# Quantum-Mechanical Second Virial Coefficient of a Hard-Sphere Gas at High Temperatures

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The high-temperature expansion of the quantum-mechanical second virial coefficient $B(T)$ of a gas of particles interacting via a hard-core pair potential is determined to fourth order in the ratio of the thermal wavelength $\lambda=(h^2/2\pi mkT)^{1/2}$ to the extension $d$ of the hard core. The result is

$$B(T)=\tfrac{2}{3}\pi d^3\left[1+\frac{3}{2\sqrt{2}}\frac{\lambda}{d}+\frac{1}{\pi}\left(\frac{\lambda}{d}\right)^2+\frac{1}{16\pi\sqrt{2}}\left(\frac{\lambda}{d}\right)^3-\frac{1}{105\pi^2}\left(\frac{\lambda}{d}\right)^4\right].$$

The first term is the classical value. The second term was found by Uhlenbeck and Beth. The third term, apart from a missing factor of 2, was obtained by Mohling. The correct value $1/\pi$, together with the fourth term, was obtained by Handelsman and Keller. Our calculation is based upon the method of Handelsman and Keller, viz., an expansion of the thermal Green's function and its boundary conditions in powers of $\lambda/d$. Our exact value for the coefficient of $(\lambda/d)^4$ confirms a numerical estimate of $-0.000965$ obtained by Boyd, Larsen, and Kilpatrick.

## I. INTRODUCTION

THE quantum-mechanical second virial coefficient $B(T)$ for a gas of hard spheres has two noteworthy features, viz., that it cannot be obtained by Wigner and Kirkwood's[1] high-temperature expansion, and moreover that at high temperatures all symmetrization effects are negligible, or, more precisely, exponentially small.[2] In a series expansion of $B(T)$ in powers of the ratio of the thermal de Broglie wavelength $\lambda=(h^2/2\pi mkT)^{1/2}$ to the hard-sphere diameter $d$ it therefore suffices to consider the spin-independent part $B_{\text{direct}}$.

We employ the expansion method of Handelsman and Keller[3] described below, with the result

$$B(T)=\tfrac{2}{3}\pi d^3\left[1+\frac{3}{2\sqrt{2}}\frac{\lambda}{d}+\frac{1}{\pi}\left(\frac{\lambda}{d}\right)^2+\frac{1}{16\pi\sqrt{2}}\left(\frac{\lambda}{d}\right)^3-\frac{1}{105\pi^2}\left(\frac{\lambda}{d}\right)^4+\cdots\right],\quad(1)$$

where the first term is the well-known classical value. The first quantum correction to this was calculated by Uhlenbeck and Beth.[4] One-half the third term was found by Mohling.[5] Handelsman and Keller[3] obtained the correct result and also evaluated the fourth term.

Boyd, Larsen, and Kilpatrick[6] calculated $B(T)$ numerically and obtained by fitting a polynomial in $\lambda/d$ to their result the value $-0.000965$ for the coefficient of $(\lambda/d)^4$. They also offered the conjecture that the exact value was $-1/105\pi^2$.

## II. CALCULATION

In terms of $G(\mathbf{r};\mathbf{r}_0;\beta)$, the propagator, or thermal Green's function, which satisfies

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

$$G=0\quad\text{for}\quad|\mathbf{r}-\mathbf{r}_c|\le d/\lambda,\quad(3)$$

$$G(\mathbf{r};\mathbf{r}_0;0-)=0,\quad(4)$$

the direct part of $B(T)$ is given as[7]

$$B_{\text{dir}}=\tfrac{1}{2}\lambda^3\int[1-2\sqrt{2}G(\mathbf{r}_0;\mathbf{r}_0;\beta)]d^3r_0$$
$$=\tfrac{2}{3}\pi d^3+\tfrac{1}{2}\lambda^3\int_{|\mathbf{r}_0-\mathbf{r}_c|\le d/\lambda}[1-2\sqrt{2}G(\mathbf{r}_0;\mathbf{r}_0;\beta)]d^3r_0$$
$$=\tfrac{2}{3}\pi d^3+2\pi\lambda^3\int_{d/\lambda}^{\infty}[1-2\sqrt{2}G(\mathbf{r}_0;\mathbf{r}_0;\beta)]\times|\mathbf{r}_0-\mathbf{r}_c|^2d(|\mathbf{r}_0-\mathbf{r}|).\quad(5)$$

Here $\beta=1/kT$ and $D=\hbar^2/m\lambda^2=1/2\pi\beta$. In the differential equation (2), $D$ and $\lambda$ are to be regarded as constants. In the last line the spherical symmetry of $G(\mathbf{r}_0;\mathbf{r}_0;\beta)$ around $\mathbf{r}_c$ is used. Now the coordinate system is chosen[3] so that the $x$ axis passes through $\mathbf{r}_c$ and

[1] E. Wigner, Phys. Rev. **40**, 747 (1932); J. G. Kirkwood, *ibid.* **44**, 31 (1933). Their expansion is essentially an expansion in powers of the gradient operator and is therefore inapplicable to the singular hard-sphere potential.

[2] S. Larsen, J. Kilpatrick, E. Lieb, and H. Jordan, Phys. Rev. **140**, A129 (1965). They show that the exchange part $B_{\text{exch}}$ satisfied

$$B_{\text{exch}}(T)\le\lambda^3 2^{-5/2}(2s+1)^{-1}\exp(-2\pi d^2/\lambda^2),$$

where $s$ is the spin value. The correct asymptotic formula was found by E. Lieb, J. Math. Phys. **8**, 43 (1967), to be

$$\ln[B_{\text{exch}}(T)\lambda^{-3}2^{5/2}(2s+1)]=-\tfrac{1}{2}\pi^3(d/\lambda)^2+O[(d/\lambda)^{2/3}].$$

[3] R. A. Handelsman and J. B. Keller, Phys. Rev. **148**, 94 (1966).

[4] G. E. Uhlenbeck and E. Beth, Physica **3**, 729 (1936).

[5] F. Mohling, Phys. Fluids **6**, 1097 (1963).

[6] M. E. Boyd, S. Y. Larsen, and J. E. Kilpatrick, J. Chem. Phys. **45**, 499 (1966).

[7] See Ref. 3. We have scaled all lengths with the thermal wavelength $\lambda$ in order to have an expansion in the dimensionless parameter $d/\lambda$ throughout the calculation.

$\mathbf{r}_0$, with $\mathbf{r}_c=(-d/\lambda, 0, 0)$ and $\mathbf{r}_0=(x_0,0,0)$. Hence

$$B_{\rm dir}=\tfrac{2}{3}\pi d^3+2\pi\lambda^3\int_0^\infty [1-2\sqrt{2}G(\mathbf{r}_0;\mathbf{r}_0;\beta)] \times(x_0+d/\lambda)^2dx_0. \quad (6)$$

In lowest approximation ($d/\lambda\to\infty$) the boundary condition (3) means that $G$ vanishes in the plane $x=0$, and further approximations are obtained by expansion of (3),

$$G[(d^2/\lambda^2-\rho^2)^{1/2}-d/\lambda, y, z; \mathbf{r}_0; \beta]=0.$$

This yields

$$G(0,y,z)-(\lambda/d)\tfrac{1}{2}\rho^2G'(0,y,z)+(\lambda/d)^2\tfrac{1}{8}\rho^2G''(0,y,z) +(\lambda/d)^3[-\tfrac{1}{8}\rho^4G'(0,y,z)-(\rho^6/48)G'''(0,y,z)] +O[(\lambda/d)^4]=0. \quad (7)$$

Here the arguments $\mathbf{r}_0$ and $\beta$ are omitted, the differentiations are with respect to $x$, and $\rho^2=y^2+z^2$. Expanding,

$$G=\sum_{n=0}(\lambda/d)^nG_n, \quad (8)$$

we obtain the following set of differential equations:

$$\partial G_0/\partial\beta-D\nabla^2G_0=\delta(\beta)\delta(\mathbf{r}-\mathbf{r}_0), \quad (9)$$

$$\partial G_n/\partial\beta-D\nabla^2G_n=0 \quad (n>0), \quad (10)$$

together with the boundary conditions

$$G_0(0,y,z)=0, \quad (11a)$$

$$G_1(0,y,z)=\tfrac{1}{2}\rho^2G_0'(0,y,z), \quad (11b)$$

$$G_2(0,y,z)=\tfrac{1}{2}\rho^2G_1'(0,y,z)-\tfrac{1}{8}\rho^4G_0''(0,y,z), \quad (11c)$$

$$G_3(0,y,z)=\tfrac{1}{8}\rho^4G_0'(0,y,z)+(1/48)\rho^6G_0'''(0,y,z) -\tfrac{1}{8}\rho^4G_1''(0,y,z)+\tfrac{1}{2}\rho^2G_2'(0,y,z), \quad (11d)$$

etc.

The solution of Eq. (9) complying with (11a) is (by the method of images)

$$G_0(\mathbf{r};\mathbf{r}_0;\beta)=\frac{\Theta(\beta)}{8(\pi D\beta)^{3/2}}\left[\exp\left(-\frac{\rho^2+(x-x_0)^2}{4D\beta}\right) -\exp\left(-\frac{\rho^2+(x+x_0)^2}{4D\beta}\right)\right], \quad (12)$$

where $\Theta(\beta)$ denotes the Heaviside step function.

Besides being the first term in (8), $G_0$ is also the Green's function for the set (10) of homogeneous equations. The standard procedure[8] using the adjoint Green's function yields the following general formula for $G_n$ in terms of the nonhomogeneous boundary condition on the plane $x=0$:

$$G_n(x,y,z;\beta)=\frac{x}{8(\pi D)^{3/2}}\int_0^\beta\frac{d\tau}{(\beta-\tau)^{5/2}} \times\int\int_{-\infty}^{+\infty}dy'dz'G_n(0,y',z';\tau) \times\exp\left[-\frac{x^2+(y-y')^2+(z-z')^2}{4D(\beta-\tau)}\right]. \quad (13)$$

Now it is in principle straightforward to calculate the $G_n$'s successively by shuttling back and forth between Eqs. (11) and (13): Equation (12) inserted in (11b) determines $G_1(0,y,z)$, which by (13) determines $G_1(\mathbf{r})$, which by (11c) determines $G_2(0,y,z)$, and so on. We find[9]

$$G_1(\mathbf{r})=\frac{xx_0}{8(D\pi\beta)^2}e^{-\rho^2/4D\beta}\int_0^\beta d\tau\,\tau^{-1/2}(\beta-\tau)^{-1/2}\left[1+\frac{\tau\rho^2}{4D\beta(\beta-\tau)}\right]\exp[-x_0^2/4D\tau-x^2/4D(\beta-\tau)], \quad (14)$$

and

$$G_2(\mathbf{r})=\frac{xx_0\exp(-\rho^2/4D\beta)}{32\beta^2(D\pi)^{5/2}}\int_0^\beta\frac{d\tau\exp(-x^2/4D(\beta-\tau))}{(\beta-\tau)^{3/2}}\int_0^\tau d\eta\frac{\exp(-x_0^2/4D\eta)}{[\eta(\tau-\eta)]^{1/2}} \times\{4D(\beta-\tau)-\tau\rho^2/\beta-(1+x_0^2/2D\eta)[4\tau\rho^2(\beta-\tau)/\beta^2+8D(\beta-\tau)^2/\beta+\tau^2\rho^4/4D\beta^3]\}. \quad (15)$$

We need only $G_3(\mathbf{r})$ for $\mathbf{r}=(x_0,0,0)$:

$$G_3(x_0,0,0)=\frac{x_0^2}{4D\pi^2\beta^4}\int_0^\beta d\tau(\beta-\tau)^{1/2}\tau^{1/2}\exp[-x_0^2\beta/4D\tau(\beta-\tau)]\Bigg\{6\tau-3\beta-(\beta-\tau)x_0^2/D\tau-\frac{\tau^{-1/2}}{\pi(\beta-\tau)} \times\int_0^\tau\frac{d\xi}{(\tau-\xi)^{1/2}}\int_0^\xi d\eta\frac{\exp[-x_0^2(\eta+\beta-\tau)/4D\eta(\beta-\tau)]}{[\eta(\xi-\eta)]^{1/2}}[8\xi\beta-3\beta^2+6\tau\beta-12\xi\tau+(x_0^2/4D\eta)(3\tau\beta^2/\xi -3\beta^2+12\xi\beta+6\tau\beta-18\xi\tau)+(x_0^4/4D^2\eta^2)(2\xi\beta-2\beta^2-\tau\beta^2/\xi+4\tau\beta-3\xi\tau)]\Bigg\}. \quad (16)$$

[8] A. G. Mackie, *Boundary Value Problems* (Oliver and Boyd, Edinburgh, 1965), Sec. 54.

[9] Equation (14) is in agreement with Handelsman and Keller [Ref. 3]. They have also found $G_2$ at the special point $\mathbf{r}=(x_0,0,0)$, and their formula agrees with our Eq. (15) at this point, except for a factor of 2 in the last term. This erroneous factor appears consistently in their formulas (2.16), (2.17), (2.18), and (3.3). In their formula (3.3), also, three signs are misprinted.

Inserting the expansion (8) for $G$ into (6) and extracting the terms of order $(\lambda/d)^4$ we obtain

$$B_{\mathrm{dir}}^{(4\text{th order})}/\tfrac{2}{3}\pi d^3 = -\left(\frac{\lambda}{d}\right)^4 6\sqrt{2} \times \int_0^\infty [x_0^2 G_1 + 2x_0 G_2 + G_3] dx_0 = (\lambda/d)^4 (I_1+I_2+I_3)\,, \tag{17}$$

where the argument of the Green's functions is $\mathbf{r}=\mathbf{r}_0 = (x_0,0,0)$. Insertion of (14)–(16) and integration over $x_0$ yields

$$I_1 = -36D^2\beta^{-3}\int_0^\beta d\tau(\beta-\tau)^2\tau^2 = -\frac{3}{10\pi^2}\,, \tag{18}$$

and

$$I_2 = -48D^2\beta^{-3/2}\pi^{-1}\int_0^\beta d\tau(\beta-\tau)^{3/2}\int_0^\tau \frac{d\eta\,\eta^{3/2}}{(\tau-\eta)^{1/2}} \times\left[\frac{(2\tau-\beta)}{(\eta+\beta-\tau)^2} - \frac{8(\beta-\tau)^2}{(\eta+\beta-\tau)^3}\right] = \frac{39}{70\pi^2}\,. \tag{19}$$

The integration in (19) is effected by introduction of the new variable $u=\eta+\beta-\tau$ instead of $\eta$, and reversion of the order of the integrations. The remaining integral,

$$I_3 = \frac{36D^2}{\beta^5}\int_0^\beta d\tau\left\{3(\beta-\tau)^4\tau^2 - (\beta-\tau)^2\tau^4 + \frac{\beta^{5/2}(\beta-\tau)}{3\pi}\int_0^\tau \frac{d\xi}{(\tau-\xi)^{1/2}}\int_0^\xi \frac{\eta\,d\eta}{(\xi-\eta)^{1/2}(\beta+\eta-\tau)^{3/2}} \right.$$
$$\times\left[-3\beta^2+8\beta\xi+6\tau\beta-12\xi\tau+\frac{9(\beta-\tau)}{2(\beta-\tau+\eta)}(4\beta\xi-\beta^2+\tau\beta^2/\xi+2\beta\tau-6\xi\tau)\right.$$
$$\left.\left. +15\left(\frac{\beta-\tau}{\beta-\tau-\eta}\right)^2(2\beta\xi-2\beta^2-\tau\beta^2/\xi+4\beta\tau-3\xi\tau)\right]\right\}\,, \tag{20}$$

is slightly more complicated. One starts best with the integration over $\xi$, followed by a few simple variable transformations. We obtain finally

$$I_3 = -(16/15)(D\beta)^2 = -4/15\pi^2. \tag{21}$$

Addition yields

$$I_1+I_2+I_3 = -1/105\pi^2\,, \tag{22}$$

as stated in the Introduction.