. With $F(y)$ in Eq. (8) expanded to second order (see, e.g., p. 112 in Ref. 10), we obtain, together with Eq. (24), the plasma dispersion

$$\omega(\vec{q})^2 = \omega_{pl}^2 + \left(\frac{3}{\beta m} - \omega_{pl}^2 G''(0)\right)q^2 \quad . \tag{27}$$

In Eq. (27), $\omega_{pl} = (4\pi Z^2 e^2 n/m)^{1/2}$ is the ordinary plasma frequency. The plasma damping may now be obtained by evaluating $\chi''(\vec{q},\omega)$ in the point $\omega(\vec{q})$. To the leading order the damping is found to be the same as the RPA result.

V. COMPRESSIBILITY SUM RULE

The static dielectric function (14) has in the limit $\vec{q}\to 0$ the form

$$\epsilon(q) = 1 + (\kappa^2/q^2)/[1-\kappa^2 G''(0)] \quad . \tag{28}$$

From the compressibility sum rule (see, e.g., p. 166 in Ref. 9), one finds

$$K_T^0/K_T = 1 - \kappa^2 G''(0) \quad , \tag{29}$$

where $K_T^0 = \beta/n$ is the isothermal compressibility of the noninteracting gas.

The isothermal compressibility can also be calculated as

$$K_T = -\frac{1}{V}\left(\frac{dP}{dV}\right)_T^{-1} \quad . \tag{30}$$

A direct differentiation according to Eq. (30) therefore gives

$$K_T^0/K_T = 1 + \tfrac{1}{3}\left(\bar{U}/NkT + \tfrac{1}{3}\Gamma\,\frac{d\bar{U}/NkT}{d\Gamma}\right) \quad . \tag{31}$$

The consistency of the two expressions (29) and (30) is investigated in Sec. VI.

VI. NUMERICAL CALCULATIONS

In the numerical calculations, we have distinguished between three different cases to be indexed I, II, and III. Case I refers to the decoupling in Eq. (4) with a static pair correlation. Case II involves the dielectric screening in accordance with Eq. (13), but with $\epsilon(\vec{q})$ approximated with the classical RPA-expression[13]

$$\epsilon_{\mathrm{RPA}}(\vec{q}) = 1 + \kappa^2/q^2 \quad . \tag{32}$$

In case III, finally, the full self-consistent dielectric screening function (14) is taken into account. In the three approximations, one then has the different forms of the function $G(\vec{q})$ written in a way that is suitable for the numerical work:

$$G_{\mathrm{I}}(\vec{q}) = -\frac{1}{8n\pi^2 q}\int_0^\infty dp\,p\,[S(p)-1]$$

$$\times \left((q^2-p^2)\ln\left|\frac{q+p}{q-p}\right| + 2pq\right) , \tag{33}$$

$$G_{\mathrm{II}}(\vec{q}) = -\frac{1}{8n\pi^2 q}\int_0^\infty dp\, p[S(p)-1] \times \left(\tfrac{1}{2}(q^2-p^2-\kappa^2)\ln\left|\frac{(p+q)^2+\kappa^2}{(p-q)^2+\kappa^2}\right| + 2pq\right) , \tag{34}$$

$$G_{\mathrm{III}}(\vec{q}) = -\frac{1}{8n\pi^2 q}\int_0^\infty \frac{dp}{\epsilon(p)p} \times[(q^2+p^2)I_1(p,q) - I_3(p,q)] . \tag{35}$$

In Eq. (35), the auxiliary functions I_1 and I_3 are defined as

$$I_n(p,q) = \int_{|p-q|}^{p+q} dx\, x^n[S(x)-1] . \tag{36}$$

The self-consistency equation (11) for $S(\vec{q})$ has been solved numerically by means of an iterative procedure, which has been started for case I and for Γ very small (the weak coupling limit). As the initial guess for $S(\vec{q})$, we have chosen the Debye-Hückel form factor (15) for q less than a certain $q_{\max}$, and $S(\vec{q}) = 1$ for $q \geq q_{\max}$. The self-consistent $S_{\mathrm{I}}(\vec{q})$ obtained in this way has then been used as the input to Eq. (11) in order to generate a consecutive $S_{\mathrm{I}}(\vec{q})$ corresponding to a slightly increased value of Γ. Proceeding in this fashion, $S_{\mathrm{I}}(q)$ has been determined for a large set of Γ values in the range (0.05, 2.5). It turns out that the resulting functions $S_{\mathrm{I}}(\vec{q})$ are insensitive to the initial cutoff at $q = q_{\max}$ and Γ very small. From case I, we have then continued to case II, using $S_{\mathrm{I}}(\vec{q})$ as the input to the iteration scheme, and from this case to III, using $S_{\mathrm{II}}(\vec{q})$ as the input. In the very weak coupling limit, the iteration procedure converges without any serious difficulties. With increasing couplings, however, strong oscillations appear. To overcome this difficulty, the "damping device"

$$S^{N+1}(\vec{q}) = pS^N(\vec{q}) + (1-p)S^{N-1}(\vec{q}) , \tag{37}$$

($p \sim 0.5$), has been found convenient.[14] The iterations have been continued until sufficient convergency has been obtained in the function $G(\vec{q})$. As for the degenerate electron gas,[7,8b] convergency in $G(\vec{q})$ reveals a very high accuracy also in $S(\vec{q})$.

In cases I, II, and III, the self-consistent functions $S(\vec{q})$ are very close to $S_{\mathrm{DH}}(\vec{q})$ for $\vec{q} \to 0$. This is because $G(\vec{q}) \simeq G''(0)\, q^2$ in the same limit and hence $\psi(\vec{q}) \to \Phi(\vec{q})$ in Eq. (11). For large $\vec{q}$ vectors the self-consistent form factors approach the value of one much faster than does $S_{\mathrm{DH}}(q)$ (see Fig. 1). The functions $G(\vec{q})$ are for the present system found to display the same general features as for the degenerate electron gas. In particular, the difference between the screened and unscreened versions is the same as that found by Singwi *et al.* (see Fig. 11 in Ref. 8b).

The self-consistent form factors have been used to calculate the static pair correlation function $g(r)$ according to

$$g(r) = 1 + \frac{1}{2\pi^2 nr}\int_0^\infty dk\, k[S(k)-1]\sin(kr) . \tag{38}$$

The results are given in the Tables I–III for $\Gamma = 0.1$, $\Gamma = \frac{1}{3}$, and $\Gamma = 1.0$. For $\Gamma = 1.0$, the results are also displayed in a graphical form (Fig. 2). For comparison, other approximate pair correlation functions are included. Among these, the nonlinear Debye-Hückel form[2]

$$g(r) = \exp\{-[(Ze)^2\beta/r]e^{-\kappa r}\} \tag{39}$$

is the simplest one. The function (39) is obtained from the derivation of $g_{\mathrm{DH}}(r)$ in Eq. (1) if a linearization is not performed at certain stages. In the method of hypernetted chains[15] (CHNC) an integral equation for $g(r)$ is obtained by a summation procedure of Mayer-type diagrams. The integral equation of Percus and Yevick[16] (PY), on the other hand, results from a collective coordinate treatment. The method of Broyles and Sahlin[17] (BS) separates the pair potential into a sum of long- and short-range part. The g corresponding to the short-range part is calculated using an equation

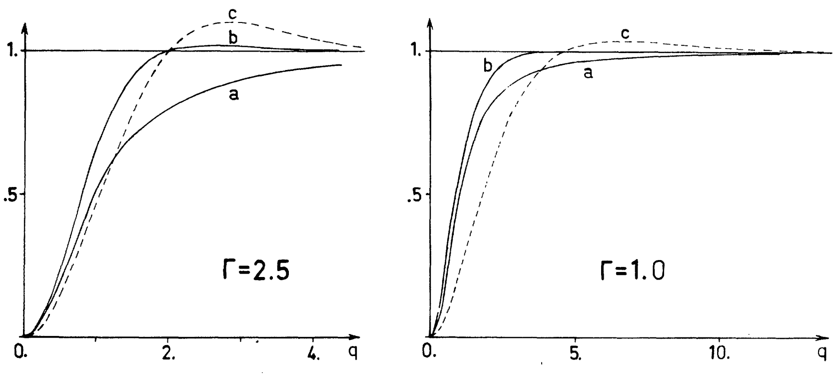

FIG. 1. Functions $S(\vec{q})$ and $G(\vec{q})$ as a function of q in units of κ; (a) is the Debye-Hückel static form factor of Eq. (15); (b) is the self-consistent $S(\vec{q})$ according to version II; and (c) is the function $G(\vec{q})$, also according to version II.

TABLE I. Radial distribution function for $\Gamma=0.1$.

r/r_s	DH[a]	Nonlinear[b] DH	CHNC[b]	PY[b]	BS[b]	MO[c]	I	II	III
0.00	$-\infty$	0.000	0.000	0.000	0.000	···	−0.011	−0.027	−0.027
0.05	−0.946	0.143	0.146	0.146	0.135	0.380	0.141	0.142	0.148
0.10	0.053	0.388	0.394	0.393	0.380	0.450	0.388	0.386	0.386
0.15	0.386	0.541	0.550	0.549	0.534	0.570	0.539	0.538	0.538
0.20	0.552	0.639	0.649	0.648	0.633	0.650	0.638	0.636	0.636
0.30	0.717	0.753	0.766	0.765	0.749	0.760	0.753	0.752	0.751
0.40	0.799	0.818	0.831	0.830	0.814	0.815	0.815	0.815	0.816
0.50	0.848	0.859	0.872	0.870	0.856	0.860	0.859	0.858	0.857
1.00	0.942	0.944	0.954	0.953	0.942	0.940	0.943	0.943	0.943
1.50	0.971	0.971	0.979	0.978	0.970	0.965	0.971	0.971	0.971
2.00	0.983	0.983	0.989	0.989	0.983	0.975	0.983	0.983	0.983
2.50	0.990	0.990	0.994	0.994	0.990	0.990	0.990	0.990	0.990

[a] Equation (1).

[b] Reference 18.

[c] Reference 3.

TABLE II. Radial distribution function for $\Gamma=\frac{1}{3}$.

r/r_s	DH[a]	Nonlinear[b] DH	CHNC[b]	PY[b]	BS[b]	MC[c]	I	II	III
0.00	$-\infty$	0.000	0.000	0.000	0.000	···	−0.009	−0.000	−0.003
0.05	−5.34	0.002	0.000	0.000	0.003	···	−0.007	−0.001	+0.001
0.10	−2.02	0.049	0.037	0.035	0.026	···	0.050	0.040	0.038
0.15	−0.913	0.147	0.128	0.120	0.104	···	0.142	0.129	0.129
0.20	−0.365	0.255	0.236	0.223	0.198	···	0.248	0.231	0.231
0.30	0.177	0.439	0.432	0.410	0.373	···	0.426	0.411	0.410
0.40	0.441	0.572	0.579	0.553	0.510	···	0.557	0.544	0.544
0.50	0.596	0.667	0.685	0.658	0.613	···	0.653	0.643	0.642
1.00	0.877	0.884	0.914	0.896	0.863	···	0.876	0.874	0.873
1.50	0.950	0.952	0.972	0.964	0.944	···	0.947	0.947	0.947
2.00	0.977	0.978	0.990	0.986	0.976	···	0.976	0.976	0.976
2.50	0.989	0.989	0.996	0.994	0.989	···	0.988	0.988	0.988

[a] Equation (1).

[b] Reference 18.

[c] Reference 3.

TABLE III. Radial distribution function for $\Gamma=1.0$.

r/r_s	DH[a]	Nonlinear[b] DH	CHNC[b]	PY[b]	BS[b]	MC[c]	I	II	III
0.00	$-\infty$	0.000	0.000	0.000	0.000	0.000	−0.010	+0.008	−0.008
0.10	−7.41	0.000	0.000	0.000	0.000	0.000	−0.003	−0.020	−0.024
0.20	−2.54	0.029	0.034	0.020	0.012	0.010	0.030	−0.044	−0.039
0.30	−0.982	0.137	0.163	0.100	0.083	0.075	0.111	0.006	0.004
0.40	−0.250	0.286	0.335	0.221	0.193	0.200	0.232	0.128	0.116
0.50	0.159	0.431	0.498	0.351	0.315	0.335	0.355	0.267	0.261
0.60	0.410	0.554	0.632	0.470	0.433	0.450	0.473	0.411	0.404
0.70	0.575	0.653	0.734	0.574	0.538	0.550	0.575	0.538	0.525
0.80	0.687	0.731	0.810	0.661	0.629	0.640	0.658	0.639	0.629
0.90	0.766	0.791	0.864	0.732	0.704	0.715	0.726	0.716	0.714
1.00	0.823	0.838	0.903	0.789	0.767	0.775	0.780	0.777	0.780
1.50	0.950	0.951	0.982	0.940	0.936	0.935	0.932	0.937	0.937
2.00	0.984	0.984	0.996	0.984	0.985	0.970	0.980	0.982	0.983
2.50	0.995	0.995	0.999	0.996	0.994	0.990	0.994	0.995	0.995

[a] Equation 1.

[b] Reference 18.

[c] Reference 3.

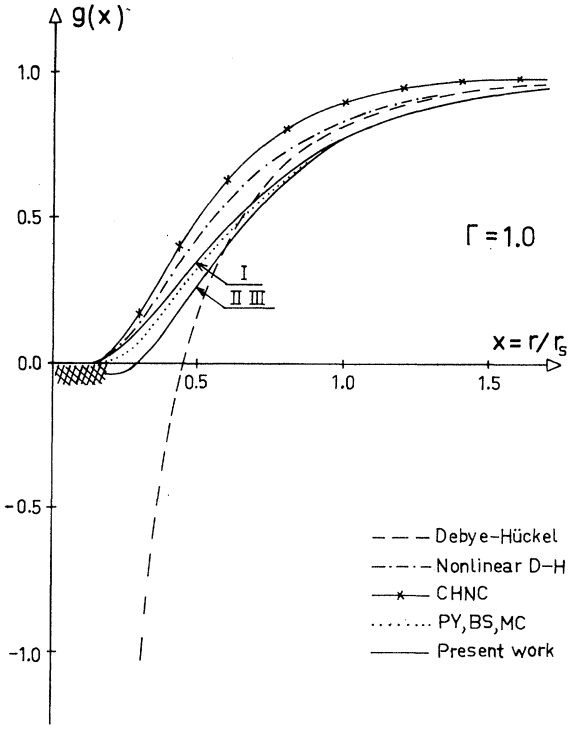

FIG. 2. Pair correlation function $g(r)$ for $\Gamma=1.0$ in different approximations. The symbols are explained in the text. The PY, BS, and MC results are represented by one curve only, as the differences between them are small and not easily pictured in a clear way. In the shaded area, the numerical accuracy is low for the present calculation.

such as the PY or CHNC. With the g thus obtained, the BS method permits the calculation of the g corresponding to the original pair potential. In the Monte Carlo (MC) method the detailed motion of a large but finite number of particles is studied The results of Brush, Sahlin, and Teller[3] refer to systems with 32–500 particles moving in a box and subject to periodic boundary conditions. Because of the long-range nature of the Coulomb interaction, the electrostatic field from the particles outside the box has been included in an average way. So far, the MC calculations in Ref. 3 represent the most extensive study of the classical one-component plasma.

The "improved" pair correlation functions for $\Gamma=0.1$ (Table I) all seem to agree reasonably well, although the MC values are surprisingly high for short distances. For large distances, all the functions approach the simple Debye-Hückel form (1). For $\Gamma=\frac{1}{3}$ (Table II) our results I, II, and III are closest to the nonlinear DH, CHNC, PY results, which form a rather well-collected group. Unfortunately, no MC results are available for this value of Γ. For $\Gamma=1.0$ (Table III and Fig. 2), our results agree mostly with the group consisting of PY, BS, and MC. The pair correlation functions calculated by means of the present methods I, II, and III therefore agree with the main group of "improved" functions in each table. As in the case of the degenerate electron gas,[7,8] it turns out that our pair correlations become increasingly negative at short distances with increasing coupling Γ. However, the region of small r is also the one which is most sensitive to numerical rounding-off errors in $S(\vec{q})$ for large $\vec{q}$ vectors. According to Eq. (38), these errors are amplified by a factor k^2 for $r=0$. Therefore, we should perhaps not emphasize the actual numbers for $g(0)$, but at the most the sign and the order of magnitude. It should be noted that small negative values are also obtained in the BS method. In Ref. 18, however, these values are set equal to zero. In all the cases in Tables I–III, the error in our functions $g(r)$ seems to be so small that it can be neglected for practical purposes. In the calculation of the total energy and pressure, for example, the effect of a small negative $g(r)$ is negligible because of a factor r in the integrand in Eq. (16). Or, equivalently, the rounding-off errors in $S(\vec{q})$ are not amplified in Eq. (17), as they are in Eq. (38). Also in another respect our results are similar to those for the electron gas, namely, it was found by Singwi *et al.*[8] that the inclusion of a static screening in the function $G(\vec{q})$ leads to worse pair correlation functions at small r.

For $\Gamma\sim 2.0$, our calculated pair correlation functions change character in an interesting way. A weak oscillatory behavior appears for large values of r, indicating the onset of a short-range order in the system. Also, in Refs. 3 and 18, oscillations in $g(r)$ appear at the same coupling strength.

The correlation energy $-\overline{U}/NkT$ corresponding to the approximations I, II, and III is listed in Table IV. In the limit of weak coupling, our results agree, as expected, with the classical RPA (or Debye-Hückel) result. For larger values of Γ the Table IV indicates in general that the present calculation gives a considerable improvement upon RPA, which overestimates the correlation energy. From the various results in Table IV, it seems, however, hard to evaluate in a strict way the accuracy of our calculated correlation energy. Nevertheless, it is pleasing that our results are in reasonable agreement with the extensive MC calculations.[3] The reason why the Table IV is terminated at $\Gamma=2.5$ is that we seem to be entering a region where the negative behavior of $g(r)$ may not be entirely neglected. In Table V, the Helmholtz free energy is given for $\Gamma\lesssim 1$. Again we note a

TABLE IV. $-\overline{U}/NkT$ as a function of Γ.

Γ	DH[a]	Nonlinear[b] DH	CHNC[b]	PY[b]	BS[b]	Abe[c]	MC[d]	I	II	III
0.05	0.00907	0.00935	0.008	0.008	0.0094	0.00988	0.0128	0.0084	0.0084	0.0084
0.10	0.0274	0.0252	0.019	0.020	0.0258	0.0257	0.0270	0.0236	0.0236	0.0236
0.20	0.0774	0.0659	0.0483	0.0509	0.0688	0.0685	···	0.0625	0.0628	0.0628
0.3	0.1423	···	···	···	···	···	···	0.1127	0.1138	0.1139
0.333	0.1667	0.129	0.0976	0.111	0.144	0.139	···	0.1316	0.1330	0.1331
0.4	0.2191	···	···	···	···	···	···	0.1694	0.1716	0.1718
0.5	0.3062	···	···	···	···	···	···	0.2267	0.2307	0.2308
0.6	0.4025	···	···	···	···	···	···	0.289	0.296	0.296
0.7	0.5072	···	···	···	···	···	···	0.355	0.364	0.365
0.8	0.6197	···	···	···	···	···	···	0.419	0.432	0.433
0.9	0.7394	···	···	···	···	···	···	0.488	0.505	0.508
1.0	0.8660	0.468	0.328	0.539	0.577	0.624	0.579	0.555	0.577	0.580
2.0	2.449	0.925	0.647	1.448	1.321	1.641	1.338	1.280	1.386	1.449
2.5	3.423	1.128	0.784	1.903	1.723	···	1.724	1.658	1.838	1.883

[a] Equation (22).
[b] Reference 18.
[c] Reference 19.
[d] Reference 3.

considerable improvement upon the Debye-Hückel result.

The expression for the plasma dispersion at small $\vec{q}$ vectors was derived in Sec. IV. It is interesting that the present approach leads to a smaller curvature in the function $\omega(\vec{q})$ at $\vec{q}\rightarrow 0$. The change to an initially decreasing dispersion, found by Singwi *et al.*[7, 8b] is, however, not recovered for the range of Γ values investigated here ($\Gamma \leq 2.5$). As in Refs. 7 and 8b, it is noted that the inclusion of screening in $G(\vec{q})$ leads to less pronounced effects in the plasma dispersion, i.e., $G_{\mathrm{I}}''(0) > G_{\mathrm{II,III}}''(0)$.

The compressibility sum rule, discussed in Sec. V, also reflects the behavior of the response function $\chi(\vec{q}, \omega)$ at small q values. The results of the numerical evaluation of relations (29) and (31) are plotted in Fig. 3. Apparently, the two different ways of obtaining the isothermal compressibility are far from being consistent, but the inclusion of screening in $G(\vec{q})$ leads to a fair improvement.

TABLE V. Helmholtz free energy $-(F-F_0)/NkT$.

Γ	DH[a]	MC[b]	I	II, III
0.1	0.0183	0.0164	0.0152	0.0152
0.2	0.0516	0.0464	0.0429	0.0431
0.3	0.0948	···	0.0770	0.0783
0.4	0.146	···	0.117	0.119
0.5	0.204	0.174	0.161	0.163
0.6	0.268	···	0.208	0.211
0.7	0.338	···	0.257	0.262
0.8	0.413	0.337	0.309	0.315
0.9	0.493	···	0.362	0.370
1.0	0.667	0.451	0.417	0.427

[a] Equation (23).
[b] Reference 3.

The general form of the broken curve denoted III in Fig. 3 seems to be the same as for the degenerate electron gas in the same approximation.[8] By numerical differentiation we have also determined from Eq. (31) the isothermal compressibility from the MC calculations.[3] The agreement with our results is satisfactory. According to Fig. 3, the isothermal compressibility becomes negative in the vicinity of $\Gamma = 3$. With the present assumptions about the uniform background the system therefore becomes thermodynamically unstable beyond this value.

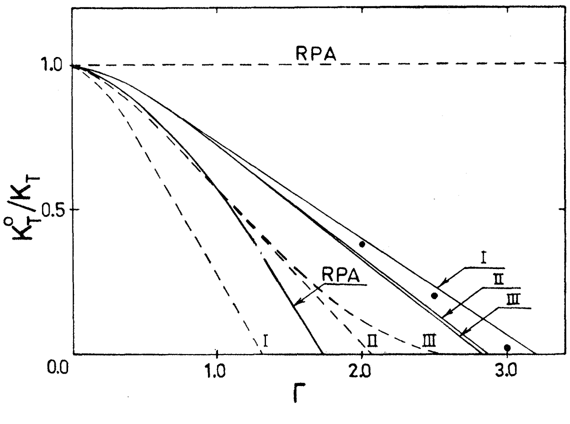

FIG. 3. Ratio between the free-particle isothermal compressibility and the compressibility of the interacting system for different values of Γ. The full curves are obtained by differentiation of the pressure [Eq. (31)] and the broken curves from the compressibility sum rule [Eq. (29)]. The broken RPA curve corresponds to $G''(0)=0$. The filled circles denote MC values, which are obtained by differentiation of energy values in Ref. 3.

VII. SUMMARY

In this paper, we have investigated the effect of particle correlations in a classical one-component plasma by means of methods which are due to Singwi *et al.*[6–8] A considerable improvement upon the Debye-Hückel theory (or, classical RPA) is found, and the comparison with the results of other calculations for quantities such as the free energy, the correlation energy, and the pair correlation functions can be said to be favorable, in particular within the region $\Gamma \leq 1.0$. At $\Gamma \sim 3.0$, the system is found to be thermodynamically unstable. As in the case of degenerate electron gas, the calculated pair correlations are negative at short distances, but $g(r)$ is so small for these r values that it for most cases can be considered to be equal to zero.

For the region $\Gamma \leq 1.0$ it is found that it is good approximation to replace the static self-consistent screening function $\epsilon(q)$ in the definition of $G(\vec{q})$ by the corresponding RPA expression in Eq. (32). The effect of using static screening functions instead of frequency dependent ones has not been investigated in this work. It seems that, at the expense of a lot more computer work and computer time, it would be possible to include also this frequency dependence.

Note added in proof. Very recently, Ichimaru (unpublished) has derived an expression for the dielectric response function starting from the second equation of the BBGKY hierarchy for the stationary values of the pair correlation function. His result is similar to ours, but the screening in the function $G(\vec{q})$ in Eq. (10) is brought about through $S(\vec{q})$, not through $1/\epsilon(\vec{q})$. We hope to report on the effect of this type of screening in a future paper.

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[1] A preliminary account of this work was presented at the Second All-Union Conference on Solid State Physics, Moscow, 1969 [FOA 4 Report No. D4118-23, Stockholm, 1969 (unpublished)].

[2] P. Debye and E. Hückel, Z. Physik 24, 185 (1923); 24, 305 (1923); see also, e.g., L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1959).

[3] S. G. Brush, H. L. Sahlin, and E. Teller, J. Chem. Phys. 45, 2102 (1966). This work contains an extensive list of references for the period 1923–1966. The very recent literature is covered in Refs. 4 and 5.

[4] F. Del Rio and H. E. De Witt, Phys. Fluids 12, 791 (1969).

[5] E. G. D. Cohen and T. J. Murphy, Phys. Fluids 12, 1404 (1969).

[6] K. S. Singwi and A. Sjölander, Note from the Institute of Theoretical Physics, Chalmers University of Technology, Gothenburg, Sweden, 1967 (unpublished).

[7] K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. 176, 589 (1968).

[8] K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, (a) Solid State Commun. 7, 1503 (1969); and (b) Phys. Rev. (to be published).

[9] See, e.g., D. Pines and P. Nozières, *The Theory of Quantum Liquids*, Vol. I (Benjamin, New York, 1966), p. 136.

[10] See, e.g., R. Balescu, in *Monographs in Statistical Physics and Thermodynamics*, Vol. 4, edited by I. Prigogine (Interscience, New York, 1963), p. 108.

[11] M. Nelkin, Phys. Rev. 183, 349 (1969).

[12] M. Nelkin and S. Ranganathan, Phys. Rev. 164, 222 (1967).

[13] In connection with this approximation, the following important observation has been made [K. S. Singwi (private communication)]: Starting from Eq. (13) and using the RPA expression (32) for $\epsilon(\vec{q})$ and for $S(\vec{q})$ the expression given by Eq. (15), one can exactly evaluate the function $G(\vec{q})$. If one now uses this $G(\vec{q})$ in Eqs. (9) and (11), one obtains a $S(\vec{q})$ which is exactly the same [or $g(r)$ for large values of r] as obtained earlier by T. O'Neil and N. Rostocker [Phys. Fluids 8, 1109 (1965); the expression $\Phi_I^{(2)}(r)$]. This is a result correct to order $\epsilon^2(\epsilon = b/L_D$ as defined by these authors).

[14] See the stabilization and convergence considerations in, e.g., F. Hermann and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Englewood Cliffs, N.J., 1963). As is known from Hartree-Fock calculations on atoms, the iterative process is usually unstable, and often divergent, when the final potential for one iteration is used as the initial potential for the next iteration. This is particularly true in the early iterations, when the potential is still far from its self-consistent limit. Similarly, oscillations occur in the present calculations when the guess of the initial $S(\vec{q})$ is too rough. Actually, one can show analytically [K. S. Singwi (private communication)] that for the case I, the choice of the Debye-Hückel form factor without cutoff leads to a logarithmic divergence in the second iteration.

[15] E. Meeron, J. Math. Phys. 1, 192 (1960); T. Morita, Progr. Theoret. Phys. (Kyoto) 23, 385 (1960); M. J. J. Van Leeuwen, J. Groenveld, and J. De Boer, Physica 25, 792 (1959).

[16] J. K. Percus and G. I. Yevick, Phys. Rev. 110, 1 (1958); J. K. Percus, Phys. Rev. Letters 8, 462 (1962); J. L. Lebowitz and J. K. Percus, J. Math. Phys. 4, 116 (1963).

[17] A. A. Broyles and H. L. Sahlin, Bull. Am. Phys. Soc. 8, 32 (1963); A. A. Broyles, H. L. Sahlin, and D. D. Carley, Phys. Rev. Letters 10, 319 (1963).

[18] D. D. Carley, Phys. Rev. 131, 1406 (1963); and

Ph.D. dissertation, University of Florida, 1963 (unpublished).

[19] R. Abe, Progr. Theoret. Phys. (Kyoto) 22, 213 (1959); J. G. Trulio and S. G. Brush, Phys. Rev. 121, 940 (1961).

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Quantum Corrections to the Second Virial Coefficient, with an Application to the Hard-Core-Plus-Square-Well Potential at High Temperatures

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A new formulation of the second-virial-coefficient problem, particularly useful for the computation of the direct second virial coefficient B_{dir} at high temperatures and as good as the phase-shift formulation at low temperatures, is given. High-temperature asymptotic expansions of B_{dir} for hard-core and hard-core-plus-square-well potentials are calculated. The exchange second virial coefficient for a hard-core-plus-square-well potential at high temperatures is investigated.

I. INTRODUCTION AND SUMMARY

A variety of approaches to the second-virial-coefficient problem can be found in the literature.[1] The phase-shift formulation developed by Gropper and by Beth and Uhlenbeck[2] is very useful at low temperatures, but difficult to handle at high temperatures because the number of phase shifts which contribute increases with temperature. The departure from Boltzmann statistics because of proper symmetrization of the wave function can be split off by expressing the second virial coefficient B as a sum $B=B_{\text{dir}}+B_{\text{exch}}$, where B_{dir} is computed using Boltzmann statistics. B_{exch} is exponentially small at high temperatures[3] for potentials more strongly repulsive than r^{-2} as $r\to 0$. B_{dir} can be calculated at high temperatures from the Wigner-Kirkwood expansion[4] in powers of $\hbar^2$ if the potential does not vary too rapidly.

The high-temperature calculation of B_{dir} when expansion in $\hbar^2$ fails has been considered by Mohling,[5] by Handelsman and Keller,[6] and by Hill.[7] The results of Mohling for the hard-core-plus-square-well potential are incorrect. The method of Handelsman and Keller and the previous method of Hill[7] are somewhat tedious to extend, either to higher order or to include an attractive well in the potential. The present formulation, based on the Laplace transform as was the previous method of Hill, is considerably less laborious to extend at high temperatures and is as useful as the phase-shift formulation at low temperatures.

Section II is devoted to the general formulation; the results are given by Eqs. (17)–(20), (27), (31), and (32). Sections III and IV are devoted to high-temperature calculations of B_{dir} for hard cores and for a hard-core-plus-square-well potential; the results are given by Eqs. (56) and (75), respectively. Section V calculates B_{exch} at high temperatures for a hard-core-plus-square-well potential; the results are given by Eqs. (76) and (91)–(95). Statements of the domain of validity of the results follow the results. Section VI traces the error in Mohling's[5] work.

II. GENERAL FORMULATION

We begin with the formulation of Boyd, Larsen, and Kilpatrick,[8] and write the second virial coefficient B in the form

$$B=B_{\text{dir}}+B_{\text{exch}}\ , \tag{1}$$

where

$$B_{\text{dir}}=2^{1/2}N\lambda^3\int d^3r\left[2^{-3/2}\lambda^{-3}-G(\vec{r},\vec{r};\beta)\right], \tag{2}$$

and

$$B_{\text{exch}}=\mp 2^{1/2}N\lambda^3(2S+1)^{-1}\int d^3r\, G(\vec{r},-\vec{r};\beta). \tag{3}$$

The minus (upper) sign in B_{exch} is associated with Bose statistics and the plus sign with Fermi statistics. Here S is the spin, $\lambda\equiv(2\pi\hbar\beta/m)^{1/2}$ is the thermal de Broglie wavelength, and $\beta=(kT)^{-1}$. G is the thermal Green's function for the relative motion:

$$G(\vec{r}',\vec{r};\beta)\equiv\langle\vec{r}'\,|\exp(-\beta H_{\text{rel}})|\,\vec{r}\rangle\ ,$$

where $H_{\text{rel}}=-(\hbar^2/m)\nabla^2+V(r)$