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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 $B_{\rm dir}$ at high temperatures and as good as the phase-shift formulation at low temperatures, is given. High-temperature asymptotic expansions of $B_{\rm dir}$ 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 $B=B_{\rm dir}+B_{\rm exch}$, where $B_{\rm dir}$ is computed using Boltzmann statistics. $B_{\rm exch}$ is exponentially small at high temperatures[3] for potentials more strongly repulsive than r^{-2} as $r\to 0$. $B_{\rm dir}$ 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 $B_{\rm dir}$ 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 $B_{\rm dir}$ 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 $B_{\rm exch}$ 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

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

where

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

and

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

The minus (upper) sign in $B_{\rm exch}$ 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:

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

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

is the Hamiltonian for the relative motion of a pair of particles of mass m. G satisfies the Bloch equation

$$\left(\frac{\partial}{\partial\beta}-\frac{\hbar^2}{m}\nabla^2+V(r)\right)G(\vec{r}',\vec{r};\beta)=0 \tag{4}$$

with initial condition

$$\lim_{\beta\to 0} G(\vec{r}',\vec{r};\beta)=\delta(\vec{r}-\vec{r}') \ . \tag{5}$$

An alternative derivation of Eqs. (1)–(5) is given in Appendix A.

The Laplace transform of G

$$\overline{G}(\vec{r}',\vec{r};W)\equiv\int_0^\infty e^{-\beta W}G(\vec{r}',\vec{r};\beta)\,d\beta \tag{6}$$

is then the Green's function of the negative-energy Schrödinger equation

$$[-(\hbar^2/m)\nabla^2+V(r)+W]\overline{G}(\vec{r}',\vec{r};W)=\delta(\vec{r}-\vec{r}'). \tag{7}$$

For spherically symmetric V, $\overline{G}$ has an expansion of the form[9]

$$\overline{G}(\vec{r}',\vec{r};W)=\sum_{l=0}^{\infty}(2l+1)P_l(\cos\Theta)\overline{g}^{(l)}(r',r;W), \tag{8}$$

where Θ is the angle between $\vec{r}$ and $\vec{r}'$ and $\overline{g}$ is the Green's function of the negative-energy radial Schrödinger equation:

$$(L_r^{(l)}+W)\overline{g}^{(l)}(r',r;W)=(4\pi r^2)^{-1}\delta(r-r') \ . \tag{9}$$

Here $$L_r^{(l)}\equiv-\frac{\hbar^2}{mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{\hbar^2 l(l+1)}{mr^2}+V(r) \ . \tag{10}$$

The Laplace inversion integral yields

$$G(\vec{r}',\vec{r};\beta)=\frac{1}{2\pi i}\int_{W_0-i\infty}^{W_0+i\infty}e^{\beta W}\overline{G}(\vec{r}',\vec{r};W)\,dW, \tag{11}$$

where W_0 lies to the right of all singularities (as a function of W with $\vec{r}'$, $\vec{r}$ fixed) of $\overline{G}$.

When $\vec{r}=\vec{r}'$, source and observer are coincident. Hence $\overline{G}(\vec{r},\vec{r};W)$ is infinite. Furthermore, for $|\vec{r}'|=|\vec{r}|$, the series (8) will at best converge only conditionally.

To circumvent this difficulty, insert (8) in (11) and interchange the order of summation and integration, which is legitimate for $|\vec{r}|<|\vec{r}'|$. After the interchange, the limit $\vec{r}\to\vec{r}'$ exists. Hence

$$G(\vec{r},\pm\vec{r};\beta)=\sum_{l=0}^{\infty}(2l+1)(\pm1)^l \times\left(\frac{1}{2\pi i}\int_{W_0-i\infty}^{W_0+i\infty}e^{\beta W}\overline{g}^{(l)}(r,r;W)\,dW\right). \tag{12}$$

In the case of free particles, denoted by a subscript 0,

$$G_0(\vec{r}',\vec{r};\beta)=2^{-3/2}\lambda^{-3}\exp\left(-\frac{\pi(\vec{r}-\vec{r}')^2}{2\lambda^2}\right), \tag{13}$$

$$\overline{G}_0(\vec{r}',\vec{r};W)=\frac{m}{4\pi\hbar^2|\vec{r}-\vec{r}'|}\exp(-\gamma|\vec{r}-\vec{r}'|), \tag{14}$$

$$\overline{g}_0^{(l)}(r,r';W)=\overline{g}_0^{(l)}(r',r;W)=\frac{m}{4\pi\hbar^2(rr')^{1/2}} \times I_{l+1/2}(\gamma r)K_{l+1/2}(\gamma r'),\quad r\le r' \tag{15}$$

where $$\gamma\equiv\hbar^{-1}(mW)^{1/2}. \tag{16}$$

Here I and K are modified Bessel functions of the first and third kinds, respectively. The use of (12) and (13) in (2) and (3) now produces

$$B_{\rm dir}=-\ 2^{1/2}N\lambda^3\Delta_+ \ , \tag{17}$$

$$B_{\rm exch}=B^0_{\rm exch}\mp 2^{1/2}N\lambda^3(2S+1)^{-1}\Delta_- \ , \tag{18}$$

where $$B^0_{\rm exch}=\mp 2^{1/2}N\lambda^3(2S+1)^{-1}\int d^3r\,G_0(\vec{r},-\vec{r};\beta)$$

$$=\mp 2^{-5/2}N\lambda^3(2S+1)^{-1} , \tag{19}$$

$$\Delta_\pm=\sum_{l=0}^{\infty}(2l+1)(\pm1)^l\left[\frac{1}{2\pi i}\int_{W_0-i\infty}^{W_0+i\infty}e^{\beta W}f^{(l)}(W)\,dW\right], \tag{20}$$

and

$$f^{(l)}(W)\equiv\int_0^\infty[\overline{g}^{(l)}(r,r;W)-\overline{g}_0^{(l)}(r,r;W)]4\pi r^2\,dr. \tag{21}$$

We now evaluate the integral in (21). Suppose

$$(L_r^{(l)}+W')u_1^{(l)}(r;W')=0 \ , \tag{22a}$$

and $$(L_r^{(l)}+W)u_2^{(l)}(r;W)=0. \tag{22b}$$

It then follows from (10) and (22) that

$$\frac{\hbar^2}{mr^2}\frac{d}{dr}\left[r^2\left(u_2^{(l)}\frac{du_1^{(l)}}{dr}-u_1^{(l)}\frac{du_2^{(l)}}{dr}\right)\right] =u_1^{(l)}L_r^{(l)}u_2^{(l)}-u_2^{(l)}L_r^{(l)}u_1^{(l)} =(W'-W)u_1^{(l)}u_2^{(l)} \ .$$

The use of this relation with $W'\ne W$ and with $W'=W$ produces the indefinite integral

$$\int u_1^{(l)}(r;W)u_2^{(l)}(r;W')r^2\,dr =\frac{\hbar^2 r^2}{m(W'-W)}\left[\left(\frac{\partial u_1^{(l)}(r;W')}{\partial r}-\frac{\partial u_1^{(l)}(r;W)}{\partial r}\right) \times u_2^{(l)}(r;W)-[u_1^{(l)}(r;W')-u_1^{(l)}(r;W)] \times\frac{\partial u_2^{(l)}(r;W)}{\partial r}\right] \ .$$

By letting $W'\to W$, it follows that

$$\int u_1^{(l)}(r;W)u_2^{(l)}(r;W)r^2\,dr =\frac{\hbar^2 r^2}{m}\left(\frac{\partial^2 u_1^{(l)}(r;W)}{\partial r\partial W}u_2^{(l)}(r;W)\right.$$

$$- \frac{\partial u_1^{(l)}(r;\,W)}{\partial W}\frac{\partial u_2^{(l)}(r;\,W)}{\partial r}\Bigg) \quad . \tag{23}$$

The differential equation (22) will in general have singular points at $r=0$ and at $r=\infty$. We now assume that $u_1^{(l)}$ is a solution which is well-behaved as $r\to 0$, and that u_2^l is well-behaved as $r\to\infty$. The Green's function $\bar{g}^{(l)}$ is then given by[9]

$$\bar{g}^{(l)}(r',r;\,W) = -\frac{m}{4\pi\hbar^2 r^2\Delta[u_1^{(l)}(r),u_2^{(l)}(r)]} \begin{cases} \times u_1^{(l)}(r)u_2^{(l)}(r'), & r\le r' \\ \times u_2^{(l)}(r)u_1^{(l)}(r'), & r\ge r' \end{cases} \tag{24}$$

where $\Delta(u_1^{(l)},\,u_2^{(l)}) \equiv u_1^{(l)}u_2'^{(l)} - u_2^{(l)}u_1'^{(l)}$ (25)

is the Wronskian of the two solutions.

For r large compared to the range of the interaction $V(r)$, $u_1^{(l)}$ and $u_2^{(l)}$ must approach linear combinations of the free-particle solutions

$$u_{10}^{(l)} = r^{-1/2}I_{l+1/2}(\gamma r) \ , \tag{26a}$$

$$u_{20}^{(l)} = r^{-1/2}K_{l+1/2}(\gamma r) \ . \tag{26b}$$

The solution $u_1^{(l)}$ can be normalized by a suitable condition imposed at $r=0$ (or at $r=a$ in the case of a hard core of diameter a). In general,

$$u_1^{(l)}(r)\to A_l(W)u_{10}^{(l)}(r)+B_l(W)u_{20}^{(l)}(r), \ \text{as } r\to\infty. \tag{27}$$

We normalize $u_2^{(l)}$ by the demand that

$$u_2^{(l)}(r)\to u_{20}^{(l)}(r), \ \text{as } r\to\infty \ . \tag{28}$$

Now $r^2\Delta$ is independent of r; hence it can be computed from (27) and (28). Thus

$$r^2\Delta_0 \equiv r^2\Delta[u_{10}^{(l)}(r),u_{20}^{(l)}(r)] = -1\,, \tag{29a}$$

$$r^2\Delta \equiv r^2\Delta[u_1^{(l)}(r),u_2^{(l)}(r)] = -A_l(W) \ . \tag{29b}$$

The use of (23) and (24) in (21) now yields

$$f^{(l)}(W) = \lim_{R\to\infty}\Bigg\{\Bigg[\frac{1}{\Delta_0}\Bigg(\frac{\partial^2 u_{10}^{(l)}}{\partial W\partial r}u_{20}^{(l)} - \frac{\partial u_{10}^{(l)}}{\partial W}\frac{\partial u_{20}^{(l)}}{\partial r}\Bigg)\Bigg]_0^R - \Bigg[\frac{1}{\Delta}\Bigg(\frac{\partial^2 u_1^{(l)}}{\partial W\partial r}u_2^{(l)} - \frac{\partial u_1^{(l)}}{\partial W}\frac{\partial u_2^{(l)}}{\partial r}\Bigg)\Bigg]_{r_0}^R\Bigg\}, \tag{30}$$

where r_0 is zero for ordinary potentials and a for hard cores of diameter a. The use of Eqs. (26)–(29) in (30) then produces

$$f^{(l)}(W) = \frac{d}{dW}\ln A_l(W) + \frac{(l+\frac{1}{2})}{2W} + h^{(l)}(W) \ , \tag{31}$$

where
$$h^{(l)}(W) = \Bigg[\frac{1}{\Delta}\Bigg(\frac{\partial^2 u_1^{(l)}}{\partial r\partial W}u_2^{(l)} - \frac{\partial u_1^{(l)}}{\partial W}\frac{\partial u_2^{(l)}}{\partial r}\Bigg)\Bigg]_{r=r_0} . \tag{32}$$

$A_l(W)$ is not yet fixed because the normalization of $u_1^{(l)}$ has not yet been prescribed. We now fix $A_l(W)$ up to a multiplicative constant independent of W by demanding that the behavior of $u_1^{(l)}$ at r_0 be such that $h^{(l)}(W)=0$. (In the case of ordinary potentials, this merely requires that the prescription of limiting behavior at the singular point $r=0$ be independent of W.)

A high-temperature expansion of $B_{\rm dir}$ can now be computed by obtaining a large W asymptotic expansion of $(d/dW)\ln A_l(W)$ which is uniformly valid in l and using (17), (20), and (31). The inverse Laplace transformation indicated in (20) can be performed term-by-term on an asymptotic series under suitable conditions[10]; the sum over l can be computed with the Euler-MacLaurin sum formula.[11] Low-temperature expansions of both $B_{\rm dir}$ and $B_{\rm exch}$ can be computed by obtaining a small W asymptotic expansion of $(d/dW)\ln A_l(W)$ and inverse Laplace transforming term by term[10]; only a small number of terms in the sum over l will contribute to a given order in the resulting large-β expansion.

The present formulation is based on an analysis carried out in Appendix C of Ref. 7 to relate the formulation of Ref. 7 to the phase-shift formulation; the relationship of the present formulation to the phase-shift formulation can be seen by examining this Appendix.

III. $B_{\rm dir}$ FOR HARD SPHERES AT HIGH TEMPERATURES

The labor involved in calculating $B_{\rm dir}$ for hard spheres by the method of Ref. 7 can be considerably reduced by exploiting the formulation of Sec. II. For hard spheres of radius a,

$$u_1^{(l)} = r^{-1/2}[K_{l+1/2}(\gamma a)I_{l+1/2}(\gamma r) - I_{l+1/2}(\gamma a)K_{l+1/2}(\gamma r)] \tag{33}$$

vanishes at $r=a$ and satisfies the condition that $h^{(l)}(W)$ as defined by (32) vanish. Hence we can take

$$A_l(W) = K_{l+1/2}(\gamma a) \tag{34}$$

for hard spheres. Then

$$f^{(l)}(W) = (2W)^{-1}[\,\nu + (\gamma a)K_\nu'(\gamma a)/K_\nu(\gamma a)] \ , \tag{35}$$

where $\nu = l+\frac{1}{2}$.

We now obtain a large-W expansion of $f^{(l)}(W)$ uniformly valid in l. It follows from the modified Bessel equation satisfied by $K_\nu(z)$ and the behavior of $K_\nu(z)$ for $z\to\infty$ that the quantity

$$S_\nu(z) \equiv z(\nu^2+z^2)^{-1/2}K_\nu'(z)[K_\nu(z)]^{-1} \tag{36}$$

satisfies the Riccati equation

$$z^{-1}(\nu^2+z^2)^{1/2}S_\nu'(z) + (\nu^2+z^2)^{-1/2}S_\nu(z) + z^{-2}(\nu^2+z^2)\{[S_\nu(z)]^2-1\} = 0 \tag{37}$$

with the boundary condition

$$\lim_{z\to\infty} S_\nu(z) = -1 \ . \tag{38}$$

We make the change of variables

$$u=\nu^2(\nu^2+z^2)^{-1} \quad , \tag{39}$$

which transforms (37) to

$$2u\left(\frac{dS_\nu}{du}\right)-S_\nu+\nu u^{-1/2}(u-1)^{-1}(S_\nu^2-1)=0\,, \tag{40}$$

with the condition

$$\lim_{u\to 0} S_\nu=-1 \quad . \tag{41}$$

A large-z asymptotic expansion of $K_\nu'(z)/K_\nu(z)$ can be obtained by looking for a formal solution to (40) in the form

$$S_\nu\sim\sum_{k=0}^{\infty} u^{k/2}\nu^{-k}\varphi_k(u) \ , \tag{42}$$

with $\varphi_0\equiv -1$. Substitution of (42) into (40) leads to the recursion relation

$$\varphi_{k+1}(u)=\tfrac{1}{2}(u-1)\{(k-1)\varphi_k(u)+2u[d\varphi_k(u)/du]\} + \tfrac{1}{2}\sum_{l=1}^{k}\varphi_l(u)\varphi_{k+1-l}(u) \tag{43}$$

for the computation of the polynomials $\varphi_k(u)$. Thus we obtain the asymptotic expansion

$$K_\nu'(z)/K_\nu(z)\sim z^{-1}(\nu^2+z^2)^{1/2} \times\sum_{k=0}^{\infty}(\nu^2+z^2)^{-k/2}\varphi_k[\nu^2/(\nu^2+z^2)]\ . \tag{44}$$

By computation from (43),

$$\begin{aligned}
\varphi_0(u)&=-1\ ,\\
\varphi_1(u)&=-\tfrac{1}{2}(1-u)\ ,\\
\varphi_2(u)&=\tfrac{1}{8}(1-u)(1-5u)\ ,\\
\varphi_3(u)&=\tfrac{1}{8}(1-u)(-1+12u-15u^2)\ ,\\
\varphi_4(u)&=\tfrac{1}{128}(1-u)(25-531u+1547u^2-1105u^3),\\
\varphi_5(u)&=\tfrac{1}{32}(1-u)(-13+426u-2124u^2 + 3390u^3-1695u^4)\ ,\\
\varphi_6(u)&=\tfrac{1}{1024}(1-u)(1073-50\,049u+373\,642u^2 - 987\,778u^3+1076\,725u^4-414\,125u^5)\ ,\\
\varphi_7(u)&=\tfrac{1}{32}(1-u)(-103+6480u-67\,080u^2+258\,672u^3 - 457\,695u^4+377\,760u^5-118\,050u^6)\ .
\end{aligned} \tag{45}$$

The use of (44) and (45) in (35) yields the required large-W asymptotic expansion of $f^{(l)}(W)$ which is uniformly valid in l:

$$f^{(l)}(W)=f_1^{(l)}(W)+f_2^{(l)}(W) \ , \tag{46}$$

where

$$f_1^{(l)}(W)=(2W)^{-1}[\nu-(\nu^2+z^2)^{1/2}-\tfrac{1}{2}z^2(\nu^2+z^2)^{-1}], \tag{47}$$

$$f_2^{(l)}(W)\sim(2W)^{-1}\sum_{k=2}^{\infty}(\nu^2+z^2)^{-(k-1)/2}\varphi_k[\nu^2/(\nu^2+z^2)]. \tag{48}$$

Here $\nu=l+\frac{1}{2}$ and $z=a\hbar^{-1}(mW)^{1/2}$; the decomposition of $f^{(l)}$ into $f_1^{(l)}$ and $f_2^{(l)}$ is motivated by the fact that the inverse Laplace transformation indicated in Eq. (20) must be performed on $f_1^{(l)}$ before summing over l, whereas with $f_2^{(l)}$ the operations can be performed in either order. The contributions of $f_1^{(l)}$ and $f_2^{(l)}$ to Δ_+ are denoted respectively by Δ_{1+} and Δ_{2+}; thus

$$B_{\rm dir}=-2^{1/2}N\lambda^3(\Delta_{1+}+\Delta_{2+})\ . \tag{49}$$

The singularities of $f_1^{(l)}(W)$ are poles and branch points at $W=-m^{-1}(\hbar\nu/a)^2$. The branch cut can be taken to run from $-\infty$ to $-m^{-1}(\hbar\nu/a)^2$; the Laplace inversion is then easily performed by deforming the integration contour in the W plane to encircle the branch cut. The result, which consists of residues at poles and an integral from the jump across the branch cut, is

$$\Delta_{1+}=\sum_{l=0}^{\infty}F_1(l+\tfrac{1}{2})\ , \tag{50}$$

where

$$F_1(\nu)\equiv-\tfrac{1}{2}\nu e^{-y} - \tfrac{1}{2}\pi^{-1/2}\nu^2\int_y^\infty x^{-3/2}e^{-x}dx \tag{51}$$

with

$$y\equiv\lambda^2\nu^2/(2\pi a^2)\ . \tag{52}$$

The sum in (50) can be performed with the aid of the Euler-MacLaurin sum formula,[11] which yields

$$\begin{aligned}
\Delta_{1+}&=\int_0^\infty F_1(\nu)\,d\nu-\int_0^{1/2}F_1(\nu)\,d\nu+\tfrac{1}{2}F_1(\tfrac{1}{2})-\frac{1}{12}\frac{dF_1}{d\nu}\Big|_{\nu=\frac{1}{2}} +\frac{1}{720}\frac{d^3F_1}{d\nu^3}\Big|_{\nu=\frac{1}{2}}-\frac{1}{30240}\frac{d^5F_1}{d\nu^5}\Big|_{\nu=\frac{1}{2}}+O\left(\frac{\lambda}{a}\right)^5\\
&=-\frac{\pi\sqrt{2}}{3}\left(\frac{a}{\lambda}\right)^3-\frac{\pi}{2}\left(\frac{a}{\lambda}\right)^2-\frac{\sqrt{2}}{24}\left(\frac{a}{\lambda}\right)-\frac{1}{48}+\frac{7\sqrt{2}}{1920\pi}\left(\frac{\lambda}{a}\right) -\frac{7}{3840\pi}\left(\frac{\lambda}{a}\right)^2+\frac{31\sqrt{2}}{193536\pi^2}\left(\frac{\lambda}{a}\right)^3 -\frac{31}{129024\pi^2}\left(\frac{\lambda}{a}\right)^4+O\left(\frac{\lambda^5}{a^5}\right)\ .
\end{aligned} \tag{53}$$

The contribution of $f_2^{(l)}(W)$ is most easily handled by performing the sum over l first. The use of (45), (48), and the Euler-MacLaurin sum formula[11] yields

$$\sum_{l=0}^{\infty}(2l+1)f_2^{(l)}(W)=\frac{ma^2}{2\hbar^2}\left[-\frac{7}{12z}-\frac{19}{20160z^3} +\frac{1}{192z^4}+\frac{1711}{4612608z^5}+\frac{3}{1120z^6}+O\left(\frac{1}{z^7}\right)\right]\ . \tag{54}$$

By performing the inverse Laplace transformation[12] of Eq. (20) on (54), it follows that

$$\Delta_{2+}=-\frac{7\sqrt{2}}{24}\left(\frac{a}{\lambda}\right)-\frac{19\sqrt{2}}{40320\pi}\left(\frac{\lambda}{a}\right)+\frac{1}{768\pi}\left(\frac{\lambda}{a}\right)^2 +\frac{1711\sqrt{2}}{27675648}\left(\frac{\lambda}{a}\right)^3+\frac{3}{17920\pi^2}\left(\frac{\lambda}{a}\right)^4+O\left(\frac{\lambda^5}{a^5}\right)\ . \tag{55}$$

The use of (53) and (55) in (49) now produces

$$B_{\rm dir} = \tfrac{2}{3}\pi N a^3\left[1+\frac{3}{2\sqrt{2}}\left(\frac{\lambda}{a}\right)+\frac{1}{\pi}\left(\frac{\lambda}{a}\right)^2 + \frac{1}{16\pi\sqrt{2}}\left(\frac{\lambda}{a}\right)^3 - \frac{1}{105\pi^2}\left(\frac{\lambda}{a}\right)^4 + \frac{1}{640\pi^2\sqrt{2}}\left(\frac{\lambda}{a}\right)^5 - \frac{2}{3003\pi^3}\left(\frac{\lambda}{a}\right)^6 + \frac{47}{215040\pi^3\sqrt{2}}\left(\frac{\lambda}{a}\right)^7 + O\left(\frac{\lambda^8}{a^8}\right)\right] \quad (56)$$

agreeing with and extending the results of other authors.[13] The simplification over the method of Ref. 7 is that only one set of polynomials need be computed [the $\varphi_k(u)$] instead of three [$\xi_k(t), \eta_k(t), \zeta_k(t)$]; furthermore φ_k is computed directly from a recursion relation rather than from multiplication or division of series which have themselves been computed recursively.

IV. $B_{\rm dir}$ FOR A HARD-CORE-PLUS-SQUARE WELL POTENTIAL

The potential considered is sketched in Fig. 1. Only the solution of the radial Schrödinger equation which obeys the inner boundary condition and makes $h_l(W)$ as defined by (32) vanish is needed for the computation of $A_l(W)$. Such a solution is

$$\begin{aligned} u_1^{(l)}(r) &= 0, \quad 0 \le r \le a \\ u_1^{(l)}(r) &= r^{-1/2}[K_{l+\frac{1}{2}}(\omega a) I_{l+\frac{1}{2}}(\omega r) - I_{l+\frac{1}{2}}(\omega a) K_{l+\frac{1}{2}}(\omega r)], \quad a \le r \le b \\ u_1^{(l)}(r) &= r^{-1/2}[A_l I_{l+\frac{1}{2}}(\gamma r) + B_l K_{l+\frac{1}{2}}(\gamma r)], \quad b \le r < \infty. \end{aligned} \quad (57)$$

Here $\omega = (\gamma^2 - u_0)^{1/2}$, (58a)

with $u_0 = mV_0/\hbar^2$. (58b)

A_l and B_l are determined by demanding continuity at $r=b$. Only A_l is needed; it is

$$A_l = \gamma b K'_{l+1/2}(\gamma b)\,[I_{l+1/2}(\omega a)K_{l+1/2}(\omega b) - K_{l+1/2}(\omega a) I_{l+1/2}(\omega b)] + \omega b K_{l+1/2}(\gamma b) \times [K_{l+1/2}(\omega a) I'_{l+1/2}(\omega b) - I_{l+1/2}(\omega a) K'_{l+1/2}(\omega b)]\,. \quad (59)$$

It is easily shown that the A_l given by (59) reduces to the hard core A_l [i.e., to $K_{l+1/2}(\gamma a)$] if either $b \to a$ or if $V_0 \to 0$ (so that $\omega \to \gamma$).

A large-W asymptotic expansion of A_l, uniformly valid in l and in $\arg W$ for $\arg W$ bounded away from $\pm\pi$, can be obtained from Debye's series[14] for $I_\nu(x)$, $K_\nu(x)$, $I'_\nu(x)$, and $K'_\nu(x)$. Define i_ν, k_ν, l_ν, m_ν by[15]

$$I_\nu(x) \equiv i_\nu(x) e^{\mu_\nu(x)}\,, \quad (60a)$$

$$K_\nu(x) \equiv k_\nu(x) e^{-\mu_\nu(x)}\,, \quad (60b)$$

$$I'_\nu(x) \equiv l_\nu(x) e^{\mu_\nu(x)}\,, \quad (60c)$$

$$K'_\nu(x) \equiv m_\nu(x) e^{-\mu_\nu(x)}\,, \quad (60d)$$

where $\mu_\nu(x) \equiv (\nu^2 + x^2)^{1/2} - \nu \sinh^{-1}(\nu/x)$. (60e)

The Debye series are then asymptotic expansions of i_ν, k_ν, l_ν, and m_ν:

$$i_\nu(x) \sim (2\pi)^{-1/2}(\nu^2+x^2)^{-1/4} \times \sum_{k=0}^{\infty}[t^{-k}u_k(t)](\nu^2+x^2)^{-k/2}, \quad (61a)$$

$$k_\nu(x) \sim (\pi/2)^{1/2}(\nu^2+x^2)^{-1/4} \times \sum_{k=0}^{\infty}[(-t)^{-k}u_k(t)](\nu^2+x^2)^{-k/2}\,, \quad (61b)$$

$$l_\nu(x) \sim (2\pi)^{-1/2}x^{-1}(\nu^2+x^2)^{+1/4} \times \sum_{k=0}^{\infty}[t^{-k}v_k(t)](\nu^2+x^2)^{-k/2}, \quad (61c)$$

$$m_\nu(x) \sim -(\pi/2)^{1/2}x^{-1}(\nu^2+x^2)^{1/4} \times \sum_{k=0}^{\infty}[(-t)^{-k}v_k(t)](\nu^2+x^2)^{-k/2}\,, \quad (61d)$$

where $t \equiv \nu(\nu^2+x^2)^{-1/2}$. (61e)

The polynomial coefficients $u_k(t)$, $v_k(t)$ are computed recursively[16] from

$$u_{k+1}(t) = \tfrac{1}{2}t^2(1-t^2)u'_k(t) + \tfrac{1}{8}\int_0^t (1-5t^2)u_k(t)\,dt\,,$$

$$v_{k+1}(t) = u_{k+1}(t) + t(t^2-1)[\tfrac{1}{2}u_k(t) + t u'_k(t)]\,, \quad (62)$$

where $u_0(t) = v_0(t) = 1$. From (31), (59), and (60) it

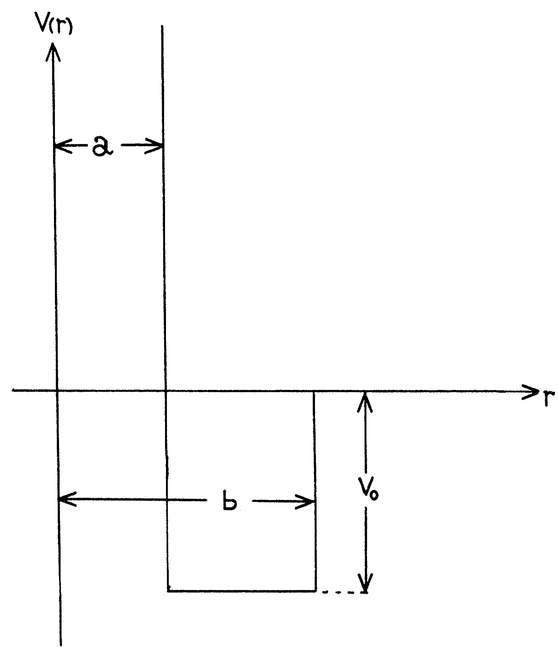

FIG. 1. Hard-core-plus-square-well potential.

follows that

$$f^{(l)}(W)=f_1^{(l)}(W)+f_2^{(l)}(W)+f_3^{(l)}(W), \qquad (63)$$

where $$f_1^{(\nu-1/2)}(W)=\frac{d}{dW}\ln[K_\nu(\gamma a)]+\frac{\nu}{2W}, \qquad (64a)$$

$$f_2^{(\nu-1/2)}(W)=\frac{d}{dW}[\mu_\nu(\omega b)-\mu_\nu(\omega a)-\mu_\nu(\gamma b)+\mu_\nu(\gamma a), \qquad (64b)$$

and

$$f_3^{(\nu-1/2)}(W)=\frac{d}{dW}\ln\{p_\nu+q_\nu\exp[2\mu_\nu(\omega a)-2\mu_\nu(\omega b)]\} \qquad (64c)$$

with $$p_\nu=[k_\nu(\gamma a)]^{-1}[-\gamma b m_\nu(\gamma b)k_\nu(\omega a)i_\nu(\omega b) + \omega b k_\nu(\gamma b)k_\nu(\omega a)l_\nu(\omega b)], \qquad (65a)$$

$$q_\nu=[k_\nu(\gamma a)]^{-1}[\gamma b m_\nu(\gamma b)i_\nu(\omega a)k_\nu(\omega b) - \omega b k_\nu(\gamma b)i_\nu(\omega a)m_\nu(\omega b)]. \qquad (65b)$$

Inasmuch as $f^{(l)}$ enters linearly in the expression for B_{dir}, each of the $f_i^{(l)}$ can be handled separately. The contribution of $f_1^{(l)}$ to B_{dir} is just the hard-sphere part computed in Sec. III. By inverse Laplace-transforming (62b) and using (20), we find that $f_2^{(l)}(W)$ makes a contribution Δ_{2+} to Δ_+ which is

$$\Delta_{2+}=\sum_{l=0}^{\infty}F_2(l+\tfrac{1}{2}), \qquad (66)$$

where

$$F_2(\nu)\equiv(e^{\beta V_0}-1)\frac{\nu^2}{2\pi^{1/2}}\int_{[\lambda^2\nu^2/(2\pi b^2)]}^{[\lambda^2\nu^2/(2\pi a^2)]}x^{-3/2}e^{-x}\,dx. \qquad (67)$$

The use of the Euler-MacLaurin sum formula[11] now produces

$$\Delta_{2+}=\frac{\sqrt{2}}{3}\pi\frac{(b^3-a^3)}{\lambda^3}(e^{\beta V_0}-1)+O(\lambda). \qquad (68)$$

The first term in (68), which equals $\int_0^\infty F_2(\nu)d\nu$, yields the classical contribution of the square well to the second virial coefficient.

It follows from (58a), (61), (62), and (65) that, for large γ,

$$p_\nu=1+\frac{u_0a^2}{4[\nu^2+(\gamma a)^2]}+O\left(\frac{1}{\gamma^3}\right), \qquad (69a)$$

$$q_\nu=-\frac{u_0b^2}{4[\nu^2+(\gamma b)^2]}+O\left(\frac{1}{\gamma^3}\right). \qquad (69b)$$

By inserting (69) in (64c), expanding the logarithm, and inserting the result in (20), we obtain a contribution Δ_{3+} to Δ_+ which is

$$\Delta_{3+}=\sum_{l=0}^{\infty}F_3(l+\tfrac{1}{2}), \qquad (70)$$

where

$$F_3(\nu)=\frac{\nu}{\pi i}\int_{\gamma_0-i\infty}^{\gamma_0+i\infty}d\gamma\exp\left(\frac{\lambda^2\gamma^2}{2\pi}\right)\frac{d}{d\gamma}\left(\frac{u_0a^2}{4[\nu^2+(\gamma a)^2]} - \frac{u_0b^2}{4[\nu^2+(\gamma b)^2]}\exp[2\mu_\nu(\omega a)-2\mu_\nu(\omega b)]\right). \qquad (71)$$

The second term in the integrand of (71) is exponentially small except as $b\to a$, when it cancels the first term. For $(b-a)\ll a$ and γa large, it is a good approximation to replace the second term of the parenthesis in (71) by

$$-\frac{u_0a^2}{4(\nu^2+\gamma^2a^2)}\exp\left[-2(\nu^2+\gamma^2a^2)^{1/2}\left(\frac{b-a}{a}\right)\right]$$

to obtain

$$F_3(\nu)\cong-\frac{u_0\lambda^2\nu}{4\pi}\exp\left(-\frac{\lambda^2\nu^2}{2\pi a^2}\right)\mathrm{erf}\left((2\pi)^{1/2}\frac{(b-a)}{\lambda}\right), \qquad (72)$$

where $$\mathrm{erf}(x)\equiv 2\pi^{-1/2}\int_0^x e^{-t^2}dt, \qquad (73)$$
$$\mathrm{erf}(0)=0,\ \mathrm{erf}(\infty)=1.$$

The use of (72) in (70) with the sum replaced by an integral yields

$$\Delta_{3+}=-\frac{u_0a^2}{4}\mathrm{erf}\left[(2\pi)^{1/2}\left(\frac{b-a}{\lambda}\right)\right]+O(\lambda). \qquad (74)$$

Addition of the contributions of Δ_{2+} and Δ_{3+} as given by (68) and (74) to the hard-sphere result computed in Sec. III yields finally

$$B_{\mathrm{dir}}=\tfrac{2}{3}\pi Na^3\left\{1+\frac{3}{2\sqrt{2}}\left(\frac{\lambda}{a}\right)+\frac{1}{\pi}\left(\frac{\lambda}{a}\right)^2+\frac{1}{16\pi\sqrt{2}}\left(\frac{\lambda}{a}\right)^3 + [1-(b/a)^3](e^{\beta V_0}-1)+\frac{3}{2\sqrt{2}}\left(\frac{\lambda}{a}\right)\beta V_0 \times\mathrm{erf}\left[(2\pi)^{1/2}\left(\frac{b-a}{\lambda}\right)\right]+O(\lambda^4/a^4)\right\}. \qquad (75)$$

Clearly this reduces to the hard-sphere result when $V_0\to 0$ or when $b\to a$. The result (75) is valid to the stated order in (λ/a) for $(b-a)/a$ and $(mV_0a^2)/(2\pi\hbar^2)$ fixed, uniformly in $(b-a)/a$. The result is not uniformly valid for $(mV_0a^2)/(2\pi\hbar^2)$ large.[17]

V. B_{exch} FOR A HARD-CORE-PLUS-SQUARE-WELL POTENTIAL

A general method for the computation of the exchange second virial coefficient at high temperatures has been given by Hill. The relevant results [Eqs. (57)–(60) of Ref. 18] are

$$B_{\mathrm{exch}}=\mp\frac{N}{2S+1}\sum_n C_n, \qquad (76)$$

where $$C_n=-2^{3/2}i\lambda^3\int_{\gamma_0-i\infty}^{\gamma_0+i\infty}g_n(\gamma)e^{f_n(\gamma)}d\gamma \qquad (77)$$

with $$g_n(\gamma)=\alpha_n(\gamma)\partial\alpha_n(\gamma)/\partial\gamma \qquad (78)$$

and $$f_n(\gamma)=\frac{\lambda^2\gamma^2}{2\pi}-\ln[2\cosh\pi\alpha_n(\gamma)]. \qquad (79)$$

In (76), the minus (upper) sign is associated with Bose statistics and the plus sign with Fermi statistics. The function $\alpha_n(\gamma)$ is the nth value of $-i\nu$

for which the solution $u_1(\nu)$ which satisfies the inner boundary condition also satisfies the outer boundary condition. Thus the $\alpha_n(\gamma)$ are the roots of

$$A_{(i\alpha_n - 1/2)}(\hbar^2\gamma^2/m) = 0 \ , \tag{80}$$

where, for the potential of Fig. 1, A_l is given by Eq. (59) [the extension from integral l to arbitrary complex l is made via the differential equation (9)].

The poles at $\nu = i\alpha_n$ arise from bound states of the centrifugal potential, which is attractive for ν pure imaginary. For large negative energies, these bound states occur for $|\nu|$ large. In the crudest approximation, they first occur when the minimum of the potential equals the energy, i.e., for

$$-W = -[\hbar^2(\alpha_n^2 + \tfrac{1}{4})/(ma^2)] - V_0 \ ,$$

which yields $\alpha_n \approx \gamma a - u_0/2\gamma a$. (81)

Although this approximation yields only the first term of the large γ expansion of α_n and the first correction to α_n for the presence of the attractive well correctly, it does show that the effect of the attractive well can be treated as a small perturbation on the hard-core result $\alpha_n^0(\gamma)$, which is[19]

$$\alpha_n^0(\gamma) = \gamma a + \beta_n(\gamma a)^{1/3} + \tfrac{1}{30}\beta_n^2(\gamma a)^{-1/3} + (\tfrac{1}{70} - \tfrac{1}{350}\beta_n^3)(\gamma a)^{-1} + O(\gamma^{-5/3}) \ , \tag{82}$$

where $-2^{1/3}\beta_n$ is the nth root of the Airy function $\mathrm{Ai}(-2^{1/3}\beta_n) = 0$.

By Taylor-expanding[20] (59) in powers of

$$(\omega - \gamma) = -u_0/(2\gamma) + O(\gamma^{-3}) \ ,$$

$$A_{\nu - 1/2}(\hbar^2\gamma^2/m) \approx K_\nu(\gamma a) - \tfrac{1}{2}u_0 a\gamma^{-1}K_\nu'(\gamma a) - \tfrac{1}{2}u_0 b^2 I_\nu(\gamma a) \times \{[K_\nu'(\gamma b)]^2 - [1 + \nu^2/(\gamma b)^2][K_\nu(\gamma b)]^2\} + \tfrac{1}{2}u_0 b^2 K_\nu(\gamma a) \times \{I_\nu'(\gamma b)K_\nu'(\gamma b) - [1 + \nu^2/(\gamma b)^2]I_\nu(\gamma b)K_\nu(\gamma b)\} \ . \tag{83}$$

The use of $K_{i\alpha_n^0(\gamma)}(\gamma a) = 0$ in the Wronskian relation[21] for I_ν and K_ν shows that

$$I_{i\alpha_n^0}(\gamma a) = -[\gamma a K'_{i\alpha_n^0}(\gamma a)]^{-1} \ . \tag{84}$$

By differentiating $K_{i\alpha_n^0(\gamma)}(\gamma a) = 0$ with respect to γ and using (82), it can be shown that

$$\left.\frac{\partial K_\nu(\gamma a)}{\partial \nu}\right|_{\nu = i\alpha_n^0} = -aK'_{i\alpha_n^0}(\gamma a)[i\partial\alpha_n^0/\partial\gamma]^{-1} \approx iK'_{i\alpha_n^0}(\gamma a) \ . \tag{85}$$

Because the attractive well is a small perturbation on the hard-core result, we set $\nu = i\alpha_n = i(\alpha_n^0 + \Delta\alpha_n)$ and expand (80) in powers of $\Delta\alpha_n$. The use of Eqs. (82)–(85) shows that, to lowest order,

$$\Delta\alpha_n = -u_0 a/(2\gamma)[1 - \theta_n(\gamma a, \gamma b)] \ , \tag{86}$$

where

$$\theta_n(\gamma a, \gamma b) = [K'_{i\alpha_n^0}(\gamma a)]^{-2} \times \{b^2a^{-2}[K'_{i\alpha_n^0}(\gamma b)]^2 - (a^2b^{-2} - 1)[K_{i\alpha_n^0}(\gamma b)]^2\} \ . \tag{87}$$

When $b \to a$, $\theta_n \to 1$, and $\Delta\alpha \to 0$. The general behavior of θ_n can be seen with the aid of the uniform asymptotic approximations[22]

$$K_{ip}(x) \sim 2^{1/2}\pi e^{-\pi p/2}[\xi(x,p)/(x^2 - p^2)]^{1/4}\,\mathrm{Ai}[\xi(x,p)] \ , \tag{88a}$$

$$K'_{ip}(x) \sim 2^{1/2}\pi x^{-1}e^{-\pi p/2}[\xi(x,p)/(x^2 - p^2)]^{-1/4}\,\mathrm{Ai}'[\xi(x,p)] \ , \tag{88b}$$

where $\tfrac{2}{3}[\xi(x,p)]^{3/2} = (x^2 - p^2)^{1/2} - p\sec^{-1}(x/p)$. (88c)

For $(\frac{b}{a} - 1) \ll 1$, $\xi(\gamma b, \alpha_n^0) \approx y - 2^{1/3}\beta_n$, (89a)

where $y \equiv 2^{1/3}(\gamma a)^{2/3}[(b/a) - 1]$. (89b)

It now follows from the large-z asymptotic approximations to the Airy functions[23]

$$\mathrm{Ai}(z) \sim \tfrac{1}{2}\pi^{-1/2}z^{-1/4}\exp(-\tfrac{2}{3}z^{3/2}) \ ,$$

$$\mathrm{Ai}'(z) \sim -\tfrac{1}{2}\pi^{-1/2}z^{1/4}\exp(-\tfrac{2}{3}z^{3/2})$$

that θ_n is exponentially small for $y \gg 1$. Hence θ_n is negligible when the approximation (89a) fails. The use of (88) and (89) in (87) yields

$$\theta_n(\gamma a, \gamma b) \approx \varphi_n(y) \ , \tag{90}$$

where

$$\varphi_n(z) \equiv [\mathrm{Ai}'(-2^{1/3}\beta_n)]^{-2} \times \{[\mathrm{Ai}'(z - 2^{1/3}\beta_n)]^2 + z[\mathrm{Ai}(z - 2^{1/3}\beta_n)]^2\} \ . \tag{91}$$

The integral in Eq. (77) can now be evaluated by steepest descent for (λ/a) small as in Sec. VA of Ref. 18; the result is

$$C_n = 4\pi^3 a^3 h_n e^{f_n} \ , \tag{92}$$

where

$$h_n = 1 + \tfrac{14}{9}\beta_n\left(\frac{\pi a}{\lambda}\right)^{-4/3} + \tfrac{130}{405}\beta_n^2\left(\frac{\pi a}{\lambda}\right)^{-8/3} + O\left[\left(\frac{a}{\lambda}\right)^{-10/3}\right] \tag{93}$$

and

$$f_n = -\pi\left\{\tfrac{1}{2}\left(\frac{\pi a}{\lambda}\right)^2 + \beta_n\left(\frac{\pi a}{\lambda}\right)^{2/3} + \tfrac{4}{45}\beta_n^2\left(\frac{\pi a}{\lambda}\right)^{-2/3} + (\tfrac{1}{70} - \tfrac{268}{14175}\beta_n^3)\left(\frac{\pi a}{\lambda}\right)^{-2} - \tfrac{1}{2}u_0 a^2[1 - \varphi_n(x)]\left(\frac{\pi a}{\lambda}\right)^{-2} + O\left[\left(\frac{a}{\lambda}\right)^{-8/3}\right]\right\} \tag{94}$$

with $x \equiv 2^{1/3}(\pi a/\lambda)^{4/3}[(b/a) - 1]$. (95)

Numerical values of B_{exch} at high temperatures can now be calculated by using Eqs. (91)–(95) to evaluate the $n = 1$ term of Eq. (76). The results (91)–(95) are uniformly valid in $(b - a)/a$ to the stated order in (λ/a), but are not uniform in $(mV_0a^2)/(2\pi\hbar^2)$ for $(mV_0a^2)/(2\pi\hbar^2)$ large.

VI. MOHLING'S METHOD

Because Mohling's method[5] may be of use for other problems if suitably modified, it seems worthwhile to trace the difficulties in his original work. We restrict our analysis to the hard-sphere case. In brief, there are three errors in Mohling's work: (a) The integral equations he iterates would, if solved correctly, yield a quantum correction too large by a factor of 2. (b) The iteration scheme he used is not a high-temperature iteration scheme as claimed; all orders in his iteration contribute to a given order in (λ/a). (c) The evaluation of the second order (in his iteration scheme) was incorrect. The difficulties (a) and (b) compensate in first order to give the (λ/a) term found by Beth and Uhlenbeck; a correct evaluation of the second order yields an additional (λ/a) term.

The relation between the notation of the present paper and the notation of Mohling's paper is as follows:

$$G(\vec{r}', \vec{r}; \beta) \equiv \langle \vec{r}' | e^{-\beta H_0^{\prime}} | \vec{r} \rangle \ , \tag{96a}$$

$$G_0(\vec{r}', \vec{r}; \beta) \equiv \langle \vec{r}' | e^{-\beta H_0} | \vec{r} \rangle \ . \tag{96b}$$

We now proceed to obtain an equation for comparison with Mohling's Eq. (20a). Make the definitions

$$G_S(\vec{r}', \vec{r}; \beta) \equiv G(\vec{r}', \vec{r}; \beta) - G_0(\vec{r}', \vec{r}; \beta) \tag{97a}$$

and $\bar{G}_S(\vec{r}', \vec{r}; W) \equiv \bar{G}(\vec{r}', \vec{r}; W) - \bar{G}_0(\vec{r}', \vec{r}; W)$. (97b)

Green's theorem is

$$\int d\vec{S}'' \cdot [u(\vec{r}'')\nabla'' v(\vec{r}'') - v(\vec{r}'')\nabla'' u(\vec{r}'')] = \int d^3\vec{r}'' [u(\vec{r}'')\nabla''^2 v(\vec{r}'') - v(\vec{r}'')\nabla''^2 u(\vec{r}'')] \ .$$

Put $u(\vec{r}'') = (\hbar^2/m)\bar{G}_0(\vec{r}', \vec{r}''; W)$, $v(\vec{r}'') = \bar{G}_S(\vec{r}'', \vec{r}; W)$ and let the volume considered in Green's theorem be that exterior to the sphere $|\vec{r}''| = a$. Then

$$d\vec{S}'' \cdot \nabla'' = -d^3r''\delta(r'' - a^+)\partial/\partial r''$$

and

$$-\int d^3r''\,\delta(r''-a^+)\left(\frac{\hbar^2}{m}\bar{G}_0(\vec{r}', \vec{r}''; W)\frac{\partial}{\partial r''}\bar{G}_S(\vec{r}'', \vec{r}; W) - \frac{\hbar^2}{m}\bar{G}_S(\vec{r}'', \vec{r}; W)\frac{\partial}{\partial r''}\bar{G}_0(\vec{r}', \vec{r}''; W)\right)$$
$$= \int d^3r''\left[\bar{G}_0(\vec{r}', \vec{r}''; W)\frac{\hbar^2}{m}\nabla''^2\bar{G}_S(\vec{r}'', \vec{r}; W) - \bar{G}_S(\vec{r}'', \vec{r}; W)\frac{\hbar^2}{m}\nabla''^2\bar{G}_0(\vec{r}', \vec{r}''; W)\right.$$
$$= \bar{G}_S(\vec{r}', \vec{r}; W) \ , \tag{98}$$

where the last equality follows from the fact that $\bar{G}_0$ satisfies (7) with $V(r) = 0$ while $\bar{G}_S$ satisfies (7) with $V(r) = 0$ and zero right-hand side. A similar application of Green's theorem with $u(\vec{r}'') = \bar{G}_0(\vec{r}', \vec{r}'', W)$ and $v(\vec{r}'') = \bar{G}_0(\vec{r}'', \vec{r}; W)$ yields

$$\int d^3r''\,\delta(r'' - a^+)[\bar{G}_0(\vec{r}', \vec{r}''; W)\frac{\partial}{\partial r''}\bar{G}_0(\vec{r}'', \vec{r}; W) - \bar{G}_0(\vec{r}'', \vec{r}; W)\frac{\partial}{\partial r''}\bar{G}_0(\vec{r}', \vec{r}''; W)] = 0 \ . \tag{99}$$

The use of (99) and the fact that $G_S = -G_0$ for $r'' = a$ (a consequence of $G = 0$ for $r'' = a$) in (98) produces

$$\bar{G}_S(\vec{r}', \vec{r}; W) = \int d^3r''\,\bar{G}_0(\vec{r}', \vec{r}''; W) \times[-(\hbar^2/m)\delta(r'' - a^+)\partial/\partial r''] \times[\bar{G}_0(\vec{r}'', \vec{r}; W) + \bar{G}_S(\vec{r}'', \vec{r}; W)] \ . \tag{100}$$

Eq. (100) can be inverse-Laplace-transformed with the aid of the faltung (convolution) theorem for the Laplace transform; the result is

$$G_S(\vec{r}', \vec{r}; \beta) = \int_0^\beta dt \int d^3r''\,G_0(\vec{r}', \vec{r}''; \beta - t) \times[-(\hbar^2/m)\delta(r'' - a^+)\partial/\partial r''] \times[G_0(\vec{r}'', \vec{r}; t) + G_S(\vec{r}'', \vec{r}; t)]. \tag{101}$$

Comparison of Eq. (101) with Mohling's Eq. (20a) for $U_R(\beta)$ shows that

$$\langle \vec{r}' | U_R(\beta) | \vec{r} \rangle = G_S(\vec{r}', \vec{r}; \beta) \tag{102}$$

[the $\theta(t^-)$ which appears in Mohling's Eq. (20a) was set equal to 1 before calculation in his work]. The fact that

$$\langle \vec{r} | U_L(\beta) | \vec{r}' \rangle = \langle \vec{r}' | U_R(\beta) | \vec{r} \rangle \ ,$$

taken together with $G_S(\vec{r}'; \vec{r}; \beta) = G_S(\vec{r}, \vec{r}'; \beta)$

yields $\langle \vec{r}' | U_L(\beta) | \vec{r} \rangle = G_S(\vec{r}', \vec{r}; \beta)$, (103)

a result which is also obtainable by using Green's theorem to derive an equation for comparison with Mohling's (20b). Eqs. (102) and (103) contradict Mohling's Eq. (23), which implies that $U_R + U_L = G_S$. Since in fact $U_R + U_L = 2G_S$, quantum corrections computed from Mohling's Eq. (24) with correct solutions of Mohling's equations for U_R and U_L would be too large by a factor of 2. The same conclusion can be reached by solving Mohling's Eqs. (20a) and (20b) by Laplace transformation [to get equations like Eq. (100)] followed by an expansion of the Laplace transforms of U_R and U_L in partial waves: A comparison with the partial-wave expansion of G [given by Eqs. (9) and (21) of Ref. 3] again yields the results (102) and (103).

Next we investigate the character of iterative solutions of Mohling's (20a) and (20b). Since (20a) and Eq. (101) of the present paper are identical, we examine (101), which has the iterative solution

$$G_S(\vec{r}', \vec{r}, \beta) = \sum_{n=1}^{\infty} G_n(\vec{r}', \vec{r}; \beta) \quad , \tag{104}$$

where the G_n are calculated recursively from

$$G_n(\vec{r}', \vec{r}; \beta) = \int_0^\beta d^3r''\, G_0(\vec{r}', \vec{r}'', \beta - t) \times\left(-(\hbar^2/m)\delta(r''-a^+)\frac{\partial}{\partial r''}\right) G_{n-1}(\vec{r}'', \vec{r}; t) \quad . \tag{105}$$

The leading term in (λ/a) at each order of the iteration is preserved by the crude approximation of replacing the sphere by a plane. In rectangular coordinates with the plane at $z''=a$, Eqs. (104) and (105) are then replaced by

$$G_S(\vec{r}', \vec{r}; \beta) \cong G_S'(\vec{r}', \vec{r}; \beta) = \sum_{n=1}^{\infty} G_n'(\vec{r}', \vec{r}; \beta) \quad , \tag{106}$$

where

$$G_n'(\vec{r}', \vec{r}; \beta) = \int_0^\beta \int_{-\infty}^{\infty} dx'' \int_{-\infty}^{\infty} dy''\, G_0(\vec{r}', \vec{r}; \beta - t) \times[-(\hbar^2/m)\partial/\partial z'']G_{n-1}'(\vec{r}'', \vec{r}, t)\big|_{z''=a} \quad . \tag{107}$$

The recursive computation of the G_n' [with $G_0' = G_0$ given by (13)] yields

$$G_n' = -2^{-n-3/2}\lambda^{-3/2} \exp\{-\tfrac{1}{2}\pi\lambda^{-2}[(x'-x)^2 + (y'-y)^2 + (z'+z-2a)^2]\} \quad . \tag{108}$$

Substitution of (108) into (106) leads to a geometric series which is readily summed to give

$$G_S' = -2^{-3/2}\lambda^{-3/2} \exp\{-\tfrac{1}{2}\pi\lambda^{-2}[(x'-x)^2 + (y'-y)^2 + (z'+z-2a)^2]\} \quad , \tag{109}$$

a result which could also have been obtained by the method of images. The expression (108) makes it clear that the expansion parameter for Mohling's iteration scheme is actually $[\frac{1}{2} + O(\lambda/a)]$ rather than $\{(\lambda/a) + O[(\lambda/a)^2]\}$ as claimed by Mohling. The iteration can be carried out explicitly to all orders on the exact equations (104) and (105) by Laplace-transforming and making a partial-wave expansion; the methods of Ref. 3 can then be used to reach the same conclusions about the character of the iteration.

Care must be taken when calculating the iterates G_n from Eq. (105) to insure that the limit of $(\partial/\partial r'')G_{n-1}(\vec{r}'', \vec{r}; t)$ is obtained correctly as r'' approaches a from the exterior of the sphere. We illustrate the problem by considering the case $n=2$, for which Eq. (105) yields

$$G_2(\vec{r}, \vec{r}; \beta) = \left(\frac{\lambda^2}{2\pi}\right)^2 \int_0^1 dt \int d^3r''\, G_0(\vec{r}, \vec{r}''; \beta t) \times \delta(r''-a^+)\frac{\partial}{\partial r''}\left(\int_0^{1-t} ds \int d^3r'\,\delta(r'-a) \times G_0[\vec{r}'', \vec{r}'; \beta(1-s-t)]\,\frac{\partial}{\partial r'}\,G_0(\vec{r}', \vec{r}; \beta s)\right)$$

$$= 2^{-13/2}\lambda^{-9}\int_0^1 dt\, t^{-3/2} \times \lim_{\epsilon\to 0}\int_0^{1-t} ds\, s^{-5/2}(1-s-t)^{-5/2}F(s, t; \epsilon) \,, \tag{110}$$

where

$$F(s, t; \epsilon) = \int d^3r'\,\delta(r'-a)\int d^3r''\,\delta(r''-a)(\vec{r}'/r') \times(\vec{r}'-\vec{r})(\vec{r}''/r'')\cdot(\vec{r}''+\epsilon\vec{r}''-\vec{r}') \times \exp\{-\tfrac{1}{2}\pi\lambda^{-2}[t^{-1}(\vec{r}-\vec{r}'')^2 + (1-s-t)^{-1} \times(\vec{r}''+\epsilon\vec{r}''-\vec{r}')^2 + s^{-1}(\vec{r}'-\vec{r})^2]\} \,. \tag{111}$$

Here $\vec{r}''$ has been increased by $\epsilon\vec{r}''$ where it appears in $(\partial/\partial r'')G_0[\vec{r}'', \vec{r}'; \beta(1-s-t)]$ to insure a correct calculation of the $r''\to$ a limit, *which must be taken after integrating over s* as a consequence of the nonuniform behavior near $s = 1-t$. Because of the rapid fall-off of the exponential in (111) for $\lambda/a \ll 1$, the major contribution to the integral comes from the neighborhood of $\vec{r}'' = \vec{r}' = a(\vec{r}/r)$. With this in mind, we choose polar coordinates with the z axis along the $\vec{r}$ direction for the integration over $\vec{r}'$ and $\vec{r}''$. Such a choice, followed by the substitutions $x = 2\sin(\theta'/2)$, $y = 2\sin(\theta''/2)$, $\varphi''-\varphi' = \varphi$ yields

$$F(s, t; \epsilon) \cong 2\pi a^5 \int_0^{2\pi} d\varphi \int_0^\infty x\,dx \int_0^\infty y\,dy \times(a - r + \tfrac{1}{2}rx^2)[\epsilon + \tfrac{1}{2}(x^2+y^2) - xy\cos\varphi - \psi(x, y, \varphi)] \times\exp\left\{-\frac{\pi}{2\lambda^2}\left[\frac{\epsilon^2 a^2}{1-s-t} + \frac{(s+t)}{st}(r-a)^2 + \left(\frac{ar}{s} + \frac{a^2}{1-s-t}\right)x^2 - \frac{2a^2}{1-s-t}\,xy\cos\varphi + \left(\frac{ar}{t} + \frac{a^2}{1-s-t}\right)y^2 - \frac{2a^2}{1-s-t}\,\psi(x, y, \varphi)\right]\right\} \,, \tag{112}$$

where $\psi(x, y, \varphi) \equiv xy[(1-\frac{1}{4}x^2)^{1/2} \times(1-\frac{1}{4}y^2)^{1/2} - 1]\cos\varphi + \frac{1}{4}x^2y^2$.

In the derivation of (112) from (111), a term $-\frac{1}{2}\pi(a/\lambda)^2\epsilon(1-s-t)^{-1}(x^2+y^2-xy\cos\varphi-\psi)$ has been dropped from the exponent (because it does not contribute in the $\epsilon\to 0$ limit) and the upper limits on the x and y integrations have been replaced by ∞ (because most of the contribution comes from the neighborhood of $x=y=0$). The integrations over x, y, and φ in (112) can be performed by making the definition

$$I(A, B, C) \equiv \int_0^{2\pi} d\varphi \int_0^\infty x\,dx \int_0^\infty y\,dy \times\exp[-(Ax^2 + 2Bxy\cos\varphi + Cy^2)] \quad . \tag{113}$$

It is shown in Appendix B that

$$I(A,B,C)=\tfrac{1}{2}\pi(AC-B^2)^{-1} \quad . \tag{114}$$

We discard terms like ψ which are of fourth degree in x and y because they do not contribute to the first two orders in (λ/a). Then (112) becomes

$$F(s,t;\epsilon)\cong-(2\pi a^5)\exp\left\{-\frac{\pi}{2\lambda^2}\left[\frac{\epsilon^2a^2}{1-s-t}+\frac{(s+t)}{st}(r-a)^2\right]\right\}\left\{\epsilon\left[(r-a)+\tfrac{1}{2}r\frac{\partial}{\partial A}\right]+\tfrac{1}{2}(r-a)\times\left(-\frac{\partial}{\partial A}+\frac{\partial}{\partial B}-\frac{\partial}{\partial C}\right)\right\} I(A,B,C), \tag{115}$$

where I and its derivatives are evaluated at

$$A=\tfrac{1}{2}\pi\lambda^{-2}a[(r/s)+a(1-s-t)^{-1}] \quad ,$$
$$B=-\tfrac{1}{2}\pi\lambda^{-2}a^2(1-s-t)^{-1} \quad ,$$
$$C=\tfrac{1}{2}\pi\lambda^{-2}a[(r/t)+a(1-s-t)^{-1}] \quad .$$

By carrying out the indicated operations in (115) and inserting the result into (110), one obtains

$$G_2(\vec{r},\vec{r};\beta)\cong G_2^{(1)}(\vec{r},\vec{r};\beta)+G_2^{(2)}(\vec{r},\vec{r};\beta) \quad , \tag{116}$$

where

$$G_2^{(1)}(\vec{r},\vec{r};\beta)=-2^{-9/2}\lambda^{-3}ar^{-1}\times\int_0^1 dt\,t^{-1/2}(1-t)^{-3/2}\,[a(r-a)\lambda^{-2}-t(1-t)\pi^{-1}]\times\exp[-\tfrac{1}{2}\pi\lambda^{-2}t^{-1}(1-t)^{-1}(r-a)^2]\times\{\lim_{\epsilon\to0}\epsilon\int_0^{1-t}ds\,(1-s-t)^{-3/2}\times\exp[-\tfrac{1}{2}\pi\lambda^{-2}\epsilon^2a^2(1-s-t)^{-1}]\} \tag{117}$$

and

$$G_2^{(2)}(\vec{r},\vec{r};\beta)=-2^{-11/2}\lambda^{-3}\pi^{-1}a^2\times(r-a)r^{-1}\int_0^1 dt\int_0^{1-t}ds\,t^{-3/2}s^{-3/2}\times(1-s-t)^{-1/2}[t(s+t)][(1-s-t)r+(s+t)a]^{-2}\times\exp[-\tfrac{1}{2}\pi\lambda^{-2}(s+t)s^{-1}t^{-1}(r-a)^2] \quad . \tag{118}$$

In (118), symmetry between s and t can be exploited to replace the factor $[t(s+t)]$ by $\frac{1}{2}(s+t)^2$. If this is done, the contribution $G_2^{(2)}$ can be recognized as half of the contribution given by Mohling's Eq. (33) [the factor of $\frac{1}{2}$ arises because $G_2(\vec{r},\vec{r};\beta)=\frac{1}{2}\langle\vec{r}|U^{(2)}(\beta)|r\rangle$]. In (117), the integration over s can be performed by noting that for ϵ small all the contribution comes from the neighborhood of $s=(1-t)$, a fact which has been used to replace s by $(1-t)$ where appropriate in obtaining (117). The integration over t can be done with the aid of the faltung theorem for the Laplace transform to give

$$G_2^{(1)}(\vec{r},\vec{r};\beta)=-2^{-7/2}\lambda^{-3}ar^{-1}\{\exp[-\tfrac{1}{2}\pi\lambda^{-2}(2r-2a)^2]-2^{-3/2}(\lambda/a)\mathrm{erfc}[2^{1/2}\pi^{1/2}\lambda^{-1}(r-a)]\}. \tag{119}$$

The leading term for $r\to a$ of (119) agrees with the result of the plane approximation given by Eq. (108), and contributes to the second virial coefficient, a term of the same order in (λ/a) as the first quantum correction found by Beth and Uhlenbeck.

It is the term $G_2^{(1)}$ which was neglected in Mohling's calculation of the second iterate.

APPENDIX A: ALTERNATIVE DERIVATION OF EQS. (1)–(5)

The grand partition function is

$$e^{-\Omega/(kT)}=\sum_{N=0}^{\infty}z^NQ_N \quad , \tag{A1}$$

where z is the absolute activity and Q_N the canonical partition function for N particles. For the ideal Boltzmann gas

$$Q_N=(N!)^{-1}[V(2\pi mkT/h^2)^{3/2}]^N$$

so that $\Omega=-zkTV(2\pi mkT/h^2)^{3/2}$. Since $N=-[z/(kT)]\partial\Omega/\partial z$, it follows that at high temperatures and low densities, where the ideal Boltzmann-gas model is a good first approximation, $z\approx\rho(2\pi mkT/h^2)^{-3/2}$. Thus the virial expansion of the equation of state can be obtained by inverting the power series in z for $\rho=-[z/(VkT)]\partial\Omega/\partial z$ to get $z(\rho)$ as a power series in ρ to be substituted for z in $PV=-\Omega$. Such a procedure makes no assumptions about the presence of quantum effects in Q_N. The algebraic manipulations are carried out in an elegant and general manner in T. L. Hill's textbook.[24] The first terms can be obtained as easily by pedestrian methods; the result we need is

$$P/(\rho kT)=1+(B/N)\rho+O(\rho^2) \quad , \tag{A2}$$

where the second virial coefficient B is

$$B=-Q_1^{-2}NV(Q_2-\tfrac{1}{2}Q_1^2) \quad . \tag{A3}$$

The partition functions Q_1 and Q_2 can be evaluated by introducing a complete orthonormal set of single-particle functions $\varphi_n(\vec{r})\chi_s(\sigma)$ where φ and χ are the spatial and spin parts. The members of a complete set of two-particle functions then have the form

$$[2^{-1/2}+(2^{-1}-2^{-1/2})\delta_{m,n}\delta_{s,t}][\varphi_n(\vec{r}_1)\varphi_m(\vec{r}_2)\chi_s(\sigma_1)\chi_t(\sigma_2)\pm\varphi_m(\vec{r}_1)\varphi_n(\vec{r}_2)\chi_t(\sigma_1)\chi_s(\sigma_2)] \quad ,$$

where the upper (plus) sign is for bosons and the lower (minus) sign is for fermions. Using these functions to evaluate the trace,

$$Q_2-\tfrac{1}{2}Q_1^2=\tfrac{1}{2}(2S+1)^2\sum_{m,n}\int d^3\vec{r}_1\int d^2\vec{r}_2\varphi_n^*(\vec{r}_1)\varphi_m^*(\vec{r}_2)$$

$$\times\{\exp[-H_2(\vec{r}_1,\vec{r}_2)/(kT)][\varphi_n(\vec{r}_1)\varphi_m(\vec{r}_2) \pm(2S+1)^{-1}\varphi_m(\vec{r}_1)\varphi_n(\vec{r}_2)]-\exp[-H_1(\vec{r}_1)/kT]\times\exp[-H_1(\vec{r}_2)/kT]\varphi_n(\vec{r}_1)\varphi_m(\vec{r}_2)\}\ , \qquad (A4)$$

where S is the spin of the particles and H_1, H_2 are the one- and two-particle Hamiltonians. We now change to relative $[\vec{r}=\vec{r}_1-\vec{r}_2]$ and center-of-mass $[\vec{R}=\frac{1}{2}(\vec{r}_1+\vec{r}_2)]$ variables and interchange the sum over spatial quantum numbers with the integration. The integration over $\vec{R}$ and sum over the c.m. complete set can then be performed by using free-particle wave functions for the c.m. complete set to give

$$Q_2-\tfrac{1}{2}Q_1^2=2^{1/2}V\lambda^{-3}(2S+1)^2\int d^3r\,[G(\vec{r},\vec{r};\beta)-G_0(\vec{r},\vec{r};\beta)\pm(2S+1)^{-1}G(\vec{r},-\vec{r};\beta)]\ , \qquad (A5)$$

where

$$G(\vec{r}\,',\vec{r};\beta)\equiv\sum_n\psi_n^*(\vec{r}\,')\exp[-\beta H_{\rm rel}(\vec{r})]\psi_n(\vec{r})\ ,$$

$$G_0(\vec{r}\,',\vec{r};\beta)\equiv\sum_n\psi_n^*(\vec{r}\,')\exp[-\beta H_{\rm rel}^{(0)}(\vec{r})]\psi_n(\vec{r})\ . \qquad (A6)$$

Here the $\psi_n(\vec{r})$ are some complete set of orthogonal functions,

$$H_{\rm rel}{}^{(0)}(\vec{r})=-(\hbar^2/m)\nabla^2,\quad H_{\rm rel}(\vec{r})=H_{\rm rel}^{(0)}(\vec{r})+V(r),$$

$$\lambda=(2\pi mkT/h^2)^{-1/2},\quad \text{and}\quad \beta=(kT)^{-1}.$$

It is easily shown by using plane waves for the ψ_n that $G_0(\vec{r}\,',\vec{r};\beta)$ is given by Eq. (13), and that

$$Q_1=(2S+1)V\lambda^{-3}\ . \qquad (A7)$$

Equations (1)–(3) now follow from using (A5) and (A7) in (A3) and noting [from (13)] that $G_0(\vec{r},\vec{r};\beta)=2^{-3/2}\lambda^{-3}$. Equations (4) and (5) follow from the definition (A6) and the completeness of the ψ_n.

APPENDIX B: EVALUATION OF $I(A,B,C)$

In the definition (113) of $I(A,B,C)$ regard x and y as the magnitudes of two-dimensional vectors $\vec{x}$, $\vec{y}$ with φ the angle between them. Then

$$I=\frac{1}{2\pi}\int d^2\vec{x}\int d^2\vec{y}\exp[-(Ax^2+2B\vec{x}\cdot\vec{y}+Cy^2)]\ , \qquad (B1)$$

where $\vec{x}$, $\vec{y}$ ranges over the entire two-space. Change view points again and regard $\vec{x}$ as the first two components and $\vec{y}$ as the second two components of a four-dimensional vector $\vec{z}$. Then

$$I=\frac{1}{2\pi}\int d^4\vec{z}\ \exp\left(-\sum_{i=1}^{4}\sum_{j=1}^{4}A_{ij}z_iz_j\right)\ , \qquad (B2)$$

where $\vec{z}$ ranges over the entire Euclidean four-space. Here $A_{11}=A_{22}=A$, $A_{33}=A_{44}=C$, $A_{13}=A_{24}=A_{31}=A_{42}=B$, and all other elements A_{ij} are zero. The matrix A_{ij} can, in principle, be diagonalized by an orthogonal transformation. With A_{ij} diagonal, the integration is easily done to obtain

$$I=\tfrac{1}{2}\pi(\det A_{ij})^{-1/2}\ . \qquad (B3)$$

But $\det A_{ij}$, which is invariant under orthogonal transformation, is just $(AC-B^2)^2$. The result (114) now follows.

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*Work of Secs. IV and V was contained in an M.S. thesis, University of Delaware, 1968 (unpublished); a preliminary report was given at the American Physical Society meeting [Bull. Am. Phys. Soc. 13, 646 (1968)]. The work of Sec. VI will appear as part of a Ph.D. thesis University of Delware (unpublished).

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[7]R. N. Hill, J. Math. Phys. 9, (1968), Secs. II–IV.

[8]M. Boyd, S. Larsen, and J. Kilpatrick, Ref. 6, Eqs.

(12)–(14).

[9]This method of obtaining Green's functions is discussed by P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Vol. I, pp. 825–833.

[10]See Sec. II of Ref. 7. Theorems useful for justifying term-by-term inverse Laplace transformation of large-W expansions to get small-β expansions and of small-W expansions to get large-β expansion have been given by J. Lavoine, Ann. Inst. Henri Poincaré 4, 49 (1966).

[11]J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, 1940), p. 431; E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge U. P., Cambridge, England, 1952), 4th ed., pp. 127–128.

[12]The $|z|\to\infty$ asymptotic expansion (44) is uniformly valid in ν for ν real and in either $\arg z^2$ as $|z|\to\infty$ with $\mathrm{Re}\, z^2 \geq 0$ or in $\mathrm{Re}\, z^2$ as $\mathrm{Im}\, z^2 \to\infty$ with $\mathrm{Re}\, z^2 \leq 0$. Hence (54) is valid uniformly in $\arg z^2$ as $|z|\to\infty$ with $\mathrm{Re}\, z^2 \geq 0$ and in $\mathrm{Re}\, z^2$ as $\mathrm{Im}\, z^2\to\infty$ with $\mathrm{Re}\, z^2 \leq 0$, thus justifying term-by-term inverse Laplace transformation (see Ref. 10).

[13]G. Uhlenbeck and E. Beth, Ref. 10, obtained the (λ/a) term. The $(\lambda/a)^2$ term, apart from a missing factor 2, was obtained by F. Mohling, Ref. 5. The correct coefficient $1/\pi$, together with the $(\lambda/a)^3$ term, was obtained by Handelsman and Keller, Ref. 6; the $(\lambda/a)^4$ term was obtained by Hemmer and Mork, Ref. 6. The $(\lambda/a)^5$ term was obtained by R. N. Hill, Ref. 3; the $(\lambda/a)^6$ term was obtained by Trygve S. Nilsen, J. Chem. Phys. 51, 4675 (1969), using the method given by Hill in Ref. 3.

[14]W. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Springer, Berlin, 1966), p. 140; M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover, New York, 1965), p. 378.

[15]For γ large, the difference between ω and γ is $O(\gamma^{-1})$, which suggests Taylor-expanding the modified Bessel functions of arguments ωa and ωb about γa and γb. Such an expansion, however, is not uniformly valid in ν. After the factor $\exp[\pm\mu_\nu(x)]$ has been separated off, such a Taylor expansion on i_ν, k_ν, l_ν, and m_ν is uniformly valid in ν.

[16]M. Abramowitz and I. A. Stegun, Ref. 14, p. 366.

[17]While the present paper was being typed, one of the authors received preprints by Trygve S. Nilsen and by Alba Theumann reporting work on quantum corrections to B_{dir} for a hard-core-plus-square-well potential. Both Nilsen and Theumann managed to handle the nonuniformity for $(mV_0a^2)/(2\pi\hbar^2)$ large by keeping all orders in

$$\beta V_0 = [(mV_0a^2)/(2\pi\hbar^2)](\lambda/a)^2$$

at a given order in λ/a. They did not, however, handle the nonuniformity for $(b-a)/a$ small, which has the consequence that they do not recover the hard-sphere result when $b\to a$. An expansion of their result in powers of βV_0 agrees with Eq. (75) when $\mathrm{erf}[(2\pi)^{1/2}(b-a)/\lambda]\approx 1$. For helium, both $(b-a)/a$ and $(mV_0a^2)/(2\pi\hbar^2)$ are near 1, so that neither nonuniformity need be handled. A complete high-temperature exploration of the model, of course, requires the handling of both nonuniformities.

[18]R. N. Hill, J. Math. Phys. 9, 1534 (1968).

[19]R. N. Hill, J. Math. Phys. 9, 1534 (1968), Eq. (62).

[20]Such Taylor expansion, although not permissible in Sec. IV (see Ref. 15), is permissible here because the ratio of order to argument is bounded for the modified Bessel functions which appear.

[21]Magnus and Oberhettinger, Ref. 14, p. 68.

[22]C. B. Balogh, thesis, Oregon State University, 1965 (unpublished), pp. 58–59 and 62–63. See also C. B. Balogh, Bull. Am. Math. Soc. 72, 40 (1966); C. B. Balogh, SIAM J. Appl. Math. 15, 1315 (1967). These approximations are uniformly valid in x for $|\arg x|$ bounded away from π and p large.

[23]Magnus and Oberhettinger, Ref. 14, pp. 75 and 139.

[24]T. L. Hill, in *Statistical Mechanics, Principles and Selected Applications* (McGraw-Hill, New York, 1956), Chap. 5.