RADIAL DISTRIBUTION FUNCTIONS FOR LONG-RANGE FORCES*

A. A. Broyles, H. L. Sahlin, and D. D. Carley

University of Florida, Gainesville, Florida

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A recent Letter by Percus[1] presents a new derivation of integral equations for obtaining the radial distribution function $g(r)$ for a monatomic fluid whose particles interact pairwise. A paper by Broyles, Chung, and Sahlin[2] indicates that, of the Born-Green, convolution-hypernetted chain (CHNC), and Percus-Yevick (PY) equation, the PY equation appears to give the better agreement with Monte Carlo calculations for the Lennard-Jones 6-12 potential. Percus[1] gives his reasons for expecting good results from the PY equation for short-range potentials. The question is left open, however, as to the performance of these equations for long-range potentials of the Coulomb type. To answer this question, we present here one set of results for the radial distribution function for a classical electron gas calculated from the PY equation, the CHNC equation, and from a new method sketched below.

The PY and CHNC equations yield essentially the same results for short-range pair potentials in many cases but give considerably different answers for the long-range pair potentials. Our method makes possible the calculations of $g(r)$ for a long-range potential when the radial distribution function for a short-range potential, $g^{sr}(r)$, is given. For this method we employ the real and imaginary parts of the collective coordinates introduced by Bohm and Pines,[3]

$$\rho_{\vec{k}} = \sum_{i=1}^{N} \exp(i\vec{k}\cdot\vec{r}_i) = (X_{\vec{k}} + iX_{-\vec{k}})2^{-1/2}. \quad (1)$$

The Fourier transform of the radial distribution function is given by

$$g_{\vec{k}} = \frac{V}{Z}\int\cdots\int \exp\left\{i\vec{k}\cdot(\vec{r}_1 - \vec{r}_2) - \frac{U}{KT}\right\} \prod_{j=1}^{N} d\vec{r}_j, \quad (2)$$

where Z is the value of the integral in Eq. (2) when k is zero, and U is the potential energy of the system. Separating the pair potential into a sum of a long-range and a short-range part[4] and expressing the long-range part of the total potential energy in terms of the $X_{\vec{k}}$'s, we obtain

$$g_{\vec{k}} = \tfrac{1}{2}VZ_{sr}[N(N-1)Z]^{-1}\int\cdots\int(X_{\vec{k}}^2 + X_{-\vec{k}}^2)$$

$$\times\exp(-\sum_{\vec{k}}A_{\vec{k}}X_{\vec{k}}^2/2)J\prod_{\vec{k}}dX_{\vec{k}},$$

$$J = Z_{sr}^{-1}\int\cdots\int \exp(-U^{sr}/KT)\prod_{\vec{k}}\delta(X_{\vec{k}} - X_{\vec{k}}(\vec{r}_1\cdots\vec{r}_n))$$

$$\times\prod_{j=1}^{N}d\vec{r}_j,$$

$$A_{\vec{k}} = \phi_{\vec{k}}^{lr}/VKT, \quad (3)$$

where $\phi_{\vec{k}}^{lr}$ is the Fourier transform of the long-range part of the pair potential, and V is the volume of the system of N particles.

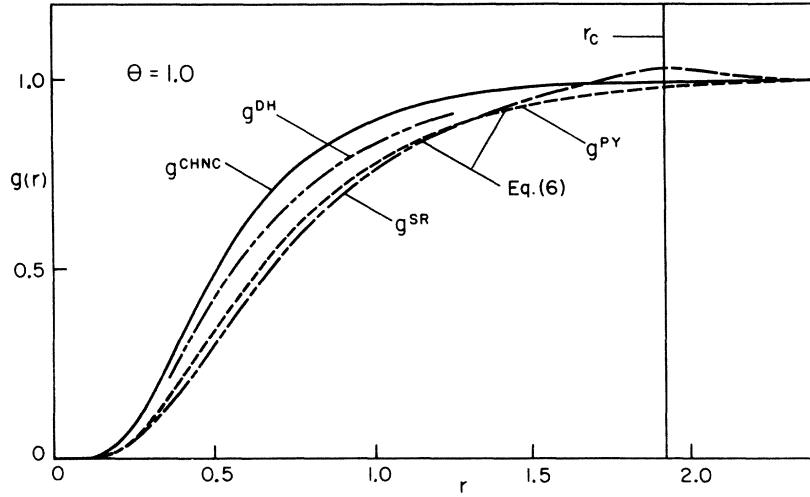It is known from the work of Bohm and Pines[3]

FIG. 1. Radial distribution functions. For $r/a > 1.3$, g from Eq. (6) is nearly equal to g^{PY}, while for $r/a < 1.3$, it is nearly equal to g^{sr}.

that a first approximation to J is given by

$$J = \prod_{\vec{k}} \exp(-\tfrac{1}{2} X_{\vec{k}}^2 / \langle X_{\vec{k}}^2 \rangle_J)(2\prod \langle X_{\vec{k}}^2 \rangle_J)^{-1/2}, \quad (4)$$

where $\langle \ \rangle_J$ means "quantity averaged over the weight function J." In cases usually found in the literature, $\exp(-U^{sr}/KT)$ is not included in the definition of J and consequently $\langle X_{\vec{k}}^2 \rangle_J = N$. For the more general case given here, one obtains

$$\langle X_{\vec{k}}^2 \rangle_J = N(N-1) V^{-1} g_{\vec{k}}^{sr} + N. \quad (5)$$

Substituting Eq. (5) into (4) and Eq. (4) into (3) gives, to a first approximation,

$$g_{\vec{k}} = \frac{\gamma}{N-1} \left\{ \frac{(N-1)V^{-1} g_{\vec{k}}^{sr} + 1}{N\beta V^{-1} \phi_{\vec{k}}^{lr}[(N-1)V^{-1} g_{\vec{k}}^{sr} + 1] + 1} - 1 \right\}.(6)$$

If J is expanded in a series of Hermite polynomials,[4] it is possible to obtain higher order terms for $g_{\vec{k}}$.

Radial distribution functions computed with the aid of Eq. (6) are shown in Fig. 1 together with the solutions to the PY and CHNC equations. For comparison the g given by the Debye-Hückel (DH) theory is also shown. The unit of length is the ion sphere radius a given by $a = (3V/4\pi N)^{1/3}$. A dimensionless parameter is defined by $\theta = aKT/q^2$ which is the temperature with the unit of energy equal to the potential energy of two ions separated by a unit distance. The g^{sr} shown in Fig. 1 is

computed for a short-range potential

$$\phi^{sr} = q^2(r^{-1} - r_c^{-1}), \quad r \le r_c,$$

$$= 0, \quad r > r_c. \quad (7)$$
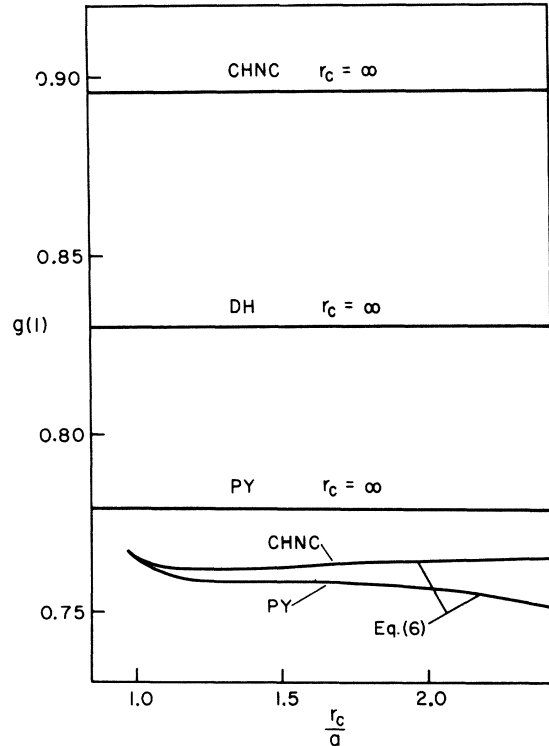
For the curve shown, $r_c = 1.9$. Figure 2 shows

FIG. 2. $g(1.0)$ from Eq. (6) as a function of r_c. For comparison, the corresponding g^{DH}, g^{PY}, and g^{CHNC} are also plotted for $r_c = \infty$.

the behavior of $g(1.0)$ from Eq. (6) as a function of r_c. Also shown for comparison are $g^{CHNC}(1.0)$, $g^{PY}(1.0)$, and $g^{DH}(1.0)$. The lables CHNC and PY on the lowest curves in Fig. 2 indicate the results obtained with Eq. (6) when g^{sr} is calculated with the CHNC and PY equations, respectively.

Any errors in g from Eq. (6) might be expected to vary with r_c. When these errors are negligible, g will be independent of r_c. For this reason, we believe that the flat region of g in Fig. 2 (where the CHNC and PY equations are producing almost the same g^{sr}) may be very close to the exact value of g. This value compares much more favorably with g^{PY} than with g^{CHNC} (with $r_c = \infty$).

In conclusion then, we are lead to believe that the PY equation is superior to the CHNC equation for long-range potentials as well as short-range at the temperatures and densities we have investigated. In addition, the procedure described here may provide a means of determining a nearly exact g in cases where it shows a region independent of r_c.

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EXACT SOLUTION OF THE PERCUS-YEVICK INTEGRAL EQUATION FOR HARD SPHERES*

M. S. Wertheim†

Courant Institute of Mathematical Sciences, New York University, New York, New York

An increasing body of numerical computations has given strong evidence for the adequacy, over an extensive range of parameters, of various approximate integral equations for the radial distribution function of a classical fluid. The simplest, and on the basis of comparisons thus far made, the most satisfactory of these, is due to Percus and Yevick (PY).[1] Despite its simplicity, this equation until now has not been solved rigorously in any special situation, so that its basic properties have not been ascertained. It is the purpose of this Letter to obtain in closed form the pair distribution and equation of state of the PY equation for the prototype of interacting hard spheres.

The PY equation[1] for hard spheres is given by

$$\tau(\vec{r}) = 1 + n\int_{|\vec{r}\,'| < R} \tau(\vec{r}\,')d\vec{r}\,'$$

$$- n\int_{|\vec{r}\,'| < R,} \tau(\vec{r}\,')\,\tau(\vec{r} - \vec{r}\,')d\vec{r}\,', \qquad (1)$$

$$|\vec{r} - \vec{r}\,'| > R$$

where R is the hard-sphere diameter, n is the particle density. The function $\tau(\vec{r})$ of PY[1] is related to the pair distribution function $g(\vec{r})$ and the direct correlation function $C(\vec{r})$ of Ornstein and Zernike[2] by

$$g(\vec{r}) = 0 \qquad (r < R),$$
$$g(\vec{r}) = \tau(\vec{r}) \qquad (r > R),$$
$$C(\vec{r}) = -\tau(\vec{r}) \qquad (r < R),$$
$$C(\vec{r}) = 0 \qquad (r > R). \qquad (2)$$

If we take the one-side Laplace transform of (1), defining

$$F(t) = R^{-2}\int_0^R r\tau(r)\exp(-sr)dr,$$

$$G(t) = R^{-2}\int_R^\infty r\tau(r)\exp(-sr)dr,$$

$$K = R^{-3}\int_0^R \tau(r)r^2 dr,$$

$$\eta = \tfrac{1}{6}\pi R^3 n, \qquad sR = t,$$

we obtain

$$t[F(t) + G(t)] = t^{-1}[1 + 24\,\eta K]$$

$$- 12\,\eta[F(-t) - F(t)]G(t), \qquad (3)$$

where the real part of s must be greater than zero.

On expanding the PY equation in powers of the density, one finds that in second order $C(r)$ retains the functional form obtained in first order, namely, a cubic polynomial with quadratic term absent. This suggests trying a solution of the form

$$-C(x) = \alpha + \beta x + \gamma x^2 + \delta x^3, \qquad (4)$$

where $x = (r/R)$, computing $F(t)$ and $F(-t)$ and solving Eq. (3) for $G(t)$. One can show directly from (1) that $\tau^{(n)}(r)$, with the superscript denoting differentiation, is continuous at $r = R$ for $n = 0, 1, 2$, and that $\tau(0) = 1 + 24\,\eta K$. The values of