DISCUSSION

As now developed, the slice method is accurate enough for studies in liquid-drop nuclear fission. This is being done and preliminary results will be published shortly. With its extension to elliptical disks the method should also be useful for further calculations of the equilibrium shapes of liquid-drop nuclei with high angular momentum[6,9] and for the dynamics of close binary stars.

[9] B. C. Carlson and Pao Lu, in *Proceedings of the Rutherford Jubilee International Conference, Manchester, 1961*, edited by J. B. Berks (Academic Press Inc., New York, 1961).

ACKNOWLEDGMENTS

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Computations of Radial Distribution Functions for a Classical Electron Gas*

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The radial distribution functions g for a classical electron gas computed using the Percus-Yevick (PY) equation, convolution hypernetted chain (CHNC) equation, and the Broyles-Sahlin (BS) method, have been compared with the Debye-Hückel (DH) theory. The quantities $E\equiv\bar{U}/Nkt$ and $P\equiv p/\bar{n}kT$ have been computed from these g's. Computations have been made for values of θ of 20, 10, 5, 3, and 1; $\theta=kTa/q^2$, where a is the ion sphere radius. The PY and BS results show the best agreement, particularly at $\theta<3$. The BS method has been of particular value in this study of a long-range potential. In the range of θ studied, g never exceeds one, that is, there is no oscillatory behavior of g.

I. INTRODUCTION

In a classical one-component fluid having an average number density $\bar{n}=N/V$, where N is the number of particles and V the volume, the average number density $n(r)$ about a given particle is, in general, not constant. The radial distribution function $g(r)$ is the factor by which $n(r)$ differs from $\bar{n}$ and is defined by $n(r)=\bar{n}g(r)$. As a result of the Maxwell-Boltzmann classical distribution law, $g(r)$ may be written, in the limit as N approaches infinity, as[1]

$$g(r)=V^2Z^{-1}\int_V\cdots\int e^{-U/kT}dr_3\cdots dr_N,$$
$$Z=\int_V\cdots\int e^{-U/kT}dr_1\cdots dr_N, \tag{1}$$

where U is the potential energy. In the following, U will be assumed to be the sum of pair potentials $\phi(r)$.

The radial distribution function is important because thermodynamic quantities can be calculated once $g(r)$ and $\phi(r)$ are known. Of particular interest here are the relations for the pressure and mean potential energy,[1]

$$E\equiv\bar{U}/NkT=2\pi\bar{n}(kT)^{-1}\int_0^\infty\phi(r)g(r)r^2dr, \tag{2}$$

$$P\equiv p/\bar{n}kT=1-2\pi\bar{n}(3kT)^{-1}\int_0^\infty r^3g(r)\frac{d\phi(r)}{dr}dr. \tag{3}$$

$\bar{U}/N$, the mean potential energy per particle, is often referred to as the correlation energy.

A direct evaluation of Eq. (1) to determine g is not practical and, consequently, several approximate methods have been developed; there are four methods which are of interest here. Using a collective coordinate technique Percus and Yevick[2] formed an integral equation (PY) for g. A second integral equation was obtained by a summation procedure of Mayer-type diagrams and has been given the name convolution hypernetted chain equation (CHNC).[3] A third method,

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[1] Terrell L. Hill, *Introduction to Statistical Thermodynamics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1960).

[2] J. K. Percus and G. J. 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).

[3] E. Meeron, J. Math. Phys. **1**, 192 (1960); T. Morita, Progr. Theoret. Phys. (Kyoto) **23**, 385 (1960); J. M. J. Van Leeuwen, J. Groeneveld, and J. DeBoer, Physica **25**, 792 (1959); M. S. Green, Tech. Rept. Hughes Aircraft Corporation (unpublished).

the Broyles-Sahlin[4] method (BS), separates the pair potential into a sum of a long and short range part. The g corresponding to the short-range part is calculated using an equation 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. The fourth method, Debye-Hückel (DH), applies only to Coulomb interactions.[5] This theory provides an explicit equation for g which is valid for low densities and high temperatures. In spite of the limited range of the DH theory, it is important because it is relatively simple to use.

Similar calculations have already been made comparing integral equations for g for a short-range (Lennard-Jones) potential.[6] Here we extend the computations and comparisons to a long-range interaction, the Coulomb interaction.

II. THE CLASSICAL ELECTRON GAS

We consider a system of particles of the same charge imbedded in a neutralizing uniform background of charge of opposite sign. It is convenient to choose as the unit of length the ion sphere radius a given by

$$a=[3/(4\pi\bar{n})]^{1/3} \tag{4}$$

and to define a dimensionless parameter θ by

$$\theta=kTa/q^2. \tag{5}$$

For the system considered and in terms of θ with a as the unit of length, Eqs. (2) and (3) are specialized to

$$E=3(2\theta)^{-1}\int_0^\infty r[g(r)-1]dr, \tag{6}$$

$$P=1+(2\theta)^{-1}\int_0^\infty r[g(r)-1]dr. \tag{7}$$

From (6) and (7) it is seen that

$$P=1+\tfrac{1}{3}E. \tag{8}$$

The relationship (8) also follows directly from the virial theorem. The -1 in $[g-1]$ in (6) and (7) comes from the uniform background.

III. THE EQUATIONS AND NUMERICAL SOLUTIONS

The PY and CHNC integral equations may be written in the form[6]

$$H(r)=2\pi\bar{n}\int_0^\infty\int_{t=|s-r|}^{t=s+r} I(t)G(s)dtds;$$

$$\begin{aligned} &G(r)=r(1-g);\\ &I(r)=H-r(g-1);\\ &g(r)=(1+H/r)\exp[-\phi(r)], \quad \text{(PY)}\\ &g(r)=\exp(H/r)\exp[-\phi(r)], \quad \text{(CHNC)}. \end{aligned} \tag{9}$$

The iteration procedure used to solve Eq. (9) is discussed in Ref. 6.

For the Coulomb problem the basic equation of the BS method is

$$F(k)=3^{-1}\left\{\frac{3F^{\rm sr}(k)+1}{q^{-2}3\theta^{-1}\Phi^{\rm lr}(k)[3F^{\rm sr}(k)+1]+1}-1\right\}, \tag{10}$$

$f(r)=g(r)-1$ is the correlation function.

The functions of k are transforms of the functions of r and are denoted by the corresponding capital letters, so that

$$F(k)=\frac{1}{k}\int_0^\infty r\sin(kr)f(r)dr \tag{11}$$

$$f(r)\equiv\frac{2}{\pi}\frac{1}{r}\int_0^\infty k\sin(kr)F(k)dk. \tag{12}$$

The superscript sr refers to short range and lr to long range.

The g's for the BS method were calculated in the following manner. The potential was separated into two parts:

$$\begin{aligned} &\phi(r)=\phi^{\rm sr}(r)+\phi^{\rm lr}(r),\\ &\phi^{\rm sr}=q^2(r^{-1}-r_c^{-1}), \quad \phi^{\rm lr}=q^2r_c^{-1} \quad \text{for} \quad r<r_c,\\ &\phi^{\rm sr}=0 \qquad\qquad \phi^{\rm lr}=q^2r^{-1} \quad \text{for} \quad r>r_c. \end{aligned} \tag{13}$$

The radial distribution function $g^{\rm sr}$ was calculated using $\phi^{\rm sr}$ in the PY or CHNC equation. Having thus obtained $g^{\rm sr}$, g was readily obtained using Eqs. (10)-(13). The computations were carried out on an IBM 709 digital computer. H. L. Sahlin has pointed out that if we take $r_c=0$, then we get

$$g(r)=1-(r\theta)^{-1}\exp[-r(3/\theta)^{1/2}]. \tag{14}$$

This is the linearized Debye-Hückel solution. [Compare with Eq. (15).]

The equation from Debye-Hückel theory is an explicit equation for g. In our system of units it is

$$g(r)=\exp\{-(r\theta)^{-1}\exp[-r(3/\theta)^{1/2}]\}. \tag{15}$$

A comparison of the four approximations may be made by looking at the forms of the direct correlation function $C(\bar{r})$. The correlation function $f(\bar{r})$ and direct correlation function are related by the Ornstein and Zernicke equation

$$f(\bar{r})=C(\bar{r})+\bar{n}\int f(\bar{s})C(\bar{s}-\bar{r})d\bar{s}. \tag{16}$$

In the respective methods, the direct correlation func-

[4] 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).

[5] P. Debye and E. Hückel, Physik. Z. **24**, 185 (1923).

[6] A. A. Broyles, S. U. Chung, and H. L. Sahlin, J. Chem. Phys. **37**, 2462 (1962).

tion is given by

$$\begin{aligned} &C(r)=-\phi(r)/kT, \quad \text{DH (linearized)} \\ &C(r)=g(r)-1-\ln g(r)-\phi(r)/kT, \quad \text{CHNC} \\ &C(r)=[1-\exp(\phi(r)/kT)]g(r), \quad \text{PY} \\ &C(r)=C^{\text{sr}}(r)-\phi^{\text{lr}}(r)/kT, \quad \text{BS}. \end{aligned} \tag{17}$$

It is interesting to compare the form $C(r)$ of the BS method with that of the DH (linearized). It should be re-emphasized that our DH calculations were carried out using Eq. (15) and not the linearized form of Eq. (14).

IV. DISCUSSION OF RESULTS

The computed g's are listed in Tables I through V. The quantity $-E$ was computed from Eq. (6) by numerical integration and the results are listed in Table VI. The quantity P was then determined using (8) and the results are given in Fig. 1. In the Tables we have generally followed the custom of retaining one uncertain figure. It is unfortunate that small errors in g tend to be magnified into rather large errors in E, particularly at the higher θ's.

It should be noted that g is negative for some values of r in the BS method. This failure at small r is characteristic of the collective coordinate approach as used in the BS method. However, the error in P and E is negligible because the error in g is small and because r is small in the region of error [see Eq. (6)].

We note that at $\theta=20$ the g's are nearly the same for all methods. The small differences may not be significant because of the errors introduced in the numerical computations. However, at the other extreme, the differences in the g's for $\theta=1$ are very significant. We find the PY and BS g's nearly the same, but in disagreement with CHNC and DH. For reasons discussed in Ref. 4, we believe that the BS method is providing a good approximation to g in the range of θ presented here.

The BS method offers certain computational advantages. In calculating g by means of the CHNC or PY equations, computational errors are dependent upon the interval spacing and range of the numerical integration. For a long-range potential such as the Coulomb potential, the effect of terminating the integration at a finite point is particularly important. Near the termination point the error in g is large, but diminishes as r decreases. In the CHNC and PY equations it is necessary to choose an integration range of r much larger than

TABLE I. Radial distribution function for $\theta=20.0$.

	Radial distribution function			
r/a	DH	CHNC	PY	BS ($r_c=2.34a$)
0.00	0.000	0.000	0.000	0.000
0.05	0.375	0.375	0.375	0.368
0.01	0.618	0.621	0.621	0.614
0.15	0.730	0.734	0.734	0.727
0.20	0.793	0.798	0.798	0.791
0.30	0.862	0.867	0.867	0.860
0.40	0.898	0.904	0.904	0.897
0.50	0.921	0.926	0.926	0.920
1.00	0.966	0.971	0.971	0.966
1.50	0.982	0.985	0.985	0.981
2.00	0.988	0.991	0.991	0.988
2.50	0.992	0.994	0.994	0.992

TABLE II. Radial distribution function for $\theta=10.0$.

	Radial distribution function			
r/a	DH	CHNC	PY	BS ($r_c=2.34a$)
0.00	0.000	0.000	0.000	0.000
0.05	0.143	0.146	0.146	0.135
0.10	0.388	0.394	0.393	0.380
0.15	0.541	0.550	0.549	0.534
0.20	0.639	0.649	0.648	0.633
0.30	0.753	0.766	0.765	0.749
0.40	0.818	0.831	0.830	0.814
0.50	0.859	0.872	0.870	0.856
1.00	0.944	0.954	0.953	0.942
1.50	0.971	0.979	0.978	0.970
2.00	0.983	0.989	0.989	0.983
2.50	0.990	0.994	0.994	0.990

TABLE III. Radial distribution function for $\theta=5.0$.

	Radial distribution function			
r/a	DH	CHNC	PY	BS ($r_c=2.34a$)
0.00	0.000	0.000	0.000	0.000
0.05	0.021	0.024	0.024	0.014
0.10	0.157	0.164	0.162	0.147
0.15	0.305	0.317	0.314	0.293
0.20	0.424	0.441	0.436	0.412
0.30	0.589	0.612	0.606	0.577
0.40	0.693	0.718	0.711	0.681
0.50	0.762	0.788	0.781	0.752
1.00	0.912	0.933	0.929	0.907
1.50	0.959	0.974	0.971	0.957
2.00	0.979	0.988	0.987	0.978
2.50	0.988	0.995	0.994	0.988

TABLE IV. Radial distribution function for $\theta=3.0$.

	Radial distribution function			
r/a	DH	CHNC	PY	BS ($r_c=2.34a$)
0.00	0.000	0.000	0.000	0.000
0.05	0.002	0.000	0.000	0.003
0.10	0.049	0.037	0.035	0.026
0.15	0.147	0.128	0.120	0.104
0.20	0.255	0.236	0.223	0.198
0.30	0.439	0.432	0.410	0.373
0.40	0.572	0.579	0.553	0.510
0.50	0.667	0.685	0.658	0.613
1.00	0.884	0.914	0.896	0.863
1.50	0.952	0.972	0.964	0.944
2.00	0.978	0.990	0.986	0.976
2.50	0.989	0.996	0.994	0.989

the range in which one is interested because a portion near the cutoff, where the error is large, must be discarded. This is important since the computation time increases very rapidly with the range of integration. In computing g^{sr} we use a short-range potential which is zero beyond r_c and the effect of terminating the integration at a finite point is no longer important. Thus, almost the entire range of g^{sr} is available for use in the BS procedure; this results in a considerable saving in computer time.

TABLE V. Radial distribution function for $\theta=1.0$.

	Radial distribution function			
r/a	DH	CHNC	PY	BS ($r_c=1.87a$)
0.00	0.000	0.000	0.000	0.000
0.10	0.000	0.000	0.000	0.000
0.20	0.029	0.034	0.020	0.012
0.30	0.137	0.163	0.100	0.083
0.40	0.286	0.335	0.221	0.193
0.50	0.431	0.498	0.351	0.315
0.60	0.554	0.632	0.470	0.433
0.70	0.653	0.734	0.574	0.538
0.80	0.731	0.810	0.661	0.629
0.90	0.791	0.864	0.732	0.704
1.00	0.838	0.903	0.789	0.767
1.50	0.951	0.982	0.940	0.936
2.00	0.984	0.996	0.984	0.985
2.50	0.995	0.999	0.996	0.994

TABLE VI. $-E\equiv-\bar{U}/NkT$ as a function of θ.

	$-E$				
θ	DH	CHNC	PY	BS	Abe
20	0.00935	0.008	0.008	0.0094	0.00988
10	0.0252	0.019	0.020	0.0258	0.0257
5	0.0659	0.0483	0.0509	0.0688	0.0685
3	0.129	0.0976	0.111	0.144	0.139
1	0.468	0.328	0.539	0.577	0.624

E and P as calculated from the BS g show close agreement with results from Abe's[7] work. The values of E listed in Table VI under "Abe" are approximate numbers obtained from interpolation of the values listed by Trulio and Brush.[8] With the possible exception of $\theta=1$, the differences are not significant; i.e., E as calculated by the BS method and the Abe method are the same within the accuracy of our calculations.

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

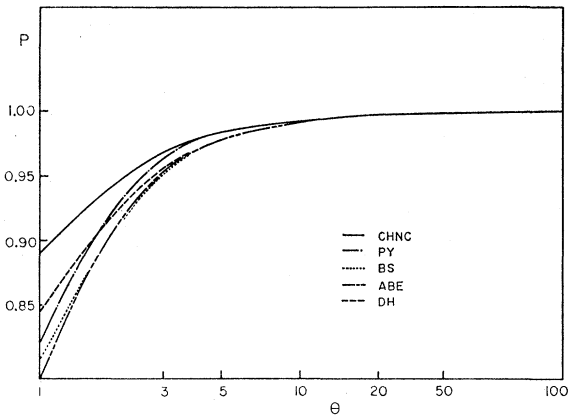

FIG. 1. The function $P\equiv p/\bar{n}kT$ as a function of θ for the PY, CHNC, BS, DH, and Abe theories.

If we assume that the BS procedure gives nearly the correct results, then we may note the following points. First, the CHNC and PY equations give nearly the same results at high θ but the PY equation is superior at lower θ. Second, in the range of θ studied, the asymptotic value of g for large r is simply the DH value. Third, in the range of θ studied g does not exceed one, that is, there is no oscillatory behavior of g. Fourth, the DH theory gives good results for θ equal to and greater than five. At $\theta=5$ the error in E is only 4.2%.

As θ is lowered, the solutions to the integral equations (9) become more difficult to obtain; in our iterative procedure the convergence becomes slower and less stable. Preliminary results in these lower θ regions indicate that g begins to exceed one and, hence, to show oscillatory behavior in the neighborhood of $\theta\approx0.5$. We plan to study this interesting region of θ further and are particularly interested in determining whether the BS method continues to be independent of r_c over a range of cutoff values.

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