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Quantum-mechanical radial distribution function for a hard-sphere gas at low density and high temperature

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A high-temperature expansion is obtained for the density-independent part of the radial distribution function (pair-correlation function) for a quantum-mechanical gas of hard spheres. Explicit expressions are given for the first five terms in this series. Comparison with the numerical values obtained by Larsen shows that our expansion is accurate for all values of the radial distance at moderately high temperatures.

I. INTRODUCTION AND STATEMENT OF RESULTS

The radial distribution function (or pair-correlation function) $g(r)$ is a quantity of central importance in the theory of both classical and quantum fluids.[1-4] It occurs in the expressions for both equilibrium and transport properties.[2] It can also be experimentally determined by x-ray and neutron-diffraction techniques.[3]

At low densities, $g(r)$ can be replaced by its density-independent part $g_0(r)$, which is determined by binary interactions only.[1] In the classical case, this is simply[1]

$$g_0^{\text{cl}}(r) = e^{-\beta v(r)}, \tag{1}$$

where $\beta = 1/kT$ and $v(r)$ is the pair intermolecular potential. In the quantum case, $g_0(r)$ can be expressed in terms of the two-body wave function,[1,5] and as such is amenable to numerical calculation.[6-11] Usually such numerical treatments are supplemented by the Wigner-Kirkwood (WK) method.[12] This gives an expansion for $g_0(r)$ in powers of $\hbar^2$,[1,13-15] which holds at moderately high temperatures and at large separations r. However, for a potential $v(r)$ which is a nondifferentiable function of r the WK expansion breaks down,[16] and we must look for an alternative method.

In the present paper, we consider the case of a dilute gas of hard spheres. Numerical calculations of $g_0(r)$ for this system have been performed by Larsen[7] and Miller and Poll.[8] The WK series does not exist for hard spheres. However, using a method devised by Handelsman and Keller[17] for the second virial coefficient of a hard-sphere gas, we have obtained the following high-temperature expansion for $g_0(r)$ for hard spheres of diameter a and mass m:

$$\begin{aligned} g_0(r) &= 0\,, && r<a \\ &= 1+\gamma_0+\gamma_1+\gamma_2+\gamma_3+\dots\,, && r>a\,. \end{aligned} \tag{2}$$

Let

$$R = r/a\,, \tag{3}$$

$$Q = (2\pi)^{1/2}(a/\lambda)(R-1)\,, \tag{4}$$

where

$$\lambda = (2\pi\hbar^2\beta/m)^{1/2} \tag{5}$$

is the thermal wavelength. Then the explicit expressions for the γ_i's, as obtained in Sec. III below, are

$$\gamma_0 = -e^{-Q^2}\,, \tag{6}$$

$$\gamma_1 = (1/\sqrt{2})(\lambda/a)Q^2\operatorname{erfc}Q\,, \tag{7}$$

$$\gamma_2 = (1/3\pi)(\lambda/a)^2Q^2[(1+Q^2)e^{-Q^2} - (3+Q^2)\sqrt{\pi}Q\operatorname{erfc}Q]\,, \tag{8}$$

$$\begin{aligned}\gamma_3 = {} & (1/24\sqrt{2})\pi^{-3/2}(\lambda/a)^3Q^3 \\ & \times[-(16+26Q^2+4Q^4)e^{-Q^2} + (39+28Q^2+4Q^4)\sqrt{\pi}Q\operatorname{erfc}Q]\,. \end{aligned} \tag{9}$$

erfc$x$ is the complementary error function, defined by

$$\operatorname{erfc}x = \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-t^2}dt\,. \tag{10}$$

At moderately high temperatures, the series (2) gives good agreement with Larsen's[7] numerical results over the entire range of r.

II. RADIAL DISTRIBUTION FUNCTION

Let H_N be the Hamiltonian for a system of N particles in volume V. The pair distribution function, defined in the canonical ensemble, is[1]

$$\begin{aligned}\rho^{(2)}(\vec{r}_1,\vec{r}_2) = {} & \frac{N(N-1)}{Q_N} \\ & \times\int\langle\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N|e^{-\beta H_N}|\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N\rangle \\ & \times d\vec{r}_3\dots d\vec{r}_N\,, \end{aligned} \tag{11}$$

where Q_N is the partition function

$$Q_N = \int \langle \vec{r}_1, \ldots, \vec{r}_N | e^{-\beta H_N} | \vec{r}_1, \ldots, \vec{r}_N \rangle \, d\vec{r}_1 \ldots d\vec{r}_N . \tag{12}$$

$\rho^{(2)}(\vec{r}_1, \vec{r}_2)$ gives the probability of finding one molecule at $\vec{r}_1$ and another at $\vec{r}_2$. In a fluid, it depends only on the distance $r = |\vec{r}_1 - \vec{r}_2|$ and on the density, and it is customary to write

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho^2 g(r) , \tag{13}$$

where $\rho = N/V$ is the number density, and $g(r)$ is the radial distribution function, or pair-correlation function.

$g(r)$ is still a function of ρ. It can be expanded as a power series in the density,[1]

$$g(r) = g_0(r) + \rho g_1(r) + \rho^2 g_2(r) + \ldots . \tag{14}$$

For dilute gases, only the first term $g_0(r)$ (the density-independent part) need be kept. It is given by[1,5,6]

$$\begin{aligned} g_0(r) &= \lambda^6 \langle \vec{r}_1, \vec{r}_2 | e^{-\beta H_2} | \vec{r}_1, \vec{r}_2 \rangle \\ &= 2^{3/2}\lambda^3 \langle \vec{r} | e^{-\beta H_2^{\mathrm{rel}}} | \vec{r} \rangle . \end{aligned} \tag{15}$$

where H_2^{rel} is the Hamiltonian for the relative motion of two particles:

$$H_2^{\mathrm{rel}} = -(\hbar^2/m)\nabla^2 + v(r) . \tag{16}$$

In the limit of classical statistical mechanics, (15) reduces to $g_0^{\mathrm{cl}}(r)$ as given by (1).

In the above, we have not taken the quantum statistics into account (i.e., we have treated the case of Boltzmann statistics). For particles of spin s obeying quantum statistics, (15) should be replaced by[6]

$$g_0(r) = g_0^{\mathrm{dir}}(r) \pm (2s+1)^{-1} g_0^{\mathrm{exch}}(r) , \tag{17}$$

where

$$g_0^{\mathrm{dir}}(r) = 2^{3/2}\lambda^3 \langle \vec{r} | e^{-\beta H_2^{\mathrm{rel}}} | \vec{r} \rangle , \tag{18}$$

$$g_0^{\mathrm{exch}}(r) = 2^{3/2}\lambda^3 \langle -\vec{r} | e^{-\beta H_2^{\mathrm{rel}}} | \vec{r} \rangle . \tag{19}$$

In (17), the plus refers to Bose-Einstein statistics and the minus to Fermi-Dirac statistics.

From Eqs. (17)–(19), we see that $g_0(r)$ can be expressed in terms of two-body wave functions. A partial-wave decomposition leads to[5,6]

$$g_0^{\mathrm{dir}}(r) = \sum_{l=0}^{\infty} (2l+1) g_{0,l}(r) , \tag{20}$$

$$g_0^{\mathrm{exch}}(r) = \sum_{l=0}^{\infty} (-1)^l (2l+1) g_{0,l}(r) , \tag{21}$$

where

$$g_{0,l}(r) = 2^{3/2}\lambda^3 (4\pi r^2)^{-1} \left(\frac{2}{\pi} \int_0^\infty dk \, e^{-\beta\hbar^2 k^2/m} |R_{kl}(r)|^2 + \sum_n e^{-\beta\epsilon_{nl}} |R_{nl}(r)|^2 \right) . \tag{22}$$

The radial wave function $R_{kl}(r)$ is for a continuum state with wave number k, and $R_{nl}(r)$ is for a bound state of energy ϵ_{nl}. Equations (20)–(22) have been used in numerical calculations of g_0 for hard spheres,[7-9] for ^{4}He,[6] and for H_2.[10]

This is a satisfactory method at low temperatures. At higher temperatures, a large number of partial waves have to be included in the sum, and also the range of the k integration in (22) has to be increased. Thus it is desirable to supplement this scheme with some alternative method at high temperatures. In the case of g_0^{dir}, this is supplied by the WK method.[12] This gives an expansion in powers of $\hbar^2$ about the classical limit[13,14]:

$$g_0^{\mathrm{dir}}(r) = e^{-\beta v(r)} [1 + \hbar^2 \omega_1(r) + \hbar^4 \omega_2(r) + \ldots] , \tag{23}$$

where $\omega_i(r)$ are functions of the derivatives of $v(r)$.

If $v(r)$ is not differentiable, this method fails, and g_0^{dir} does not have an expansion in powers of $\hbar^2$.[16] An extreme case is that of hard spheres. We investigate this case below, and find an alternative expansion which is useful for calculating g_0^{dir} at high temperatures.

For g_0^{exch}, the WK method is not useful (even if the potential is differentiable). This is because the presence of a steep repulsive core in the potential causes g_0^{exch} to decrease rapidly with increasing temperature, becoming negligible above a few degrees Kelvin. This effect has been discussed by a number of authors.[6-10,18] Thus, except at very low temperatures, it is sufficient to calculate g_0^{dir} only, and we do not discuss g_0^{exch} further in this paper.

III. HARD SPHERES

We wish to find an expansion for $g_0^{\mathrm{dir}}(r)$ for a system of hard spheres about its classical limit:

$$\begin{aligned} g_0^{\mathrm{cl}}(r) &= 0, \quad r < a \\ &= 1, \quad r > a . \end{aligned} \tag{24}$$

The first term in such an expansion was given many years ago by Uhlenbeck and Beth.[19] They replaced the hard sphere by a hard wall, and found

$$g_0^{\mathrm{dir}}(r) \sim 1 - \exp[-2\pi(r-a)^2/\lambda^2] , \quad r > a . \tag{25}$$

Recently, Bruch[20] has shown that the right-hand side of Eq. (25) is a lower bound for g_0^{dir}.

A method for obtaining higher terms in such an expansion has been given by Handelsman and Keller.[17] They were principally interested in obtaining a high-temperature series for the second virial coefficient $B_{\rm dir}(T)$, which is related to the distribution function by

$$B_{\rm dir}(T)=\tfrac{1}{2}\int[1-g_0^{\rm dir}(r)]\,d\vec{r}\,. \tag{26}$$

Thus they left the terms in their expansion of $g_0^{\rm dir}$ in the form of multiple integrals, preferring to do the r integration in Eq. (26) before the other integrals. We show that it is possible to obtain explicit expressions for these terms, which can be easily evaluated for a range of values of r and λ/a.

Our method is basically the same as that of Handelsman and Keller.[17] (See also Ref. 21.) We write

$$g_0^{\rm dir}(r)=2^{3/2}\lambda^3 G(\vec{r};\vec{r};\beta)\,, \tag{27}$$

where

$$G(\vec{r};\vec{r}_0;\beta)=\langle\,\vec{r}\,|\,e^{-\beta H_2^{\rm rel}}\,|\,\vec{r}_0\,\rangle\,. \tag{28}$$

Then $G(\vec{r};\vec{r}_0;\beta)$ satisfies

$$\partial G/\partial\beta - D\nabla^2 G=\delta(\beta)\delta(\vec{r}-\vec{r}_0)\,, \tag{29}$$

$$G(\vec{r};\vec{r}_0;\beta)=0 \quad \text{for } \beta<0\,, \tag{30}$$

and the boundary conditions that $G(\vec{r};\vec{r}_0;\beta)$ vanishes when $r\leqslant a$ and when $r\to\infty$. $G(\vec{r};\vec{r}_0;\beta)$ is the Green's function for diffusion past a sphere, with center $\vec{r}=0$ and radius a, with $\vec{r}_0$ the source point, β the time, and $D\equiv\hbar^2/m$ the diffusion constant.[22]

We wish to expand $G(\vec{r};\vec{r}_0;\beta)$ in powers of $1/a$. As a first step, a new origin is taken at the surface of the sphere, on the line joining the center and the source point. A Cartesian coordinate system xyz is introduced, with the x axis passing through the center of the sphere and the source point. The yz plane is then tangent to the sphere at the origin. Relative to this coordinate system, $\vec{r}=(x,y,z)$, $\vec{r}_0=(x_0,0,0)$, and the sphere center is at $(-a,0,0)$. The boundary condition that G vanishes on the hemisphere $x>-a$ is now

$$G(\,(a^2-d^2)^{1/2}-a,y,z;\vec{r}_0;\beta\,)=0\,, \tag{31}$$

where

$$d^2=y^2+z^2\,. \tag{32}$$

Expanding $G(\vec{r};\vec{r}_0;\beta)$ in powers of $1/a$,

$$G=G_0+G_1a^{-1}+G_2a^{-2}+\ldots\,, \tag{33}$$

substituting in (29), and equating powers of $1/a$ gives

$$\partial G_0/\partial\beta - D\nabla^2 G_0=\delta(\beta)\delta(\vec{r}-\vec{r}_0)\,, \tag{34}$$

$$\partial G_n/\partial\beta - D\,\nabla^2 G_n=0,\quad n>0\,. \tag{35}$$

The appropriate boundary conditions are found by expanding (31) in powers of $1/a$. This leads to

$$G_0(0,y,z;\vec{r}_0;\beta)=0\,, \tag{36}$$

$$G_1(0,y,z;\vec{r}_0;\beta)=\tfrac{1}{2}d^2G_0'(0,y,z;\vec{r}_0;\beta)\,, \tag{37}$$

etc., where the prime denotes differentiation with respect to x. In general, $G_n(0,y,z;\vec{r}_0;\beta)$ can be expressed in terms of G_m and its derivatives at $x=0$, where $m<n$.

Equation (34) is easily solved to give

$$G_0(\vec{r};\vec{r}_0;\beta)=\frac{1}{8(\pi D\beta)^{3/2}}\left[\exp\left(-\frac{d^2+(x-x_0)^2}{4D\beta}\right)-\exp\left(-\frac{d^2+(x+x_0)^2}{4D\beta}\right)\right]. \tag{38}$$

This gives the Uhlenbeck-Beth approximation [Eq. (25)] to $g_0^{\rm dir}$. From (35), one obtains the equation[23]

$$G_n(x,y,z;\vec{r}_0;\beta)=\frac{x}{8(\pi D)^{3/2}}\int_0^\beta\frac{d\tau}{(\beta-\tau)^{5/2}}\times\iint_{-\infty}^{\infty}dy'\,dz'\,G_n(0,y',z';\vec{r}_0;\tau)\times\exp\left(-\frac{x^2+(y-y')^2+(z-z')^2}{4D(\beta-\tau)}\right). \tag{39}$$

This follows either from standard Green's-function methods, using G_0 as the Green's function for the homogeneous equation,[24] or alternatively by taking a double Fourier transform of (35) with respect to y and z, and then a Laplace transform with respect to β.

One can now use this equation to calculate G_1, using $G_1(0,y,z;\vec{r}_0;\beta)$ as given by (37), and then repeat the procedure for G_2, G_3, etc. This is the method used in Refs. 17 and 21, and gives the G_n's as multiple integrals. It is possible to do the integration explicitly in these expressions for G_1 and G_2, but the process becomes increasingly difficult. We therefore adopt the following more systematic procedure.

It can be shown (by induction) that G_n can be written in the form

$$G_n(\vec{r};\vec{r}_0;\beta)=\left(\sum_{l=0}^{n}A_l^{(n)}(x;x_0;\beta)d^{2l}\right)e^{-d^2/4D\beta}\,, \tag{40}$$

where $A_l^{(n)}$ is independent of y and z. Inserting (40) into (39) shows that $A_l^{(n)}$ satisfies

$$A_l^{(n)}(x;x_0;\beta)=\frac{x}{\sqrt{\pi}}\sum_{k=l}^{n}\frac{(4D)^{k-l-1/2}}{\beta^{k+l+1}}\left(\frac{k!}{l!}\right)^2\frac{1}{(k-l)!}$$
$$\times\int_0^\beta d\tau A_k^{(n)}(0;x_0;\tau)$$
$$\times(\beta-\tau)^{k-l-3/2}\tau^{k+l+1}e^{-x^2/4D(\beta-\tau)}\,. \tag{41}$$

We note that we are finally only interested in

$$G_n(x;x;\beta)\equiv G_n(x,0,0;x,0,0;\beta)$$
$$=A_0^{(n)}(x;x;\beta)\,, \tag{42}$$

but it is necessary to calculate the other $A_l^{(n)}$ for the intermediate steps. Equation (41) can be written as

$$A_l^{(n)}(x;x_0;\beta)=\sum_{k=l}^{n}\beta^{-k-l-1}I_{l,k}^{(n)}\,, \tag{43}$$

where

$$I_{l,k}^{(n)}=C_{l,k}\int_0^\beta d\tau A_k^{(n)}(0;x_0;\tau)\tau^{k+l+1}$$
$$\times(\beta-\tau)^{k-l-3/2}e^{-x^2/4D(\beta-\tau)}\,, \tag{44}$$

and

$$C_{l,k}=\frac{x}{\sqrt{\pi}}(4D)^{k-l-1/2}\left(\frac{k!}{l!}\right)^2\frac{1}{(k-l)!}\,. \tag{45}$$

We now observe that (44) is in the form of a convolution integral, and this suggests using Laplace transforms. Let

$$L_p\equiv\int_0^\infty d\beta\,e^{-\beta p} \tag{46}$$

denote the operation of taking the Laplace transform with respect to β. Applying this to (44) gives

$$L_p(I_{l,k}^{(n)})=C_{l,k}L_p[\beta^{k+l+1}A_k^{(n)}(0;x_0;\beta)]$$
$$\times L_p(\beta^{k-l-3/2}e^{-x^2/4D\beta})\,. \tag{47}$$

The transforms on the right-hand side can be done, and their product inverted to give $I_{l,k}^{(n)}$. To illustrate the method, we give the details for $A_0^{(1)}(x;x_0;\beta)$. From (43),

$$A_0^{(1)}(x;x_0;\beta)=\beta^{-1}I_{0,0}^{(1)}+\beta^{-2}I_{0,1}^{(1)}\,. \tag{48}$$

Substituting (40) into (37) gives

$$A_0^{(1)}(0;x_0;\beta)=0\,, \tag{49}$$

$$A_1^{(1)}(0,x_0;\beta)=\tfrac{1}{2}A_0^{(0)\prime}(0;x_0;\beta)$$
$$=\frac{x_0}{16\pi^{3/2}(D\beta)^{5/2}}e^{-x_0/4D\beta}\,. \tag{50}$$

From (44) and (49),

$$I_{0,0}^{(1)}=0\,. \tag{51}$$

From (47),

$$L_p(I_{0,1}^{(1)})=C_{0,1}L_p[\beta^2A_1^{(1)}(0;x_0;\beta)]$$
$$\times L_p(\beta^{-1/2}e^{-x^2/4D\beta})\,. \tag{52}$$

Using (50) and doing the transforms gives

$$L_p(I_{0,1}^{(1)})=\frac{xx_0}{8\pi D^2}\frac{1}{p}e^{-(x+x_0)(p/D)^{1/2}}\,. \tag{53}$$

Inverting the transform gives

$$I_{0,1}^{(1)}=\frac{xx_0}{8\pi D^2}\operatorname{erfc}\left(\frac{x+x_0}{(4D\beta)^{1/2}}\right)\,. \tag{54}$$

Thus, by (40),

$$G_1(x;x;\beta)=\frac{x^2}{8\pi D^2\beta^2}\operatorname{erfc}\left(\frac{x}{(D\beta)^{1/2}}\right)\,. \tag{55}$$

Higher terms are calculated in a similar manner. We have evaluated two more terms, the results being

$$G_2(x;x;\beta)=\frac{X^2}{12\pi^{3/2}(D\beta)^{1/2}}$$
$$\times[(1+X^2)e^{-X^2}-(3+X^2)\sqrt{\pi}X\operatorname{erfc}X]\,, \tag{56}$$

$$G_3(x;x;\beta)=\frac{X^3}{96\pi^{3/2}}[-(16+26X^2+4X^4)e^{-X^2}$$
$$+(39+28X^2+4X^4)\sqrt{\pi}X\operatorname{erfc}X]\,, \tag{57}$$

where $X\equiv x(D\beta)^{-1/2}$.

These results are still in terms of the special

TABLE I. Contributions to g_0^{dir} for $\lambda/a=1.0$.

R	γ_0	γ_1	γ_2	γ_3	g_0^{dir}
1.0625	−0.9758	0.0143	0.0008	−0.0001	0.039
1.125	−0.9065	0.0457	−0.0014	−0.0003	0.138
1.1875	−0.8018	0.0791	−0.0089	0.0009	0.269
1.25	−0.6752	0.1043	−0.0198	0.0039	0.411
1.3125	−0.5414	0.1163	−0.0306	0.0085	0.549
1.375	−0.4133	0.1148	−0.0385	0.0135	0.670
1.4375	−0.3004	0.1028	−0.0416	0.0175	0.770
1.5	−0.2079	0.0848	−0.0401	0.0195	0.847
1.5625	−0.1370	0.0649	−0.0350	0.0194	0.903
1.625	−0.0859	0.0464	−0.0281	0.0174	0.941
1.6875	−0.0513	0.0311	−0.0209	0.0142	0.966
1.75	−0.0292	0.0196	−0.0144	0.0108	0.981
1.8125	−0.0158	0.0117	−0.0093	0.0076	0.990
1.875	−0.0081	0.0065	−0.0057	0.0049	0.995
1.9375	−0.0040	0.0035	−0.0032	0.0030	0.998
2.0	−0.0019	0.0017	−0.0017	0.0017	0.999

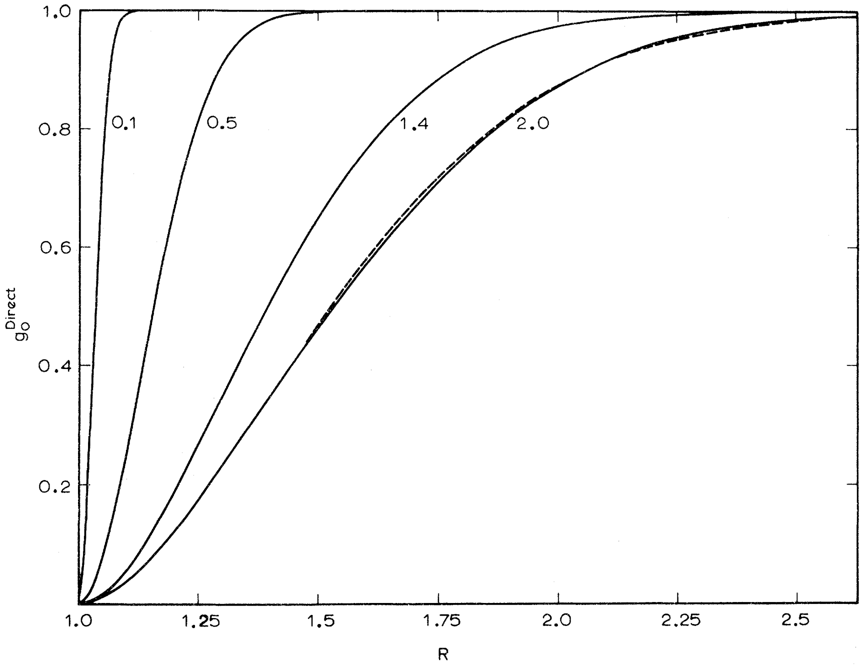

FIG. 1. Direct correlation function g_0^{dir} for $\lambda/a = 0.1$, 0.5, 1.4, and 2.0. Solid lines: obtained from our high-temperature expansion. Broken line: Larsen's numerical result for $\lambda/a = 2.0$.

coordinate system, with origin on the sphere surface. Transforming back to the original coordinate system gives the result stated in the Introduction [Eqs. (2)–(9)].

IV. DISCUSSION OF RESULTS

One check that can immediately be performed on our series for g_0^{dir} is to insert it in Eq. (26) for the direct part of the second virial coefficient. This yields

$$B_{\text{dir}} = \frac{2\pi a^3}{3}\left[1 + \frac{3}{2\sqrt{2}}\left(\frac{\lambda}{a}\right) + \frac{1}{\pi}\left(\frac{\lambda}{a}\right)^2 + \frac{1}{16\sqrt{2}\pi}\left(\frac{\lambda}{a}\right)^3 - \frac{1}{105\pi^2}\left(\frac{\lambda}{a}\right)^4 + O((\lambda/a)^5)\right], \tag{58}$$

in agreement with previous results.[17,21,25]

We expect the series (2) to be useful for calculating $g_0^{\text{dir}}(r)$ for small values of λ/a (i.e., high temperatures). However, (2) is not simply an asymptotic series in powers of λ/a, since Q depends on λ/a. In fact, $(\lambda/a)Q = (2\pi)^{1/2}(R-1)$; so inspection of (6)–(9) suggests that the expansion may work best for R close to 1. This indeed turns out to be the case. However, the expansion also holds for larger values of R, since the γ_i's behave like e^{-Q^2}, and consequently decrease rapidly as R increases. To illustrate the behavior of the terms, we give in Table I the values of the γ_i's for $\lambda/a = 1$, and a range of values of R. We note that the terms alternate in sign (except for R close to 1), and in calculating g_0^{dir} we have used the standard procedure of including only half the last term.

Figure 1 shows g_0^{dir}, as calculated from our high-temperature series, for $\lambda/a = 0.1$, 0.5, 1.4, and 2.0. The general features of such curves have already received adequate discussion in the literature[7,8]; so we will not repeat it here.

At the two lowest temperatures, given by $\lambda/a = 2.0$ and 1.4, we can compare our results with the accurate numerical values of Larsen,[7] obtained by summing the partial-wave series. For $\lambda/a = 2.0$, there is some deviation for larger values of R, and Larsen's results are shown as a broken line in Fig. 1. For $\lambda/a = 1.4$, the error is too small to show on the graph, the difference between our results and Larsen's being less than 1% for the entire range of R.

We conclude that our series gives an accurate representation of g_0^{dir} for all r at moderately high temperatures ($\lambda/a \lesssim 1.4$). At somewhat lower temperatures it is still quantitatively accurate for small r, and at least qualitatively correct for larger r.

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