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Quantum-Mechanical Second Virial Coefficient at High Temperatures

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An expression is obtained for the quantum-mechanical second virial coefficient in the form of an inverse Laplace transform of the logarithmic derivative of the Jost function. This form is useful for the calculation of the direct part of the virial coefficient at high temperatures in cases where the Wigner-Kirkwood expansion breaks down. Explicit calculations are presented for hard spheres, the square-well potential, and the square-well potential with a hard core.

I. INTRODUCTION

The straightforward method of calculating the direct part of the second virial coefficient at high temperatures uses the Wigner-Kirkwood (WK) expansion.[1] This essentially is a perturbation expansion of the Hamiltonian in powers of the kinetic energy and leads to an expression for the second virial coefficient as a power series in $\hbar^2$. However, for a large class of potentials, the WK expansion breaks down. This class includes all potentials $V(r)$ which are nondifferentiable functions of r, as well as potentials such as the exponential potential for which higher coefficients in the WK expansion diverge. DeWitt[2] has analyzed the quantum corrections to the second virial coefficient for a number of these potentials and has found that they involve nonanalytic forms of $\hbar^2$. The particular case of hard spheres has received some attention,[3–6] and Mohling[5] has also treated the case of a square-well potential with a hard core. In these instances, expansions in powers of $\hbar$ are obtained.

The related problem of calculating the exchange second virial coefficient at high temperatures has also been studied by several authors,[3,7,8] and recently Hill[6] has given a general method for determining the exchange contribution when the potential is more singular than r^{-2} at the origin.

In the present paper, we derive an expression for the second virial coefficient in the form of an inverse Laplace transform of the logarithmic derivative of the Jost function.[9,10] The asymptotic behavior of the Jost function can then be used to determine the behavior of the virial coefficient at high temperatures. The general method is the same as that of Hill.[6] However, our expression for the direct second virial coefficient is simpler in that the coordinate-space integration has been performed explicitly at the outset, and only the inverse-transform and partial-wave summation remain to be done. Provided these are carried out in the correct order, there are no convergence difficulties, and one does not have to subtract off "singular parts" and evaluate them by a different method, as in Hill's treatment.

In Secs. III–V, we present calculations of the direct second virial coefficient for hard spheres, the square-well potential, and the square-well potential with a hard core. In the last case, we obtain an expression which only partially agrees with a result of Mohling.

II. DERIVATION OF BASIC EQUATIONS

The second virial coefficient can be expressed in the form[3]

$$B = B_{\text{direct}} + B_{\text{exch}} , \tag{1}$$

where

$$B_{\text{direct}} = -\tfrac{1}{2} N\, 2^{3/2}\lambda^3 \int d^3r \langle \vec{r}\,| e^{-\beta H} - e^{-\beta H_0} |\,\vec{r}\rangle, \tag{2}$$

$$B_{\text{exch}} = \mp \tfrac{1}{2} N(2s+1)^{-1} 2^{3/2}\lambda^3 \times \left(\int d^3r \langle -\vec{r}\,| e^{-\beta H} - e^{-\beta H_0} |\,\vec{r}\rangle + \tfrac{1}{8}\right) . \tag{3}$$

H is the Hamiltonian for the relative motion of two particles, each of mass m interacting via a potential $V(r)$, and H_0 is the corresponding Hamiltonian in the absence of interaction; s is the spin of a particle and $\lambda = (2\pi\hbar^2\beta/m)^{1/2}$, where $\beta \equiv 1/kT$, is the thermal wavelength; B_{exch} is the contribution from the quantum statistics, the upper sign being for Bose statistics and the lower sign for Fermi statistics.

It has been shown by Koppe[11] and Watson[12] that the statistical operator $e^{-\beta H}$ is related to the resolvent $(z-H)^{-1}$ by a Laplace transform. If we write

$$G(\vec{r}\,', \vec{r}; z) = \langle \vec{r}\,' |(z-H)^{-1}|\vec{r}\rangle , \tag{4}$$

then $$\langle \vec{r}\,' | e^{-\beta H} | \vec{r}\rangle = -L_\beta^{-1}[G(\vec{r}\,', \vec{r}; -p)] , \tag{5}$$

where $$L_\beta^{-1} \equiv (1/2\pi i)\int_{c-i\infty}^{c+i\infty} dp\, e^{\beta p} \tag{6}$$

is the inversion operator for the Laplace transform; $c > (-E_L)$, where E_L is the least eigenvalue of H. Use of (5) in (2) and (3) gives

$$B_{\text{direct}} = \tfrac{1}{2} N 2^{3/2}\lambda^3 \int d^3r\, L_\beta^{-1} \times [G(\vec{r}, \vec{r}; -p) - G_0(\vec{r}, \vec{r}; -p)] , \tag{7}$$

$$B_{\text{exch}} = \pm \tfrac{1}{2} N(2s+1)^{-1} 2^{3/2}\lambda^3 \{ \int d^3r\, L_\beta^{-1} \times [G(-\vec{r}, \vec{r}; -p) - G_0(-\vec{r}, \vec{r}; -p)] - \tfrac{1}{8}\} , \tag{8}$$

where $G_0(\vec{r}\,', \vec{r}; z)$ is the Green's function for the noninteracting system. We now substitute the partial-wave expansion

$$G(\vec{r}\,', \vec{r}; z) = \sum_{l=0}^{\infty} (2l+1) P_l(\hat{\vec{r}}\,'\cdot\hat{\vec{r}}) g_l(r', r; z), \tag{9}$$

and obtain

$$B_{\text{direct}} = -2^{1/2} N\lambda^3 \Delta_+ , \tag{10}$$

$$B_{\text{exch}} = B^0_{\text{exch}} \mp 2^{1/2} N\lambda^3 (2s+1)^{-1} \Delta_- , \tag{11}$$

where $$\Delta_\pm = \sum_{l=0}^{\infty} (\pm)^l (2l+1) B_l , \tag{12}$$

$$B_l = -L_\beta^{-1}\{\int_0^\infty 4\pi r^2 dr\, [g_l(r, r; -p) - g_{0l}(r, r; -p)]\} , \tag{13}$$

$$B^0_{\text{exch}} = \mp 2^{-5/2} N\lambda^3 (2s+1)^{-1} . \tag{14}$$

B^0_{exch} is the ideal-gas contribution. Equations (10)–(14) are equivalent to Eqs. (C1)–(C5) of Hill.[6]

The radial Green's function is given by

$$g_l(r, r'; z) = \frac{m}{4\pi\hbar^2}\,\frac{1}{rr'}\,\frac{1}{W(y_1, y_2)}\; y_1(k, r_<)\, y_2(k, r_>) , \tag{15}$$

where y_1, y_2 are solutions of

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - \frac{m}{\hbar^2} V(r) + k^2\right) y(k, r) = 0 , \tag{16}$$

where $k^2 \equiv (m/\hbar^2) z$ is complex, with $\mathrm{Im}k > 0$.

$$W(y_1, y_2) \equiv y_1 \frac{\partial y_2}{\partial r} - \frac{\partial y_1}{\partial r} y_2 \tag{17}$$

is the Wronskian of the two solutions, and $r_<$ ($r_>$) equals the lesser (greater) of r' and r. For y_1 and y_2 we can choose any two independent solutions of (16) such that y_1 satisfies the inner boundary condition and y_2 satisfies the outer boundary condition. We take

$$y_1 = \varphi_l(k, r), \tag{18}$$

$$y_2 = f_l(-k, r) , \tag{19}$$

where $\varphi_l(k, r)$ is the regular solution defined by

$$\lim (2l+1)!!\, r^{-l-1} \varphi_l(k, r) = 1, \quad \text{as } r \to \infty , \tag{20}$$

and $f_l(k, r)$ is the Jost solution defined by

$$\lim e^{ikr} f_l(k, r) = i^l , \quad \text{as } r \to \infty. \tag{21}$$

The Wronskian is

$$W[\varphi_l(k,r),f_l(-k,r)]=(-1)^{l+1}f_l(-k)/k^l\ , \qquad (22)$$

where $f_l(k)$ is the Jost function, and so

$$g_l(r,r';z)=(m/4\pi\hbar^2)(1/rr')(-1)^{l+1} \times[k^l/f_l(-k)]\varphi_l(k,r_<)f_l(-k,r_>)\ . \qquad (23)$$

For the noninteracting case, this becomes

$$g_{0l}(r,r';z)=(m/4\pi\hbar^2)(-i)kj_l(kr_<)h_l^{(1)}(kr_>)\ , \qquad (24)$$

where $j_l(z)\equiv(\pi/2z)^{1/2}J_{l+1/2}(z)$,

$h_l^{(1)}(z)\equiv(\pi/2z)^{1/2}H_{l+1/2}^{(1)}(z)$

are spherical Bessel functions. If we substitute (23) and (24) in (13), the integration over r can be done explicitly. In Appendix A, we show that

$$\int_0^\infty 4\pi r^2dr\,[g_l(r,r;z)-g_{0l}(r,r;z)] =-(m/\hbar^2)\,(1/2k)f_l'(-k)/f_l(-k)\ , \qquad (25)$$

where the prime denotes differentiation with respect to the argument. Equation (25) holds even in the case where the potential has a hard core. Equations (25) and (13) give

$$B_l=L_\alpha^{-1}\{\,(1/2i\gamma)\,[f_l'(-i\gamma)/f_l(-i\gamma)]\}\ , \qquad (26)$$

where $\gamma\equiv p^{1/2}$, and $\alpha=\lambda^2/2\pi$. Equation (26), in combination with (10)–(12), is our final expression for the second virial coefficient. The advantage of this form lies in the fact that the large-p behavior of the integrand determines the behavior of B_l for small values of α (i.e., high temperatures). This remains true in the case of potentials $V(r)$ which are nondifferentiable functions of r, and for which the WK expansion fails.

Although the above formulation is formally correct for both the direct and exchange parts of B, in practice it is only useful for calculating B_{direct} at high temperatures. In the exchange part, large cancellations occur between the contributions from the various partial waves, making summation difficult. Hill[6] has shown that in the case of B_{exch}, the Sommerfeld-Watson transform can be used to do the partial-wave summation before the inversion of the Laplace transform, at least for potentials more singular than r^{-2} at the origin. His result can be obtained by applying the Sommerfeld-Watson transform to our equations (11), (12), and (26), although care must be taken in interchanging the order of $\sum_l$ and L_α^{-1}.

The equivalence of (26) to the usual phase-shift formula of Beth and Uhlenbeck[13] is easily demonstrated. The transformation $p=\gamma^2$ gives

$$B_l=-\frac{1}{2\pi}\int_{\gamma_0-i\infty}^{\gamma_0+i\infty}d\gamma\, e^{\alpha\gamma^2}\frac{f_l'(-i\gamma)}{f_l(-i\gamma)}\ , \qquad (27)$$

where the contour lies to the right of all the singularities of the integrand. $f_l(k)$ as a function of k is analytic for $\operatorname{Im}k<0$,[14] and has simple zeros on the imaginary axis at $k=-ik_n$ corresponding to bound states of energy $\epsilon_n=-(\hbar^2/m)k_n^2$. It is continuous on the real axis and has no zeros there except possibly at $k=0$. Therefore, $f_l'(-i\gamma)/f_l(-i\gamma)$ is analytic for $\operatorname{Re}\gamma>0$, except for simple poles at $\gamma=k_n$. Thus we may shift the integration contour in (27) to the left to lie along the imaginary axis, picking up the residues at the bound-state poles as we go. This gives

$$B_l=\sum_n e^{-\beta\epsilon_n}-\frac{1}{2\pi}\,P\int_{-i\infty}^{+i\infty}d\gamma\, e^{\alpha\gamma^2}\frac{f_l'(-i\gamma)}{f_l(-i\gamma)}$$

$$=\sum_n e^{-\beta\epsilon_n}-\frac{1}{2\pi i}\int_0^\infty dk\, e^{-\alpha k^2}\left(\frac{f_l'(-k)}{f_l(-k)}+\frac{f_l'(k)}{f_l(k)}\right). \qquad (28)$$

Using the relation between the Jost function and the phase shift $\delta_l(k)$

$$f_l(k)/f_l(-k)=e^{2i\delta_l(k)}\ , \qquad (29)$$

we obtain the usual expression

$$B_l=\sum_n e^{-\beta\epsilon_n}+\frac{1}{\pi}\int_0^\infty dk\, e^{-\alpha k^2}\,\frac{d\delta_l}{dk}\ . \qquad (30)$$

III. HARD SPHERES

For hard spheres of radius a, the Jost function is

$$f_l(k)=-ik^l(\tfrac{1}{2}\pi ka)^{1/2}H_{l+1/2}^{(2)}(ka)\ . \qquad (31)$$

This gives

$$f_l(-i\gamma)=(2a/\pi)^{1/2}\gamma^\nu K_\nu(\gamma a)\ , \qquad (32)$$

where $\nu\equiv l+\frac{1}{2}$ and $K_\nu(x)$ is a modified Bessel function. Substitution in (26) then gives

$$B_l=\tfrac{1}{2}L_\alpha^{-1}\left(\frac{\nu}{\gamma^2}+\frac{a}{\gamma}\,\frac{K_\nu'(a\gamma)}{K_\nu(a\gamma)}\right)\ . \qquad (33)$$

In order to evaluate this for small α, we require the asymptotic expansion of the integrand for large γ. This is obtained from the Debye expansions for the modified Bessel functions,[15] which are uniformly valid for $0\le\nu\le\infty$. These are

$$I_\nu(x)\sim(2\pi)^{-1/2}(\nu^2+x^2)^{-1/4}e^{\mu} \times\sum_{k=0}^\infty[t^{-k}u_k(t)](\nu^2+x^2)^{-k/2}\ , \qquad (34)$$

$$K_\nu(x)\sim(\tfrac{1}{2}\pi)^{1/2}(\nu^2+x^2)^{-1/4}e^{-\mu} \times\sum_{k=0}^\infty[(-t)^{-k}u_k(t)](\nu^2+x^2)^{-k/2}\ , \qquad (35)$$

$$I_\nu'(x)\sim(2\pi)^{-1/2}x^{-1}(\nu^2+x^2)^{1/4}e^{\mu} \times\sum_{k=0}^\infty[t^{-k}v_k(t)]\,(\nu^2+x^2)^{-k/2}\ , \qquad (36)$$

$$K_\nu'(x) \sim -(\tfrac{1}{2}\pi)^{1/2} x^{-1} (\nu^2+x^2)^{1/4} e^{-\mu} \times \sum_{k=0}^{\infty} [(-t)^{-k} v_k(t)] (\nu^2+x^2)^{-k/2} , \quad (37)$$

where $\mu = (\nu^2+x^2)^{1/2} - \nu \sinh^{-1}(\nu/x)$, (38)

$$t = \nu(\nu^2+x^2)^{-1/2} . \quad (39)$$

$u_k(t)$ and $v_k(t)$ are polynomials in t. [We give the series for $I_\nu(x)$ for later reference – only (35) and (37) are required for hard spheres.]

From (35) and (37), one obtains[6]

$$\frac{K_\nu'(x)}{K_\nu(x)} \sim -\frac{1}{x} \sum_{k=0}^{\infty} \frac{t^{-k}\zeta_k(t)}{(x^2+\nu^2)^{(k-1)/2}} , \quad (40)$$

where

$$\zeta_0(t) = 1 ,$$

$$\zeta_k(t) = (-1)^k v_k(t) - \sum_{l=0}^{k-1} (-1)^{k-l} u_{k-l}(t)\, \zeta_l(t). \quad (41)$$

The explicit expressions for coefficients ζ_0 to ζ_5 are given by Hill.[6] The series (40) is now substituted in (33) to give

$$B_l = \tfrac{1}{2} e^{-\Lambda\nu^2} \sum_{k=0}^{\infty} L_\Lambda^{-1} [h_k(\tau)] , \quad (42)$$

where

$$h_0(\tau) = \frac{\nu}{\gamma^2-\nu^2} - \frac{1}{\gamma^2-\nu^2} \frac{\zeta_0(\tau)}{\gamma-1} = \frac{-1}{\gamma+\nu} , \quad (43)$$

$$h_k(\tau) = -\frac{1}{\gamma^2-\nu^2} \frac{\tau^{-k}\zeta_k(\tau)}{\gamma^{k-1}} , \quad k \geq 1 . \quad (44)$$

Here we have set $\tau = \nu/\gamma$, $\Lambda = (\lambda/a)^2/2\pi$. In deriving (42), we have used the translation property of the inverse Laplace transform:

$$L_\beta^{-1} [F(p+c^2)] = e^{-\beta c^2} L_\beta^{-1}[F(p)]. \quad (45)$$

The inverse transforms in (42) can be performed using[16]

$$L_\beta^{-1} [(p^{1/2}+c)^{-1}] = \pi^{-1/2}\beta^{-1/2} - c e^{\beta c^2} \operatorname{erfc}(\beta^{1/2}c), \quad (46)$$

$$L_\beta^{-1} [(p+c^2)^{-\mu}] = e^{-\beta c^2} \beta^{\mu-1}/\Gamma(\mu) , \quad (47)$$

where $\operatorname{erfc}(x) = 2\pi^{-1/2} \int_x^\infty e^{-t^2} dt$. (48)

This leads to

$$B_l \sim \tfrac{1}{2} \nu \operatorname{erfc}(\nu \Lambda^{1/2}) + \tfrac{1}{2} e^{-\Lambda\nu^2} \sum_{n=0}^{\infty} \nu^{2n} \theta_n(\Lambda) , \quad (49)$$

where

$$\theta_0 = -\pi^{-1/2}\Lambda^{-1/2} - \tfrac{1}{2} + \tfrac{1}{4}\pi^{-1/2}\Lambda^{1/2} - \tfrac{1}{8}\Lambda + \tfrac{25}{96}\pi^{-1/2}\Lambda^{3/2} - \tfrac{13}{64}\Lambda^2 + O(\Lambda^{5/2}) ,$$

$$\theta_1 = -\tfrac{5}{6}\pi^{-1/2}\Lambda^{3/2} + \tfrac{3}{4}\Lambda^2 - \tfrac{177}{80}\pi^{-1/2}\Lambda^{5/2} + \tfrac{71}{32}\Lambda^3 + O(\Lambda^{7/2}) ,$$

$$\theta_2 = -\tfrac{5}{16}\Lambda^3 + \tfrac{221}{120}\pi^{-1/2}\Lambda^{7/2} - \tfrac{177}{64}\Lambda^4 + O(\Lambda^{9/2}) , \quad (50)$$

$$\theta_3 = -\tfrac{221}{756}\pi^{-1/2}\Lambda^{9/2} + \tfrac{113}{128}\Lambda^5 + O(\Lambda^{11/2}) ,$$

$$\theta_4 = -\tfrac{113}{1536}\Lambda^6 + O(\Lambda^{13/2}) .$$

The next step is to perform the summation over l. In Appendix B, we obtain the results

$$\sum_{l=0}^{\infty} \nu e^{-\Delta\nu^2} \sim \frac{1}{2\Lambda} + \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{B_{2n+2}}{2(n+1)} (1-2^{-2n-1}) \Lambda^n, \quad (51)$$

$$\sum_{l=0}^{\infty} \nu^2 \operatorname{erfc}(\nu\Lambda^{1/2}) \sim \tfrac{1}{3}\pi^{-1/2}\Lambda^{-3/2} - \pi^{-1/2} \times \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{B_{2n+4}}{(n+2)(2n+1)} (1-2^{-2n-3}) \Lambda^{n+1/2}, \quad (52)$$

where B_{2n} are the Bernoulli numbers. The other series required can be obtained by differentiating (51) with respect to Λ. From (10), (12), and (49)–(52), we obtain the final result

$$B_{\text{direct}}\,(\text{hard spheres}) = \tfrac{2}{3} N\pi a^3 \Bigg\{ 1 + \frac{3}{2\sqrt{2}}\left(\frac{\lambda}{a}\right) + \frac{1}{\pi}\left(\frac{\lambda}{a}\right)^2 + \frac{1}{16\pi\sqrt{2}}\left(\frac{\lambda}{a}\right)^3 - \left(\frac{1}{105\pi^2}\,\frac{\lambda}{a}\right)^4 + \frac{1}{640\pi^2\sqrt{2}}\left(\frac{\lambda}{a}\right)^5 + O\left[\left(\frac{\lambda}{a}\right)^6\right] \Bigg\}, \quad (53)$$

which is identical to that of Hill.

IV. SQUARE-WELL POTENTIAL

For the square-well potential

$$V(r) = -V_0, \quad r < b, \quad V(r) = 0, \quad r > b, \quad (54)$$

the Jost function is

$$f_l(-i\gamma) = (\gamma/\Gamma)^\nu [\Gamma b K_\nu(\gamma b) I_\nu'(\Gamma b) - \gamma b K_\nu'(\gamma b) I_\nu(\Gamma b)] , \quad (55)$$

where $\Gamma^2 = \gamma^2 - mV_0/\hbar^2$. (56)

The expansions (34)–(37) give, after some work,

$$\frac{-if_l'(-i\gamma)}{f_l(-i\gamma)} = \gamma b^2 \Bigg[\frac{-1}{\nu+(\nu^2+\gamma^2b^2)^{1/2}} + \frac{1}{\nu+(\nu^2+\Gamma^2b^2)^{1/2}} + \frac{1}{(\nu^2+\gamma^2b^2)^{1/2}(\nu^2+\Gamma^2b^2)^{1/2}} - \frac{1}{2(\nu^2+\gamma^2b^2)} - \frac{1}{2(\nu^2+\Gamma^2b^2)} + O\left(\frac{1}{(\nu^2+\gamma^2)^{3/2}}\right) \Bigg] . \quad (57)$$

The inverse Laplace transforms can be done using (46) and (47) together with[16]

$$L_\beta^{-1} [p^{-1/2}(p+c^2)^{-1/2}] = e^{-\beta c^2/2} I_0(-\tfrac{1}{2}\beta c^2) . \quad (58)$$

This gives

$$B_l = \tfrac{1}{2}(1-e^{\beta V_0})\, \nu \operatorname{erfc}(\nu\Lambda^{1/2}) + \tfrac{1}{2} e^{-\Lambda\nu^2} \times [-(1-e^{\beta V_0})\pi^{-1/2}\Lambda^{-1/2} + \tfrac{1}{2}C(\beta V_0) + O(\Lambda^{1/2})], \quad (59)$$

where $C(x) \equiv 2e^{x/2} I_0(\tfrac{1}{2}x) - 1 - e^x$. (60)

The l summation is performed with the aid of (51) and (52) and yields

$$B_{\mathrm{direct}}\,(\text{square well}) = \tfrac{2}{3}\pi N b^3 \times \left\{ (1 - e^{\beta V_0}) - \frac{3}{2\sqrt{2}}\, C(\beta V_0)\left(\frac{\lambda}{b}\right) + O\left[\left(\frac{\lambda}{b}\right)^2\right] \right\} . \quad (61)$$

We note that as $V_0 \to -\infty$, then $C(\beta V_0) \to -1$, and we obtain the first two terms of the expansion for hard spheres of radius b. In the other limiting case where βV_0 is small, we find

$$B_{\mathrm{direct}}\,(\text{square well}) = -\pi N b^3 \times \left\{ -\tfrac{2}{3}(\beta V_0) + (\beta V_0)^2 \left[\tfrac{1}{3} - 2^{-7/2}(\lambda/b)\right] + O[(\beta V_0)^3] + O\left[\left(\frac{\lambda}{b}\right)^2\right] \right\} , \quad (62)$$

which agrees with a result of DeWitt.[17]

V. SQUARE WELL WITH HARD CORE

For the potential

$$\begin{aligned} V(r) &= \infty, & r<a \\ &= -V_0, & a<r<b \\ &= 0, & r>b \end{aligned} \quad (63)$$

the Jost function is

$$f_l(-i\gamma) = -(2a/\pi)^{1/2}\gamma^\nu \Gamma b \times [C_\nu(\gamma) I_\nu(\Gamma a) - D_\nu(\gamma) K_\nu(\Gamma a)] , \quad (64)$$

where

$$C_\nu(\gamma) = K_\nu(\gamma b) K_\nu'(\Gamma b) - (\gamma/\Gamma) K_\nu'(\gamma b) K_\nu(\Gamma b) , \quad (65)$$

$$D_\nu(\gamma) = K_\nu(\gamma b) I_\nu'(\Gamma b) - (\gamma/\Gamma) K_\nu'(\gamma b) I_\nu(\Gamma b) , \quad (66)$$

and Γ is defined by (56). This can be written in the form

$$f_l(-i\gamma) = \left[\left(\frac{2a}{\pi}\right)^{1/2} \Gamma^\nu K_\nu(\Gamma a)\right]\left[\left(\frac{\gamma}{\Gamma}\right)^\nu \Gamma b D_\nu(\gamma)\right] \times \left(1 - \frac{C_\nu(\gamma) I_\nu(\Gamma a)}{D_\nu(\gamma) K_\nu(\Gamma a)}\right) . \quad (67)$$

The first bracket is the Jost function for hard spheres of radius a, with γ replaced by Γ. The second bracket is the Jost function for the square-well potential (54). Substituting (64) into (26) and using (10) and (12) gives

$$B_{\mathrm{direct}}(\text{square well} + \text{hard core}) = e^{\beta V_0} B_{\mathrm{direct}}(\text{hard spheres}) + B_{\mathrm{direct}}(\text{square well}) + B_{\mathrm{direct}}(\text{linking}) , \quad (68)$$

where the last term arises from the Jost function

$$f_l^L(-i\gamma) = 1 - C_\nu(\gamma) I_\nu(\Gamma a)/D_\nu(\gamma) K_\nu(\Gamma a) . \quad (69)$$

The expansions (34)–(37) can now be used to obtain the asymptotic form of (69). If we set

$$\omega(x) = (\nu^2 + x^2)^{1/2} , \quad (70)$$

$$\mu(x) = (\nu^2 + x^2)^{1/2} - \nu \sinh^{-1}(\nu/x) , \quad (71)$$

then

$$F_l(p) \equiv \frac{1}{2i\gamma} \frac{f_l^{L\prime}(-i\gamma)}{f_l^L(-i\gamma)} = e^{-E_\nu(\Gamma)} \frac{m}{\hbar^2} V_0 b^2 \times \frac{\omega(\Gamma b) - \omega(\Gamma a)}{\Gamma^2[\omega(\gamma b) + \omega(\Gamma b)]^2} \left[1 + O\left(\frac{1}{\omega(\gamma)}\right)\right] , \quad (72)$$

where

$$E_\nu(\Gamma) = 2[\mu(\Gamma b) - \mu(\Gamma a)] = \int_{a^2}^{b^2} \frac{(\nu^2 + \Gamma^2 t)^{1/2}}{t}\, dt . \quad (73)$$

The exponential in (72) dominates the behavior of $F_l(p)$ for large p, and leads to the conclusion that B_{direct} (linking) does not behave asymptotically like any power of α at high temperatures. This can be demonstrated by means of the following lemma.[18] Let $\bar{g}(p)$ be the Laplace transform of a function $g(\alpha)$. Assume that $\bar{g}(p)$ is analytic except on the real axis for $p<p_0$, and that $\bar{g}(p)^* = \bar{g}(p^*)$. Assume further that for some $\eta > 0$, $\lim p^{\eta+1}\bar{g}(p) = 0$, as $|p| \to \infty$, holds uniformly in $\arg p$ for $|p| \to \infty$ in the right half-plane and uniformly in Rep for Im$p \to \infty$ in the left half-plane. Then

$$\lim \alpha^{-\eta} g(\alpha) = 0, \quad \text{as } \alpha \to 0+ .$$

$F_l(p)$ satisfies the conditions of this lemma for any $\eta > 0$ and every l, so

$$\lim \alpha^{-\eta} L_\alpha^{-1}[F_l(p)] = 0, \quad \text{as } \alpha \to 0+ \quad (74)$$

for all $\eta > 0$. Also, the series

$$\sum_{l=0}^{\infty} (2l+1) L_\alpha^{-1}[F_l(p)]$$

is uniformly convergent, so we can interchange the limit and the sum. This gives

$$\lim \alpha^{-\eta} B_{\mathrm{direct}}(\text{linking}) = 0, \quad \text{as } \alpha \to 0+ \quad (75)$$

for all $\eta > 0$, and so B_{direct} (linking) does not have an expansion in any powers of α.[19]

Thus, at high temperatures the only significant contribution to B_{direct}(square well + hard core) comes from the hard-core and the square-well parts separately; and from (68), (53), and (61), we have

$$B_{\mathrm{direct}}\,(\text{square well} + \text{hard core}) = \tfrac{2}{3} N\pi a^3 e^{\beta V_0}\left[1 + \frac{3}{2\sqrt{2}}\left(\frac{\lambda}{a}\right)\right] + \tfrac{2}{3} N\pi b^3 \times \left[(1 - e^{\beta V_0}) - \frac{3}{2\sqrt{2}}\, C(\beta V_0)\left(\frac{\lambda}{b}\right)\right] + O(\lambda^2) . \quad (76)$$

Mohling[5] has also calculated B_{direct} for the square well with hard-core potential (63). He obtains the terms from the hard core and from the square well (for the case where βV_0 is small), but he also obtains additional terms

$$2^{-5/2} N\pi\lambda a^2 \{\beta V_0 + \tfrac{1}{2}(\beta V_0)^2 + O[(\beta V_0)^3]\} + O(\lambda^3) .$$

In the light of our present investigation we can only regard them as spurious.

APPENDIX A: DERIVATION OF (25)

Let $y_1(k, r)$ and $y_2(k, r)$ be two independent solutions of the differential equation

$$\left[\frac{d^2}{dr^2} - \left(\frac{l(l+1)}{r^2} + \frac{m}{\hbar^2} V(r)\right) + k^2\right] y(k, r) = 0, \quad \text{(A1)}$$

where k is complex with $\text{Im}k > 0$. It follows that

$$\int y_1(k', r) y_2(k, r) dr = [1/(k'^2 - k^2)] W[y_1(k', r), y_2(k, r)] . \quad \text{(A2)}$$

Taking the limit $k' \to k$ gives

$$\int y_1(k, r) y_2(k, r) dr = \frac{1}{2k} W\left(\frac{\partial y_1(k, r)}{\partial k}, y_2(k, r)\right). \quad \text{(A3)}$$

We require the integral

$$I_l(z) = \int_0^\infty 4\pi r^2 dr \, [g_l(r, r; z) - g_{0l}(r, r; z)] . \quad \text{(A4)}$$

Substituting the expression (23) for the Green's functions, and using (A3) gives

$$I_l(z) = (m/2\hbar^2)(-1)^{l+1} k^{l-1} \times \left[W\left(\frac{\partial \varphi_l(k, r)}{\partial k}, \frac{f_l(-k, r)}{f_l(-k)}\right) - W\left(\frac{\partial \varphi_{0l}(k, r)}{\partial k}, f_{0l}(-k, r)\right)\right]_{r=0}^{r=\infty}, \quad \text{(A5)}$$

where $\varphi_{0l}(k, r)$ and $f_{0l}(k, r)$ are the regular solution and the Jost solution in the absence of interaction. The boundary condition (20) shows that the Wronskians vanish at the lower limit. At the upper limit we use (21) and[9]

$$\varphi_l(k, r) \sim \tfrac{1}{2} i^{l+1} k^{-l-1} [f_l(-k) e^{-ikr} - (-)^l f_l(k) e^{ikr}], \quad \text{as } r \to \infty \quad \text{(A6)}$$

to obtain

$$W\left(\frac{\partial \varphi_l(k, r)}{\partial k}, \frac{f_l(-k, r)}{f_l(-k)}\right) \sim \tfrac{1}{2}(-1)^l k^{-l-1} \times \left(2k \frac{f_l'(-k)}{f_l(-k)} + (2l+1) + 2ikr\right), \quad \text{as } r \to \infty . \quad \text{(A7)}$$

For the noninteracting case, the corresponding result is

$$W\left(\frac{\partial \varphi_{0l}(k, r)}{\partial k}, f_{0l}(-k, r)\right) \sim \tfrac{1}{2}(-1)^l k^{-l-1} [(2l+1) + 2ikr], \quad \text{as } r \to \infty. \quad \text{(A8)}$$

From (A5), (A7), and (A8), we obtain the result (25).

It should be noted that (25) still holds in the case where the interaction has a hard core. The boundary condition (20) is now replaced by

$$\varphi_l(k, a) = 0, \quad \frac{\partial}{\partial r} \varphi_l(k, r)\Big|_{r=a} = 1 , \quad \text{(A9)}$$

where a is the hard-core radius. The Wronskians in (A5) still vanish at the lower limit, and the contribution from the upper limit is unchanged by the presence of the hard core.

APPENDIX B: DERIVATION OF (51) AND (52)

We wish to evaluate

$$F(\sigma) = \sum_{l=0}^{\infty} (l + \tfrac{1}{2}) \exp[-\sigma(l + \tfrac{1}{2})^2] , \quad \text{(B1)}$$

where σ is small. The Mellin transform of $F(\sigma)$ is

$$S(p) = \int_0^\infty F(\sigma) \sigma^{p-1} d\sigma , \quad \text{(B2)}$$

$$S(p) = \sum_{l=0}^{\infty} (l + \tfrac{1}{2}) \Gamma(p)/(l + \tfrac{1}{2})^{2p} , \quad \text{(B3)}$$

$$S(p) = \Gamma(p) \zeta(2p-1)(2^{2p} - 1), \quad (\text{Re}\, p > 1) \quad \text{(B4)}$$

where $\zeta(z)$ is the Riemann ζ function. The inversion theorem for the Mellin transform then gives

$$F(\sigma) = (1/2\pi i) \int_{c-i\infty}^{c+i\infty} S(p) \sigma^{-p} dp , \quad \text{(B5)}$$

where $c > 1$. Now $\zeta(2p-1)$ has a pole at $p = 1$ with residue $\frac{1}{2}$, and $\Gamma(p)$ has poles at $p = -n$ ($n = 0, 1, 2, \ldots$) with residues $(-1)^n/n!$. Thus, shifting the contour to the left and picking up the residues at the poles of the integrand gives

$$F(\sigma) \sim \frac{1}{2\sigma} + \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \zeta(-2n-1)(2^{-2n-1} - 1)\sigma^n, \quad \text{(B6)}$$

and using

$$\zeta(-2n-1) = -\tfrac{1}{2} B_{2n+2}/(n+1) , \quad \text{(B7)}$$

where the B_{2n} are the Bernoulli numbers, gives (51). The result (51) was first obtained by Mulholland[20] by a different method.

The same method can be applied to the sum

$$F(\sigma) = \sum_{l=0}^{\infty} (l + \tfrac{1}{2})^2 \,\text{erfc}[(l + \tfrac{1}{2})\sigma^{1/2}] . \quad \text{(B8)}$$

The Mellin transform is

$$S(p) = \pi^{-1/2} p^{-1} \Gamma(p + \tfrac{1}{2})(2^{2p-2} - 1)\zeta(2p-2), \quad \text{Re}\, p > \tfrac{3}{2} \quad \text{(B9)}$$

and the inversion integral now gives

$$F(\sigma) \sim \tfrac{1}{3}\pi^{-1/2}\sigma^{-3/2} - 2\pi^{-1/2} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{1}{2n+1} \times (2^{-2n-3} - 1)\zeta(-2n-3)\sigma^{n+1/2}. \quad \text{(B10)}$$

Use of (B7) then gives (52).

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Microscopic Theory of Quantum Fluids. III. Quasiparticle Ensemble for Degenerate Bose Fluid

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The analysis of the preceding two papers in this series is applied to the specific case of a degenerate Bose fluid, in which there can be macroscopic occupation of the zero-momentum state (in a system at rest). The quasiparticle ensemble of Mohling and Tuttle is incorporated into the theory in order to guarantee that Nernst's theorem for the entropy is satisfied. It is shown that a double-quasiparticle model emerges naturally from the theory, as developed earlier, and this feature is then incorporated into the quasiparticle ensemble. The general theory is prepared, with the aid of the Λ transformation, for calculational applications. A phenomenological theory of the degenerate Bose fluid, based on the double-quasiparticle model, is presented, but no significant physical implications are deduced from it.

1. INTRODUCTION

London[1] emphasized that liquid helium, nature's best example of a degenerate Bose fluid, undoubtedly undergoes Bose-Einstein condensation when it cools from the liquid I phase to the liquid II phase. Lee and Yang[2] used this concept in one of the first modern attempts to derive a quantum-statistical theory of the degenerate Bose fluid. Their x ensemble, which introduces into quantum statistics the possibility for macroscopic occupation of one quantum-mechanical single-particle state, is a stepping stone for the developments in the present paper.

We are concerned with the derivation of a quantum-statistical theory of the degenerate Bose fluid which is useful for practical applications to liquid helium II. In the preceding two papers of this series,[3] we have developed a general theory of quantum fluids and, in particular, have shown how to apply the theory to the special cases of normal Fermi and Bose fluids. For the degenerate Bose-fluid case these two papers represented a simplification and outgrowth of earlier work by Mohling[4]