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Solutions to the Percus-Yevick Equation*

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The radial distribution function for a classical fluid of particles interacting with the Lennard-Jones potential has been computed by solving the Percus-Yevick integral equation numerically. The solutions and the quantities, p/nkT and E/NkT, are compared with those obtained by Wood and Parker using Monte Carlo techniques. The radial distribution functions agree to better than 15% beyond the first points where they are unity while the thermodynamic quantities differ by, at most, 3% from the range of Monte Carlo values for cases where the system is believed to be in a liquid state. The quantity

$$K=-(1/V)(\partial V/\partial p)_{N,T},$$

has also been computed.

I. INTRODUCTION

THE radial distribution function g is proportional to the probability density that a second particle will be found to lie at a position a displacement $\mathbf{r}$ from a given particle in a system in thermal equilibrium. This paper will consider only classical fluids consisting of one kind of particles interacting pairwise with a potential energy $\phi(r)$. In this case, the radial distribution function depends upon r alone and approaches a constant at large r given by (through order N^{-1})

$$g\sim 1-nkTKN^{-1}, \tag{1}$$

where[1]

$$K=-(1/V)(\partial V/\partial p)_{N,T}. \tag{2}$$

A number of useful thermodynamic quantities can be computed from g such as

$$nkTK=1+4\pi n\int_0^{r_c}(1-g)r^2dr, \tag{3}$$

$$p/nkT=1-(2\pi n/3kT)\int_0^{\infty}\phi' g r^3 dr, \tag{4}$$

and[2,3]

$$(E/NkT)-\tfrac{3}{2}=E'/NkT=(2\pi n/kT)\int_0^{\infty}\phi g r^2 dr. \tag{5}$$

The value of r_c in Eq. (3) is much larger than unity but much smaller than the size of the system. It is necessary to cut off the integration in this way because of the terms or order N^{-1} in g as shown by Eq. (1). Several integral equations have been derived to determine g approximately. One of these was obtained by Percus and Yevick[4] using their collective coordinate techniques and will be referred to here as the PY equation. The PY equation (and others) may be written in the form

$$y(r)=1+n\int F(f(s),f(s-r),y(s),y(s-r))ds, \tag{6}$$

where

$$y=g\exp(\phi/kT) \quad \text{and} \quad f=\exp(-\phi/kT)-1.$$

For the PY equation F is given by

$$F_{PY}=f(s)y(s)[y(s-r)f(s-r)+y(s-r)-1]. \tag{7}$$

The radial distribution function for the case where ϕ is given by the Lennard-Jones potential,

$$\phi=4\epsilon[(a/r)^{12}-(a/r)^{6}], \tag{8}$$

has been computed by Wood and Parker[5] for several densities with a value of kT/ϵ equal to 2.74. It is interesting to compare the solutions of the integral equation with the Monte Carlo calculations. Such comparisons indicate the reasonableness of the approximations made in deriving the integral equations. It may also be easier in some cases to obtain radial distribution functions by numerical solution of an integral equation than by Monte Carlo techniques. A comparison has already been made between the Monte Carlo calculations and the solutions to the Born-Green equation.[6,7] It is the purpose of this paper to make the comparison between Monte Carlo and PY radial distribution functions as well as the thermodynamic quantities in Eqs. (3)-(5).

It is convenient to choose the parameter a in Eq. (8) to be the unit of length and this is done throughout this paper.

II. REDUCTION OF THE PY EQUATION

The integration of the angle between s and $s-r$ in Eq. (6) may be readily carried out to reduce the equa-

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[3] Reference 1, pp. 189, 190.

[4] J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958), p. 9, Eq. (66).

[5] W. W. Wood and F. R. Parker, J. Chem. Phys. **27**, 720 (1957).

[6] A. A. Broyles, J. Chem. Phys. **33**, 456 (1960).

[7] A. A. Broyles, J. Chem. Phys. (to be published).

TABLE I. Numerical solution to the PY equation and comparison with the Monte Carlo solution of Wood and Parker and with g_a for $na^3=2/5$ and $kT/\epsilon=2.74$.

r	h	g_{PY}	$(g_{MC}/g_{PY})-1$	$(g_a/g_{PY})-1$
0.80	1.301	0.0000		
0.85	1.296	0.0025		
0.90	1.290	0.1272	−0.016	5.806
0.95	1.277	0.6575	−0.012	0.647
1.00	1.265	1.265	−0.060	−0.018
1.05	1.254	1.575	−0.041	−0.146
1.10	1.246	1.622	−0.029	−0.141
1.15	1.237	1.539	−0.013	−0.093
1.20	1.231	1.420	0.002	−0.042
1.3	1.235	1.208	0.001	0.017
1.4	1.259	1.064	0.005	0.012
1.5	1.306	0.978	0.001	−0.018
1.6	1.380	0.936	−0.006	−0.036
1.7	1.482	0.923	−0.016	−0.027
1.8	1.617	0.937	−0.013	−0.009
1.9	1.776	0.963	−0.014	0.005
2.0	1.959	1.002	−0.012	0.000
2.1	2.112	1.023	−0.003	−0.001
2.2	2.235	1.029	0.000	−0.002

tion to

$$y(r)=1+2\pi nr^{-1}\int_{s=0}^{\infty}\int_{t=|s-r|}^{s+r}F_1(s,t)t\,dt\;\;s\,ds, \tag{9}$$

where

$$F(f(s),f(t),y(s),y(t))=F_1(s,t). \tag{10}$$

Equation (9) may now be multiplied through by r to give

$$h(r)=r+2\pi n\int_{s=0}^{\infty}\int_{t=|s-r|}^{s+r}F t\,dt\;s\,ds, \tag{11}$$

where

$$h(r)=ry=rg\exp(\phi/kT). \tag{12}$$

Differentiating Eq. (11) by r gives the equation

$$h'(r)=1+2\pi n\int_0^{\infty}[(s+r)F_1(s,s+r)+(s-r)F_1(s,|s-r|)]s\,ds. \tag{13}$$

On substituting for the F_1's, we have finally

$$h'(r)=1-2\pi n\int_0^{\infty}\{1-\exp[-\phi(s)/kT]\}h(s)\{h(s+r)\times\exp[-\phi(s+r)/kT]+h(|s-r|)\times\exp[-\phi(|s-r|)/kT][(s-r)/|s-r|]-2s\}ds. \tag{13'}$$

From Eq. (11), it can be seen that as r approaches zero, the inner integral of the last term vanishes so that $h(r)$ approaches zero. Thus we have

$$h(r)=\int_0^r h'(s)ds. \tag{14}$$

Equations (13′) and (14) were solved numerically to obtain $h(r)$ and, therefore, g through Eq. (12).

III. SERIES EXPANSION FOR h

A series expansion for $h(r)$ around $r=0$ can be obtained as follows. Equation (13) may be rewritten as

$$h'(r)=1+2\pi n\int_0^{\infty}[G(s,s+r)+G(s,s-r)]ds, \tag{15}$$

where

$$G(s,t)=stF(s,|t|). \tag{16}$$

A series expansion of G is given by

$$G(s,t)=\sum_{j=0}^{\infty}\frac{(t-s)^j}{j!}(\partial^jG/\partial t^j)_{t=s}. \tag{17}$$

If this series is substituted into Eq. (15), it reduces to

$$h'(r)=1+4\pi n\int_0^{\infty}G(s,s)ds+4\pi n\sum_{j=1}^{\infty}\frac{r^{2j}}{(2j)!}\int_0^{\infty}(\partial^jG/\partial t^j)_{t=s}ds. \tag{18}$$

TABLE II. Numerical solution to the PY equation and comparison with the Monte Carlo solution of Wood and Parker and with g_a for $na^3=5/6$ and $kT/\epsilon=2.74$.

r	h	g_{PY}	$(g_{MC}/g_{PY})-1$	$(g_a/g_{PY})-1$
0.80	3.349	0.0000		
0.85	3.017	0.0059		
0.90	2.720	0.2683	0.772	2.966
0.95	2.396	1.233	0.078	0.060
1.00	2.098	2.098	−0.083	−0.293
1.05	1.828	2.295	−0.047	−0.312
1.10	1.585	2.063	−0.041	−0.225
1.15	1.376	1.712	−0.020	−0.096
1.20	1.210	1.396	−0.016	0.033
1.3	0.992	0.970	0.020	0.183
1.4	0.921	0.778	0.060	0.117
1.5	0.978	0.733	0.036	−0.024
1.6	1.133	0.768	0.003	−0.069
1.7	1.368	0.852	0.014	−0.026
1.8	1.673	0.969	0.006	0.016
1.9	2.016	1.093	−0.007	0.010
2.0	2.276	1.164	−0.021	−0.010
2.1	2.336	1.131	−0.010	−0.005
2.2	2.270	1.045	0.004	0.009

TABLE III. Numerical solution to the PY equation and comparison with the Monte Carlo solution of Wood and Parker and with g_a for $na^3=1.0$ and $kT/\epsilon=2.74$.

r	h	g_{PY}	$(g_{MC}/g_{PY})-1$	$(g_a/g_{PY})-1$
0.80	5.345	0.0000		
0.85	4.632	0.0091		
0.90	3.959	0.3904	0.333	2.197
0.95	3.279	1.687	0.024	−0.138
1.00	2.674	2.674	−0.042	−0.408
1.05	2.117	2.659	−0.083	−0.388
1.10	1.662	2.163	−0.081	−0.267
1.15	1.295	1.612	−0.033	−0.083
1.20	1.030	1.188	0.021	0.113
1.3	0.736	0.719	0.145	0.339
1.4	0.699	0.590	0.116	0.175
1.5	0.860	0.644	0.023	−0.043
1.6	1.138	0.772	−0.042	−0.055
1.7	1.487	0.927	−0.030	0.016
1.8	1.895	1.097	−0.031	0.038
1.9	2.294	1.244	−0.033	−0.009
2.0	2.458	1.256	−0.014	−0.043
2.1	2.275	1.102	−0.002	−0.015
2.2	2.022	0.931	0.063	0.024

TABLE IV. Numerical solution to the PY equation and comparison with the Monte Carlo solution of Wood and Parker and with g_a for $na^3=10/9$ and $kT/\epsilon=2.74$.

r	h	g_{PY}	$(g_{MC}/g_{PY})-1$	$(g_a/g_{PY})-1$
0.80	7.925	0.0000		
0.85	6.599	0.0130		
0.90	5.412	0.533	−0.288	2.347
0.95	4.221	2.172	−0.263	−0.053
1.00	3.236	3.236	−0.150	−0.332
1.05	2.320	2.913	0.030	−0.278
1.10	1.649	2.147	0.164	−0.111
1.15	1.130	1.404	0.308	0.151
1.20	0.777	0.896	0.316	0.427
1.3	0.492	0.481	−0.013	0.349
1.4	0.546	0.461	−0.047	−0.317
1.5	0.850	0.637	−0.122	−0.413
1.6	1.243	0.843	−0.288	−0.150
1.7	1.667	1.039	−0.201	0.079
1.8	2.138	1.238	0.154	0.118
1.9	2.507	1.360	0.162	0.038
2.0	2.468	1.262	−0.089	−0.019
2.1	2.021	0.979	−0.132	0.009
2.2	1.691	0.778	0.027	0.021

TABLE V. Numerical solution to the PY equation for small r and comparison with two terms of the series solution for $na^3=10/9$.

na^3 / r	2/5 $h(r)$	5/6 $h(r)$	1.0 $h(r)$	10/9 $h(r)$	10/9 $h_2(r)$
0.0	0.000	0.000	0.000	0.000	0.000
0.1	0.377	1.695	3.273	5.652	5.596
0.2	0.688	2.997	5.725	9.866	8.947
0.3	0.922	3.892	7.244	12.416	7.808
0.4	1.088	4.305	7.994	13.518	−0.068
0.5	1.200	4.587	8.063	13.414	
0.6	1.266	4.293	7.560	12.242	
0.7	1.300	3.898	6.605	10.309	
0.8	1.302	3.349	5.346	7.926	

This may be integrated term by term to give a series for $h(r)$ according to Eq. (14).

IV. NUMERICAL SOLUTION

Equations (13′) and (14) were solved numerically on the IBM 650 of the University of Florida Statistical Laboratory using the techniques described in reference 6.

Solutions for $h(r)$ were checked by substituting them under the integral signs in Eqs. (13′) and (14) and comparing with the resulting $h(r)$ of Eq. (14). It is believed that $h(r)$ and, therefore, $g(r)$ have been determined to an error less than 1% for all solutions presented in Tables I–V.

These solutions were computed for parameters $kT/\epsilon=2.74$ and n (in units of "a") equal to $\frac{2}{5}$, $\frac{5}{6}$, 1.0,

TABLE VI. Parameters in the fit to g_{PY} in Eq. (19), the maximum r used for IBM 650 calculations, and thermodynamic quantities computed from the PY solution and from Monte Carlo by Wood and Parker.

na^3	2/5	5/6	1	10/9
b	−7.54	−3.10	−2.04	−3.79
α	2.53	1.49	1.12	1.16
m	5.92	6.81	7.20	7.36
c	2.36	2.91	3.00	2.85
r_m	3.5	4.0	4.5	4.975
$(nkTK)_{PY}$[a]	0.48	0.013	0.36	0.19
$(nkTK)_{PY}$[b]	0.48	0.068	0.033	0.018
$(p/nkT)_{PY}$	1.236	4.01	6.86	10.0
$(p/nkT)_{MC}$	1.2–1.5	4.01	7.03	7.8
$(E'/NkT)_{PY}$	−0.865	−1.60	−1.65	−1.47
$(E'/NkT)_{MC}$	−0.86	−1.58	−1.60	−1.90

[a] From Eq. (3).
[b] From differentiating $(p/nkT)_{PY}$.

and $\frac{10}{9}$. The parameter v/v^* used by Wood and Parker[5] is equal to n^{-1}. Tables I–IV list in the second and third columns the values of h and g obtained from the PY equation. The fourth columns of Tables I–IV compare g_{PY} from the third column with that obtained by Monte Carlo techniques[5] by listing $(g_{MC}/g_{PY})-1$. In the same manner column five compares g_{PY} to a fit to g_{PY}, g_a, given by

$$g_a=1+be^{-\alpha r}\sin(mr-c). \tag{19}$$

The first two coefficients in the series for $h(r)$ were computed for $n=\frac{10}{9}$ and it was found that the first two terms are given by

$$h_2(r)=59.70r-374.2r^3. \tag{20}$$

Values of $h_2(r)$ are listed in the last column of Table V for comparison with $h(r)$.

The parameters used in Eq. (19) are listed in Table VI together with the thermodynamic quantities in Eqs. (3)–(5). The quantity r_m contained in Table VI is the maximum of r used in the machine calculations. To evaluate the integral occurring in Eq. (3), it was necessary to assume that g was represented well by g_a for values of r beyond r_m. This may not be unreasonable since Tables I–IV indicate that g_a is a good approximation.

From Eq. (2) it is clear that $nkTK$ can also be obtained by differentiating p/nkT. This was done by plotting $(p/nkT)-1$ vs n on log-log paper and fitting the tangents of the curve to power laws. The values of $nkTK$ obtained in this way are also listed in Table VI. The agreement between the two values of $nkTK$ is extremely poor for each n greater than $\frac{2}{5}$. This is because the contribution to the integral in Eq. (3) is important at such large values of r when g is very close to one that more accuracy in g is required than is available here. For example, for $na^3=\frac{5}{6}$, the contribution to the integral is still quite important for r so large that the maximum deviation of g from unity is less than 1%.

V. DISCUSSION

The comparison between the Monte Carlo, Born-Green, and PY radial distribution function for $n=\frac{10}{9}$ has already been made in reference 8, where the results are presented graphically. As expected, the PY solutions become progressively closer to those obtained by Monte Carlo as n gets smaller. For $n=1.0$ the PY solution differs from the Monte Carlo by less than 15% to the right of the first point where it crosses unity. As already mentioned,[8] it is unable to follow the twists caused by the crystal formation at $n=\frac{10}{9}$, but even here its *maximum* difference is only around 30%.

The comparison of thermodynamic quantities in Table VI indicates that the PY equation may provide a very useful means of calculating them as long as the system is in a fluid state.

[8] A. A. Broyles, J. Chem. Phys. **34**, 1068 (1961).

VI. ACKNOWLEDGMENTS

Programming of this problem for the IBM 650 was done by Frank D. Vickers who introduced several innovations to speed its solution. The series for $h(r)$ was obtained by S. U. Chung.

VII. NOTATION

a = Parameter in the Lennard-Jones potential [Eq. (8)] and the unit of length in this paper.
b = Parameter in g_a [Eq. (19)].
c = Parameter in g_a [Eq. (19)].
E = Total internal energy.
E' = Total average potential energy.
F = Integrand of the integral equation for g [Eq. (6)].
$f=\exp(-\phi/kT)-1$.
g = Radial distribution function.
g_a = Approximate analytic expression for g_{PY} at large r.
g_{MC} = g obtained by Monte Carlo techniques by Wood and Parker.[5]
g_{PY} = g obtained from the Percus-Yevick equation.
$h(r)=rg\exp(\phi/kT)$.
$h_2(r)$ = First two terms in the series for $h(r)$ [Eq. (20)].
K = Fractional isothermal compressibility [Eq. (2)].
k = Boltzmann constant.
m = Parameter in g_a [Eq. (19)].
N = Total number of particles.
$n=N/V$.
p = Pressure.
PY = Percus-Yevick.
$\mathbf{r}$ = Displacement.
r_c = Value of r beyond which $g-1$ is negligible except for terms of order N^{-1}.
r_m = Maximum value of r used for IBM 650 calculations.
T = Temperature.
V = Volume of the system.
$y=g\exp(\phi/kT)$.
α = Parameter in g_a [Eq. (19)].
ϵ = Parameter in the Lennard-Jones potential [Eq. (8)].
ϕ = Pair potential energy.