order correction for small concentrations in terms of $b=2\pi N\sigma^3/3$ as

$$pv=NkT[1+b/v+(5/8)(b/v)^2].$$

The close packed (face-centered cubic) concentration of atoms is

$$n_1=\sqrt{2}/\sigma^3,$$

so that in terms of fractional close packing θ, where

$$\theta=N/n_1v,$$

$$pv=NkT(1+2.96190\theta+5.48300\theta^2). \qquad (31)$$

The reciprocal of the coefficient of NkT is plotted in Fig. 6.

Near $\theta=1$ each atom center is confined to a dodecahedron formed by the twelve 110 planes, and the same reasoning as for the two-dimensional case leads now to the formula

$$pv=NkT/(1-\theta^{1/3}). \qquad (32)$$

Again, this can be rigorously proved for a plain cubic array.

The appropriate formula which covers the whole range of θ is

$$pv=NkT\frac{1+2.96190\theta+5.48300\theta^2}{1-0.8517\theta^3-0.1483\theta^4}. \qquad (33)$$

NOVEMBER 15, 1936 PHYSICAL REVIEW VOLUME 50

Quantum Theory of the Equation of State at Low Temperatures*

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(Received September 28, 1936)

The quantum formulae for the second virial coefficient B are derived, for the case of Boltzmann, Einstein-Bose and Fermi-Dirac statistics. It is shown how these formulae may be expressed in terms of the phases of the Schrödinger wave function. For low temperatures the expression for B is developed in a power series of T, the temperature, which gives formal agreement with the experimental formula in the case of He. Using this series development a potential is fixed to fit the data. The potential agrees with the Slater-Margenau potential in the region where the latter is valid.

1.

IN a fundamental paper on the quantum statistics of a gas, Slater[1] has pointed out that the classical Zustands integral

$$e^{-\beta\psi}=\frac{(2\pi mKT)^{3N/2}}{(2\pi\hbar)^{3N}}\int_V\cdots\int e^{-\beta U}dx_1\cdots dz_N \qquad (1)$$

must be replaced by the Zustandsumme in the following form,

$$e^{-\beta\psi}=\int\cdots\int dx_1\cdots dz_N\sum_n e^{-\beta E_n}\,\Psi_n\Psi_n^*. \qquad (2)$$

Here ψ is the free energy of the gas from which is derived the pressure $p=-\partial\psi/\partial V$, Ψ_n is the still to be normalized, time free, wave function for a system of N molecules (we will take N to be the number of molecules in a mole of gas), U is the total potential energy of the system, E the energy, and $\hbar$ is Planck's constant divided by 2π. The integrals in (1) and (2) are over the whole volume V of the gas.

The classical expression for the second virial coefficient which is the B, in the equation of state,

$$p^V/RT=(1+B/V+C/V^2+\cdots) \qquad (3)$$

is derived from (1) and is given by,[2]

$$B_{\text{Cl.}}=2\pi N\int_0^\infty drr^2(1-e^{-\beta V}) \qquad (4)$$

for the case of monatomic gases, where the force field is radial. Here, V is now the potential between two molecules and is not to be confused with the volume.

It can be shown that the quantum expression for the second virial coefficient is given by:

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* The results of the present investigation were submitted in the form of a Letter to the Editor on March 19, 1936. —Editor.

[1] J. C. Slater, Phys. Rev. **38**, 237 (1931).

[2] See R. H. Fowler, *Statistical Mechanics*, Chap. VIII

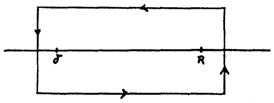

FIG. 1.

(a) Boltzmann statistics

$$B_{\mathrm{B}}=\sum_{\text{all } l}(l+\tfrac{1}{2})B_l. \tag{5}$$

(b) Einstein-Bose statistics

$$B_{\mathrm{E.B.}}=-\frac{N\pi^{\frac{3}{2}}\lambda^3}{2}+2\sum_{\text{even } l}(l+\tfrac{1}{2})B_l. \tag{6}$$

(c) Fermi-Dirac statistics

$$B_{\mathrm{F.D.}}=+\frac{N\pi^{\frac{3}{2}}\lambda^3}{2}+2\sum_{\text{odd } l}(l+\tfrac{1}{2})B_l, \tag{7}$$

where

$$B_l=16(\pi)^{\frac{1}{2}}\lambda^3N\int_0^\infty dke^{-\lambda^2k^2}\int_0^\infty dr$$
$$\times((\pi kr/2)J^2{}_{l+\frac{1}{2}}(kr)-v_l{}^2(k,r)). \tag{8}$$

Here v_l is determined from the radical wave equation in the relative coordinates of two molecules

$$d^2v/dr^2+(k^2-(m/\hbar^2)V-l(l+1)/r^2)v=0$$

and has already been normalized so as to behave asymptotically like, $v\sim\sin(kr-l\pi/2+\eta_l(k))$ where η is the phase shift in the wave due to the presence of the force field, and λ, the statistical wave-length of the molecule is given by $(\beta\hbar^2/m)^{\frac{1}{2}}$ where m is the mass of a molecule.[3]

Eqs. (5), (6) and (7), follow from (2) by the same procedure used in deriving (4) from (1). Since the rigorous proofs are long and tedious we leave them to the appendix.[1]

For an ideal gas it is clear that B_l is zero, so that B_{B} is zero, and $B_{\mathrm{E.B.}}$, $B_{\mathrm{F.D.}}$ reduce to the well-known expressions for the second virial coefficient of a degenerate, ideal, gas.

2.

With the methods of Uhlenbeck and Gropper,[4] or Kirkwood,[5] both of which depend on the invariance of the Spur,[6] plus the use of the following formulae,[7]

$$\sum_{n=0}^{\infty}(n+\tfrac{1}{2})J^2{}_{n+\frac{1}{2}}(z)=z/\pi,$$

$$\sum_{n=0}^{\infty}(2n+\tfrac{1}{2})J^2{}_{2n+\frac{1}{2}}(z)=\tfrac{1}{4}z^2\{J^2{}_{-\frac{1}{2}}(z)-J_{-\frac{3}{2}}(z)J_{\frac{1}{2}}(z)\},$$

one can verify that as λ→0 (quantum theory →classical theory) (5), (6), (7), may be evaluated in power series of λ^2,

$$B_{\mathrm{B}}=2\pi N\int_0^\infty drr^2\left\{1-e^{-\beta V}\left[1-\frac{\beta^2\lambda^2}{12}\left(\frac{dV}{dr}\right)^2+\frac{\beta^2\lambda^4}{120}\left(\left(\frac{d^2V}{dr^2}\right)^2+\frac{2}{r^2}\left(\frac{dV}{dr}\right)^2\right.\right.\right.$$
$$\left.\left.\left.+\frac{10}{9}\frac{\beta}{r}\left(\frac{dV}{dr}\right)^3-\frac{5}{36}\beta^2\left(\frac{dV}{dr}\right)^4\right)+\cdots\right]\right\}, \tag{5'}$$

$$\overset{\mathrm{E.B.}}{B_{\mathrm{F.D.}}}=B_{\mathrm{B}}\pm2\pi N\int_0^\infty drr^2e^{-\beta V}e^{-r^2/\lambda^2}\left(1+\beta r\frac{dV}{dr}+\cdots\right). \tag{6')(7'}$$

In (6′), (7′), the plus sign is for the E.B. statistics, the negative sign for the F.D. statistics. One sees from this, that as λ→0, (5′), (6′), (7′), reduce to the classical value 4.

In conjunction with Professor Uhlenbeck, the writer has made a graphical study of (5′), (6′), (7′), with different potentials, at low temperatures ($T=20°$ absolute). For such low temperatures this formulation for B is unsatisfactory because:

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[3] Formula (5) was pointed out to me without proof some years ago in a private communication from Professor Uhlenbeck to whom I wish to acknowledge my indebtedness. In a recent paper, August, 1936, in Physica, Uhlenbeck and Beth consider some of the points in this paper, though from a somewhat different point of view.

[4] Uhlenbeck and Gropper, Phys. Rev. **41**, 79 (1932).

[5] Kirkwood, Phys. Rev. **44**, 31 (1933).

[6] F. Bloch, Zeits. f. Physik **74**, 295 (1932).

[7] Watson, *Bessel Functions*, p. 152.

1. Either (5′), (6′), (7′) do not converge or converge too slowly to be useful (as is also mentioned by Uhlenbeck and Beth).

2. (5′), (6′) (7′) are extremely sensitive to the potential V, so that as Wigner[8] remarks, a change of only $\frac{1}{2}$ percent in the parameter of the exponential representing Slater's repulsive force, changes *even the classical part of B* by as much as 20 percent. And it does not seem possible to determine V theoretically to anywhere near that accuracy.

3.

In this paper we shall eliminate these objections by,

1. Deriving an alternate general expression for B.
2. Obtaining a series in power of $1/\lambda^2$ for large λ, which is relatively insensitive to V.

Point (1) depends essentially on the fact that we know the behavior of the wave function at large distances, point (2), on the fact that as $\lambda \to \infty$ we know the expression for the phase shifts.

4.

Consider first, the integral over r in (8). We may write it,

$$\begin{aligned} F &= \lim_{\substack{R\to\infty \\ \partial\to 0}} \int_{\partial}^{R} \left(\frac{\pi k r}{2} J^2_{l+\frac{1}{2}}(kr) - v_l^2 \right), \\ &= \lim_{\substack{R\to\infty \\ \partial\to 0}} \int_{\partial}^{R} dr \frac{1}{2\pi i} \oint \frac{((\pi k z/2) J^2_{l+\frac{1}{2}}(kz) - v_l^2(z))}{z-r} dz, \end{aligned} \tag{9}$$

where the z path of integration is indicated in Fig. 1. Since the integrand has no singularities, except $z=r$, in the finite portion of the z plane, we may take the sides of the rectangle as large as we please. Further, since the integral is regular and finite throughout both limits of integration ($z \neq r$), we may permute the integrals. Integrating over r we get

$$F = \lim_{\substack{R\to\infty \\ \partial\to 0}} \frac{1}{2\pi i} \oint dz \left(\frac{\pi k z}{2} J^2_{l+\frac{1}{2}}(kz) - v_l^2(z) \right) \log \left(1 + \frac{R-\partial}{z-R} \right). \tag{10}$$

Now the logarithm may be expanded in a convergent series provided

$$\left| \frac{R-\partial}{z-R} \right| = \frac{R-\partial}{((x-R)^2+y^2)^{\frac{1}{2}}} < 1.$$

But by taking the rectangle large enough we can assure this condition to be satisfied over the path of integration. Hence, letting $f(z) = ((\pi k z/2) J^2_{l+\frac{1}{2}}(kz) - v_l^2(z))$, (10) becomes

$$\begin{aligned} F &= \lim_{\substack{R\to\infty \\ \partial\to 0}} \frac{1}{2\pi i} \oint dz f(z) \left[\left(\frac{R-\partial}{z-R} \right) - \frac{1}{2} \left(\frac{R-\partial}{z-R} \right)^2 + \frac{1}{3} \left(\frac{R-\partial}{z-R} \right)^3 - \cdots \right] \\ &= \lim_{\substack{R\to\infty \\ \partial\to 0}} \left\{ (R-\partial) f(R) - \frac{(R-\partial)^2}{2!} f'(R) + \frac{(R-\partial)^3}{3!} f''(R) - \cdots \right\}, \end{aligned} \tag{11}$$

the last line following from an extension of Cauchy's theorem.

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[8] Wigner, Phys. Rev. **40**, 749 (1932).

Going to the limit $\partial=0$ (11) becomes

$$F=\lim_{R\to\infty}\{Rf(R)-(R^2/2\,!)f'(R)+(R^3/3\,!)f''(R)-\cdots\}. \tag{12}$$

Putting in the asymptotic values for $f(R)$ and its derivatives,

$$\begin{aligned}f(R)&=\sin^2(kR-l\pi/2)-\sin^2(kR-l\pi/2+\eta_l(b))\\&=(-1)^l/2[\cos 2kR(\cos 2\eta-1)-\sin 2kR\sin 2\eta],\end{aligned}$$

collecting terms, and summing the two resultant series, (12) becomes

$$F=\lim_{R\to\infty}(-1)^l/k\{-\sin 2\eta+(\cos 2\eta-1)\sin 2kR+\sin 2\eta\cos 2kR\}. \tag{13}$$

Inserting this result in (8), we find, on using the second of the Riemann-Lebesgue lemmas,[9] that the terms with sin kR and cos kR, after integrating over k, and going to the limit $R\to\infty$, vanish. There remains only the term with sin 2η which is free of R. Therefore (8) becomes

$$B_l-=4\pi^{\frac{1}{2}}\lambda^3N(-1)^l\int_0^\infty dke^{-\lambda^2k^2}\frac{\sin 2\eta_l(k)}{k}. \tag{14}$$

Substituting this in (5), (6), (7) we get

$$B_{\mathrm{B}}=-4\pi^{\frac{1}{2}}\lambda^3N\int_0^\infty dke^{-\lambda^2k^2}\sum_{\text{all } l}(-1)^l(l+\tfrac{1}{2})\frac{\sin 2\eta}{k}, \tag{5''}$$

$$B_{\mathrm{E.B.}}=-\frac{N\pi^{\frac{1}{2}}\lambda^3}{2}-8\pi^{\frac{1}{2}}\lambda^3N\int_0^\infty dke^{-\lambda^2k^2}\sum_{\text{even } l}(-1)^l(l+\tfrac{1}{2})\frac{\sin 2\eta}{k}, \tag{6''}$$

$$B_{\mathrm{F.D.}}=+\frac{N\pi^{\frac{1}{2}}\lambda^3}{2}-8\pi^{\frac{1}{2}}\lambda^3N\int_0^\infty dke^{-\lambda^2k^2}\sum_{\text{odd } l}(-1)^l(l+\tfrac{1}{2})\frac{\sin 2\eta}{k}. \tag{7''}$$

The integrals here represent a statistical average over the quantity $\sum(-1)^l(l+\frac{1}{2})\sin 2\eta/k$, which is closely related to, although not identical with, the expression for the total elastic collision cross section. Hence, if one knows the phases $\eta_l(k)$, say, from collision data, one can immediately compute the virial coefficient from (5″), (6″), (7″).[10] We shall postpone to a later paper the numerical calculation of the phases and the values of the second virial coefficient obtained with them.

5.

In the absence of a knowledge of these phases, however, we can gain some idea of the correlation between theory and experiment by expressing the second virial coefficient as a power series in $1/\lambda^2$ for the region of low temperature, and then using these expressions to derive a potential which may be compared with that already known. It will be sufficient to deal with (6″).

Letting $f=\sum_{\text{even } l}(-1)^l(l+\frac{1}{2})\sin 2\eta/k$, we have, aside from the factor, $-N\pi^{\frac{1}{2}}\lambda^3/2$, which is very small compared to experimental values, even at very low temperature, $T\leq 20°$ absolute,

$$B_{\mathrm{E.B.}}=-8\pi^{\frac{1}{2}}\lambda^3N\int_0^\infty dke^{-\lambda^2k^2}f(k). \tag{14'}$$

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[9] Whittaker-Watson, *Modern Analysis*, third edition, p. 172.

[10] These formulae are to be compared with the analogous formulae for viscosity and diffusion. See Massey and Mohr, Proc. Roy. Soc. London **141**, 734 (1933).

Now as $\lambda \rightarrow \infty$, the integrand of (14′) is different from zero only in the neighborhood $k=0$. Therefore, since most of the integral comes from the neighborhood $k=0$, we may expand $f(k)$ in a MacLaurin series. This series will certainly not represent $f(k)$ for large k, but in that case the integrand is negligible anyway because of the factor $e^{-\lambda^2 k^2}$, so that the error in using the expansion in this region does not matter. Making this expansion and integrating over k we get,

$$B_{\mathrm{E.B.}} = -4\pi\lambda^2 N f(0) - 4\pi^{\frac{1}{2}}\lambda N f'(0) - \pi N f''(0) - \cdots. \tag{15}$$

Remembering that $\lambda^2 = \hbar^2/mKT$, and rewriting (15) in terms of the temperature we have

$$B_{\mathrm{E.B.}} = -\frac{4(\pi\hbar^2/mK)Nf(0)}{T} - \frac{4(\pi\hbar^2/mK)^{\frac{1}{2}}Nf'(0)}{T^{\frac{1}{2}}} - \pi N f''(0) - \cdots. \tag{16}$$

As is shown in the appendix (2) all the odd derivative terms $f'(0)$, $f'''(0)$, etc., are zero; so that we finally have for $B_{\mathrm{E.B.}}$

$$B_{\mathrm{E.B.}} = -\frac{(4\pi\hbar^2/mK)Nf(0)}{T} - \pi N f''(0) - \cdots. \tag{17}$$

Formula (17) agrees in first approximation with the form for B in the expanded van der Waals equation

$$\frac{pV}{RT} = \left(1 + \frac{-a/RT + b}{V} + \frac{5}{8}\frac{b^2}{V^2} + \cdots\right).$$

At the same time, for T less than the boiling point of oxygen, the second virial coefficient, for He in Kammerling-Onnes units, is found to fit very closely the formula,[11]

$$B_{\mathrm{K.O.}} \times 10^3 = -18.905/T + 0.7224.$$

In terms of cc mole this is,[12] $B = -423/T + 16.2$.

The experimental formula may be looked upon as the first two terms of a rapidly converging series in T, for T small. Therefore comparing the coefficients with (17) we find, $f(0) = 4.6 \times 10^{-8}$, $f''(0) = -8.5 \times 10^{-24}$. Thus,

$$f = \sum_{\text{even } l} (-1)^l (l + \tfrac{1}{2})(\sin 2\eta / k) = f(0) + k f'(0) + (k^2/2!) f''(0) + \cdots = 4.6 \times 10^{-8} - 4.25 \times 10^{-24} k^2 + \cdots.$$

Letting $k = k_0/a_0$, where a_0 is the radius of the first Bohr orbit this becomes,

$$\sum_{\text{even } l} (-1)^l (l + \tfrac{1}{2}) \sin 2\eta = 8.75 k_0 - 29 k_0^3 + \cdots.$$

For very small values of k_0, we may replace the sum by the first term, $l=0$, and neglect the second term on the right. Thus $\sin 2\eta_0 \cong 17.5 k_0$. This formula can only be valid in the region $17.5 k_0 \leq 1$. Thus, for $17.5 k_0 = 1$ we should find $\eta_0 = \pi/4 = 0.78$. The writer is at present calculating the phases so as to compare the exact formulae (5″), (6″), (7″), with the data.

It is possible also to calculate the first coefficient of (17), $f(0)$ (Appendix 2) by means of the formula

$$f(0) = -m/\hbar^2 \int_0^\infty V r^2 dr. \tag{18}$$

Using a potential

$$V = \left\{ 7.7 e^{-2.43\rho} - e^{-b^2/\rho^2} \left(\frac{0.68}{\rho^6} + \frac{5.37}{\rho^8} + \frac{20.4}{\rho^{10}} \right) \right\} \times 10^{-10} \text{ ergs}$$

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[11] G. P. Nyhoff, Leiden Comm. Supp. No. °64C.

[12] The conversion is given by $B = (N/\nu_0) B_{\mathrm{K.O.}}$ where ν_0 is the number of molecules per cc under normal conditions.

and comparing (17) with the first coefficient of the experimental formula, we find, $b=1.71$. This potential is quite reasonable for, (1) since b is quite small it reduces to the Slater-Margenau potential in the region where the latter is known to be valid; (2) it insures that the negative part of the potential vanishes as $\rho\rightarrow 0$, as it must; (3) for large ρ the expansion of e^{-b^2/ρ^2} leaves the experimentally determined dipole-dipole term unaltered, and slightly corrects the dipole quadruple, and quadrupole-quadrupole terms.

I am indebted to Dr. I. S. Lowen for his very helpful criticism, and to Professor G. E. Uhlenbeck who first introduced me to the problem in this paper.

APPENDIX 1.

In the following we shall adopt a derivation, given by Ursell,[2] of the classical second virial coefficient as obtained from the classical Zustands integral.

Boltzmann statistics

Eq. (1) may be written

$$e^{-\beta\psi}=\int_V\cdots\int dx_1\cdots dz_N\sum_n e^{-\beta E_n}\Psi_n\Psi_n{}^*, \tag{1}$$

where the Ψ_n (still to be normalized) satisfy the Schrödinger equation

$$\sum_{r=1}^{N}\Delta_r\Psi_n+\frac{2m}{\hbar^2}(E_n-U)\Psi_n=0. \tag{2}$$

Let the integrand of (1) be called g. Let Φ^N be the wave function for a system of N free molecules and ϵ^N the corresponding energy, $\Phi^{N-2}\psi(r_ir_j)$ the wave function for $N-2$ free and two interacting molecules, $\Phi^{N-4}\psi(r_ir_j)\psi(r_kr_l)$ the wave function for $N-4$ free and two pairs of interacting molecules, etc. (r stands for the three coordinates x, y, z). Consider the expression,

$$\begin{aligned}f=&\Big[\sum_n e^{-\beta\epsilon_n{}^N}\Phi_n{}^N\Phi_n^{*N}\Big]+\Big[\sum_{i\neq j}\sum_n e^{-\beta\epsilon_n{}^{N-2}}\Phi_n{}^{N-2}\Phi_n^{*N-2}\sum_{n_in_j}e^{-\beta E_{n_in_j}}(\psi(r_ir_j)\psi^*(r_ir_j)-\varphi(r_ir_j)\varphi^*(r_ir_j))\Big]\\&+\Big[\sum_{i\neq j,\,k\neq l}\sum_n e^{-\beta\epsilon_n{}^{N-4}}\Phi_n{}^{N-4}\Phi_n^{*N-4}\sum_{n_in_jn_kn_l}e^{-\beta(E_{n_in_j}+E_{n_kn_l})}(\psi(r_ir_j)\psi^*(r_ir_j)-\varphi(r_ir_j)\varphi^*(r_ir_j))\\&\qquad\times(\psi(r_kr_l)\psi^*(r_kr_l)-\varphi(r_kr_l)\varphi^*(r_kr_l))\Big]+\cdots,\end{aligned}$$

where $\sum_{i\neq j}$ means the sum over all pairs without repetition, and the (i, j) molecules are not included in Φ^{N-2}. Similarly for the third and higher brackets. We will now show that, for the forces of the range we are considering, $f\cong g$.

The integral (1) is over all position of all the molecules.

Consider first the case when all the molecules are in a position free from each other's influence. In the region of such a set of values of the coordinates the contribution to the integrand is the same as $g_0\cong\sum_n e^{-\beta\epsilon_n{}^N}\Phi_n{}^N\Phi_n^{*N}$ in the same region. But in this region all the $\psi(r_ir_j)\cong\varphi(r_ir_j)$, so that all the brackets of f after the first vanish and we have. $f_0=g_0=\sum_n e^{-\beta\epsilon_n{}^N}\Phi_n{}^N\Phi_n^{*N}$.

Next, take the case when all molecules except one pair are in positions free from each other's influence. In the region of such a set of values of coordinates the contribution to the integrand becomes

$$g_1\cong\sum_n e^{-\beta\epsilon_n{}^{N-2}}\Phi^{N-2}\Phi^{*N-2}\sum_{n_in_j}e^{-\beta E_{n_in_j}}\psi(r_ir_j)\psi^*(r_ir_j).$$

But in this region all except one of the $\psi(r_ir_j)\cong\varphi(r_ir_j)$, so that all the brackets of f after the second vanish. Part of the second cancels with the first, and we have

$$f_1=g_1=\sum_n e^{-\beta\epsilon_n{}^{N-2}}\Phi^{N-2}\Phi^{*N-2}\sum_{n_in_j}e^{-\beta E_{n_in_j}}\psi(r_ir_j)\psi^*(r_ir_j).$$

The same considerations apply to sets of values of the coordinates where any number of pairs of molecules are under each other's influence. Thus we see for any set of values,[13] the two functions are the same. That is, if we were to plot the "graphs" of f and g they would almost coincide.

These considerations, of course, apply only to short range forces where a boundary can be drawn between the positions where the molecules are or are not under each other's influence, the limiting case being the hard sphere model. For long range forces there is no sharp boundary line, so that one cannot "count" positions of the assemblage.

Replacing g by f in (1) we can now proceed to reduce (1).

Consider the first bracket in f,

$$S_0=\sum_n e^{-\beta\epsilon_n{}^N}\Phi_n{}^N\Phi_n^{*N}=\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_N=0}^{\infty}e^{-\beta\epsilon_n{}^N}(\varphi_{n_1}{}^2\varphi_{n_2}{}^2\cdots\varphi_{n_N}{}^2).$$

For any molecule,

$$\varphi_n=\sin(n_x\pi x/L)\sin(n_y\pi y/L)\sin(n_z\pi z/L),\qquad \epsilon_n=(\hbar^2\pi^2/2mL^2)(n_x{}^2+n_y{}^2+n_z{}^2).$$

The normalization furnishes the factor $2^{3N}/V^N$. Replacing the multiple sums by integrals, integrating over the n's and then integrating over the coordinates, we find that the first bracket in f contributes to (1) the amount,[14] $(1/2\pi\lambda^2)^{3N/2}V^N$.

Coming now to the second bracket in f, and taking into account the normalization, we have,

$$S_1=\frac{2^{3(N-1)}}{V^{N-1}}\sum_{i\neq j}\sum_n e^{-\beta\epsilon_n{}^{N-2}}\Phi_n{}^{N-2}\Phi_n^{*N-2}\sum_{n_in_j}e^{-\beta E_{n_in_j}}\left(\frac{\psi(r_ir_j)\psi^*(r_ir_j)}{A}-\frac{\varphi(r_ir_j)\varphi^*(r_ir_j)}{B}\right),$$

where

$$A=\int\int_V\int d\tau\psi(r_{ij})\psi^*(r_{ij}),\qquad B=\int\int_V\int d\tau\varphi(r_{ij})\varphi^*(r_{ij}),$$

and $\psi(r_{ij})$ means the wave function for the relative motion of the (ij) molecules. Similarly for $\varphi(r_{ij})$. These will also be referred to as ψ_R and φ_R.

Summing over the free wave function, as before, and integrating over their coordinates we get

$$2^3V^{N-3}\left(\frac{1}{2\pi\lambda^2}\right)^{\frac{3}{2}(N-2)}\frac{N(N-1)}{2}\sum_{n_in_j}e^{-\beta E_{n_in_j}}\left(\frac{\psi(r_ir_j)\psi^*(r_ir_j)}{A}-\frac{\varphi(r_ir_j)\varphi^*(r_ir_j)}{B}\right).$$

The factor $N(N-1)/2$ comes from the $\Sigma_{i\neq j}$. For the (ij) molecules we separate into relative and center of gravity coordinates, sum over n and integrate over the coordinates of the latter, so that the above expression becomes

$$2^3V^{N-1}\left(\frac{1}{2\pi\lambda^2}\right)^{3N-1}(\pi\lambda^2)^{\frac{3}{2}}\frac{N(N-1)}{2}\int\int_V\int d\tau\sum e^{-\beta E_R}\left(\frac{\psi_R\psi^*{}_R}{A}-\frac{\varphi_R\varphi^*{}_R}{B}\right),$$

where ψ_R, φ_R are the relative wave functions of the two molecules, E_R the relative energy, and the integral is over their relative coordinates. Letting

$$t=2^3(\pi\lambda^2)^{\frac{3}{2}}\int\int_V\int d\tau\sum e^{-\beta E_R}\left(\frac{\psi_R\psi^*{}_R}{A}-\frac{\varphi_R\varphi_R{}^*}{B}\right),\tag{3}$$

the above expression becomes

$$V^{N-1}(1/2\pi\lambda^2)^{3N/2}(N(N-1)/2)t.$$

Coming now to the third bracket in f, the reader can verify, by a procedure similar to the evaluation of the second bracket, that its contribution to (1) is

$$V^{N-2}(1/2\pi\lambda^2)^{3N/2}(N(N-1)(N-2)(N-3)/2^2\cdot 2!)t^2.$$

The factor $N(N-1)(N-2)(N-3)/2^2\cdot 2!$ comes from the number of double pairs. And so on, for the higher brackets.

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[13] We have considered only binary collisions. Tertiary and higher collisions are completely negligible. See reference 2.

[14] A factor due to the finite size of the box, which is completely negligible, has here been omitted.

By letting $x=Nt/2V$, and by collecting together all the brackets, (1) can be written as the following series[2]

$$e^{-\beta\psi}=\frac{V^N}{(2\pi\lambda^2)^{3N/2}}\sum_{r=0}^{N/2}\frac{N!}{r!(N-2r)!N^r}x^r$$

$$=\frac{V^N}{(2\pi\lambda^2)^{3N/2}}\{1+x+O(x^2)+\cdots\}^N.$$

Taking the logarithm, and differentiating with respect to the volume, and neglecting x^2 with respect to x, we get

$$pV/RT=(1-x)=(1-(N/2V)t), \tag{4}$$

where $R=NK$, and we have replaced β by $1/KT$.
We can now reduce the quantities

$$t=2^3(\pi\lambda^2)^{\frac{3}{2}}\iiint_V d\tau\sum e^{-\beta E_R}\left(\frac{\psi_R\psi^*_R}{A}-\frac{\varphi_R\varphi^*_R}{B}\right),\qquad A=\iiint_V d\tau\psi_R\psi_R^*,\qquad B=\iiint_V d\tau\varphi_R\varphi_R^*.$$

On passing to polar coordinates and integrating over the angles, A and B become

$$A=\frac{2\pi}{(l+\frac{1}{2})}\frac{(l+m)!}{(l-m)!}\int_0^R v^2dr,\qquad B=\frac{2\pi}{(l+\frac{1}{2})}\frac{(l+m)!}{(l-m)!}\int_0^R \frac{r}{k}J_{l+\frac{1}{2}}{}^2(kr)dr,$$

where $k^2=(m/\hbar^2)E_R$ and v satisfies the equation

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

For large r, $v\rightarrow\sin\left(kr-\frac{l\pi}{2}+\eta\right)$, so the contribution near the origin to the normalization integral may be neglected, since $\sin^2\left(kr-\frac{l\pi}{2}+\eta\right)$ is always positive and R is very large, compared to the distance around the origin (where v remains finite)

$$\therefore\int_0^R v^2dr\cong R/2.$$

Similarly for large r, $J_{l+\frac{1}{2}}(kr)\rightarrow\dfrac{\sin(kr-l\pi/2)}{(\pi kr/2)^{\frac{1}{2}}}$, so that

$$\int_0^R\frac{r}{k}J_{l+\frac{1}{2}}{}^2(kr)\cong\frac{R}{\pi k^2}.$$

Inserting the resultant values of A and B in t, and going to polar coordinates in the integral for t, we have,

$$t=\frac{8(\pi\lambda^2)^{\frac{3}{2}}}{\pi R}\int_0^R\int_0^\pi\int_0^{2\pi}\sin\theta drd\theta d\varphi\sum_n e^{-\lambda^2k_n{}^2}\sum_l(l+\tfrac{1}{2})\sum_{m=-l}^{+l}\frac{(l-m)!}{(l+m)!}\Big(P_l{}^m(\cos\theta)\Big)^2\left(v_l{}^2-\frac{\pi kr}{2}J_{l+\frac{1}{2}}{}^2(kr)\right)$$

where instead of summing over the three quantum numbers, we now sum over the radial quantum number and the degenerate states.
Since[15]

$$\sum_{m=-l}^{+l}\frac{(l-m)!}{(l+m)!}\Big(P_l{}^m(\cos\theta)\Big)^2=1,$$

this reduces, after integrating over the angles, to

$$t=\frac{32(\pi\lambda^2)^{\frac{3}{2}}}{R}\int_0^R dr\sum_n e^{-\lambda^2k_n{}^2}\sum_{l=0}^{\infty}(l+\tfrac{1}{2})\left(v_l{}^2-\frac{\pi kr}{2}J_{l+\frac{1}{2}}\right)\cdot$$

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[15] Jahnke and Emde, second edition.

Converting the sum over n into an integral over k, the conversion factor being given by $dn=(R/\pi)dk$, we have

$$t=32\pi^{\frac{1}{2}}\lambda^3\int_0^\infty dkl^{-\lambda^2k^2}\sum_{l=0}^{\infty}(l+\tfrac{1}{2})\int_0^R dr\left(v_l^2-\frac{\pi kr}{2}J_{l+\frac{1}{2}}{}^2(kr)\right)\cdot$$

Substituting in (4) we have

$$pV/RT=(1+B_B/V),$$

where

$$B_B=16\pi^{\frac{1}{2}}\lambda^3N\int_0^\infty dkl^{-\lambda^2k^2}\sum_{l=0}^{\infty}(l+\tfrac{1}{2})\int_0^R dr\left(\frac{\pi kr}{2}J_{l+\frac{1}{2}}{}^2-v_l^2\right)\cdot$$

Since the waves are zero at the boundary and outside the vessel, we may extend the integral over r to ∞, and this gives the expression for B_B which was to be proven.

Einstein-Bose or Fermi-Dirac statistics

For the solutions of (2) we must take the symmetric or antisymmetric linear combinations. That is

$$\Psi_n=\sum_P(\pm 1)^P(\psi_{n_1}(r_1)\psi_{n_2}(r_2)\cdots\psi_{n_N}(r_N))$$

the sum being taken over all permutations of the coordinates keeping the quantum numbers fixed.

As before we may replace the integrand g by f. Consider the first term of f,

$$S_0=\sum_n e^{-\beta\epsilon_n{}^N}\Phi_n{}^N\Phi_n^{*N}.$$

Written more fully this is,[16]

$$S_0=\sum_{n_1\geq}\sum_{n_2\geq}\cdots\sum_{n_N}e^{-\beta(\epsilon_{n_1}+\epsilon_{n_2}+\cdots\epsilon_{n_N})}\sum_P(\pm 1)^P(\varphi n_1(r_1)\varphi n_2(r_2)\cdots\varphi n_N(r_N))\sum_{P'}(\pm 1)^{P'}(\varphi^* n_1(r_1)\varphi^* n_2(r_2)\cdots\varphi^* n_N(r_N)).$$

The normalization will introduce the factor $(2^{3N}/(N!V^N)g(n_1\cdots n_N)$ where $g(n_1\cdots n_N)$ will be defined immediately. Thus

$$S_0=\frac{2^{3N}}{N!V^N}\sum_{n_1\geq}\sum_{n_2\geq}\cdots\sum_{n_N}e^{-(\beta\hbar^2\pi^2/2m)(n_{1x}{}^2+n_{1y}{}^2+n_{1z}{}^2+\cdots)}g(n_1\cdots n_N)\Phi^N\Phi^{*N}.$$

Here $g(n_1\cdots n_N)$ is unity when all the n_i are different (in which case the integral of $(\Phi^N)^2$ consists of only $N!$ terms because of the orthogonality relations); $g(n_1\cdots n_N)=1/2!$ when two of the n_i are the same (in which case the integral of $(\Phi^N)^2$ consists of $2!N!$ terms); $g(n_1\cdots n_N)=1/3!$ when three of the n_i are the same, etc.

We now arrange the terms of $(\Phi^N)^2$ into a series of sums. The first sum will contain all those terms for the identical permutation $P=P'$; the second all those in which the permutation differs only with respect to one pair of molecules, the third with respect to two pairs of molecules, etc. Of all the sums, we write down only those which contribute to the two highest powers of V, the volume, after integration. One can verify that the sums in which the permutations differ with respect to more than one pair of molecules, do not contribute to the two highest powers of V. Writing down S_0, for the first two sums,

$$S_0=\frac{2^{3N}}{N!V^N}\sum_{n_1\geq}\sum_{n_2\geq}\cdots\sum_{n_N}e^{-\beta\epsilon_n{}^N}\sum_P\{(\varphi_{n_1}{}^2(r_1)\cdots\varphi_{n_N}{}^2(r_N))\pm(\varphi_{n_1}{}^2(r_1)\cdots\varphi_{n_{N-2}}(r_{N-2}))\sum_{i\neq j}\varphi_{n_i}(r_i)\varphi_{n_j}(r_i)\varphi_{n_j}(r_j)\varphi_{n_i}(r_j)+\cdots\}.$$

It is understood that whenever a pair of molecules occurs in the sum (ij) it is missing from the product $\varphi n_1{}^2(r_1)\cdots\times\varphi_{n_{N-2}}{}^2(r_{N-2})$. Now if we permute the order of the relation $n_1\geqq n_2\geqq\cdots n_N$ we do not change the value of the multiple sum. Thus we can take the multiple sum $N!$ times corresponding to the $N!$ permutations in $n_1\geqq n_2\geqq\cdots n_N$ and divide by the factor $N!$. The effect of this is to sum over all the n_i independently with the factor $g(n_1\cdots n_N)$ omitted. Again, since the multiple sum is the same for each permutation of the Σ_P we need only take one term and multiply by the factor $N!$, which cancels the $N!$ just introduced. Thus we get,

$$S_0=\frac{2^{3N}}{N!V^N}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_N=0}^{\infty}e^{-\beta\epsilon_n{}^N}\{(\varphi_{n_1}{}^2(r_1)\cdots\varphi_{n_N}{}^2(r_N))\pm(\varphi_{n_1}{}^2(r_1)\cdots\varphi_{n_{N-2}}{}^2(r_{N-2}))\sum_{i\neq j}\varphi_{n_i}(r_i)\varphi_{n_j}(r_i)\varphi_{n_j}(r_j)\varphi_{n_i}(r_i)+\cdots\}.$$

Letting $\lambda^2=\hbar^2\beta/m$, and carrying out these sums and integrating over the coordinates,[17] we get as the contribution of

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[16] This sum was worked out by Uhlenbeck and Gropper, Phys. Rev. **41**, 79 (1932) but we do it here explicitly since the method is used to calculate the other brackets in f. The sums with $n_1\geqq n_2\geqq n_3\geqq\cdots n_N$ insures that no state is repeated.

[17] Again, a term λ^3/V has been neglected with respect to unity, and enters only because of the finite size of the box.

the first bracket in f to (1),

$$\frac{1}{N!}\left(\frac{1}{2\pi\lambda^2}\right)^{3N/2}\left(1\pm\frac{N(N-1)}{2}\frac{\pi^{\frac{3}{2}}\lambda^3}{V}+O\left(\frac{1}{V^2},\frac{1}{V^3},\cdots\right)\right), \tag{5}$$

where O contains all those terms contributing lower powers of V.

Consider now the second bracket in f. The normalization of $\Phi^{N-2}\psi(r_ir_j)$ will furnish the factor

$$\frac{2^{3(N-1)}}{N!V^{N-1}}\frac{g(n_1\cdots n_N)}{A} \qquad \text{where} \qquad A=\underset{V}{\int\int\int}\psi_R\psi^*{}_Rd\tau$$

and ψ_R means the wave function for the relative motion of two interacting molecules.[18] The normalization of $\Phi^{N-2}\varphi(r_ir_j)$ is, as before $(2^{3N}/N!V^N)g(n_1\cdots n_N)$, which we can also write as $(2^{3(N-1)}/N!V^{N-1})(g(n_1\cdots n_N)/B)$, where

$$B=\underset{V}{\int\int\int}\varphi_R\varphi^*{}_Rd\tau$$

and φ_R means the wave function for the relative motion of two free molecules.

As with the first bracket, we write the terms of the expression

$$\Phi^{N-2}\Phi^{*N-2}\left(\frac{\psi(r_ir_j)\psi^*(r_ir_j)}{A}-\frac{\varphi(r_ir_j)\varphi^*(r_ir_j)}{B}\right)$$

as a series of sums, the first containing all terms with the identical permutations, the second, terms in which the permutations differ with respect to a single pair of molecules, etc. One can verify that terms involving permutations between two or more pair of molecules contribute powers of V lower than V^{N-1}. Of the second sum only those terms in which the quantum numbers of the (ij) molecules are permuted give terms with a factor V^{N-1}. These contributing terms are

$$\pm\sum_P(\varphi_{n_1}{}^2(r_1)\cdots\varphi_{n_{N-2}}{}^2(r_{N-2}))\left(\frac{\psi n_i(r_i)\psi^*n_j(r_i)\psi n_j(r_j)\psi^*n_i(r_j)}{A}-\frac{\varphi n_i(r_i)\varphi^*n_j(r_i)\varphi n_j(r_j)\varphi^*n_i(r_j)}{B}\right).$$

All of the terms of the first sum will give the factor V^{N-1}. They are

$$+\sum_P(\varphi_{n_1}{}^2(r_1)\cdots\varphi_{n_{N-2}}{}^2(r_{N-2}))\left(\frac{\psi n_i(r_i)\psi^*n_i(r_i)\psi n_j(r_j)\psi^*n_j(r_j)}{A}-\frac{\varphi n_i(r_i)\varphi^*n_i(r_i)\varphi n_j(r_j)\varphi^*n_j(r_j)}{B}\right).$$

As before we eliminate the factor $g(n_1\cdots n_N)$ and the sum over the permutations of the contributing terms. With these contributing terms the second bracket in f, written more fully is,

$$S_1=\frac{2^{3(N-1)}}{N!V^{N-1}}\sum_{i\neq j}\left\{\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_{N-2}}^{\infty}e^{-\beta\epsilon_n{}^{N-2}}(\varphi_{n_1}{}^2(r_1)\cdots\varphi_{n_{N-2}}{}^2(r_{N-2}))\sum_{n_in_j}e^{-\beta E_{n_in_j}}\left(\frac{W(r_ir_j)}{A}-\frac{w(r_ir_j)}{B}\right)\right\}+\cdots,$$

where

$$W(r_ir_j)=\psi n_i(r_i)\psi^*n_i(r_i)\psi n_j(r_j)\psi^*n_j(r_j)\pm\psi n_i(r_i)\psi^*n_j(r_i)\psi n_j(r_j)\psi^*n_i(r_j),$$
$$w(r_ir_j)=\varphi n_i(r_i)\varphi^*n_i(r_i)\varphi n_j(r_j)\varphi^*n_j(r_j)\pm\varphi n_i(r_i)\varphi^*n_j(r_i)\varphi n_j(r_j)\varphi^*n_i(r_j).$$

By permuting r_i and r_j we do not change the value of the sums over n_i, n_j, which then becomes

$$\tfrac{1}{2}\sum_{n_in_j}e^{-\beta En_in_j}\left(\frac{S(r_ir_j)S^*(r_ir_j)}{A}-\frac{s(r_ir_j)s^*(r_ir_j)}{B}\right),$$

where $S=\psi n_i(r_i)\psi n_j(r_j)\pm\psi n_j(r_i)\psi n_i(r_j)$, and s is the corresponding symmetric or antisymmetric function for the φ's.

Performing the multiple sum for the wave functions of the free molecules, and integrating over their coordinates, we reduce to

$$\frac{2^3V^{N-3}}{N!}\left(\frac{1}{2\pi\lambda^2}\right)^{\frac{3}{2}(N-2)}\cdot\frac{N(N-1)}{2}\cdot\frac{1}{2}\sum_{n_in_j}e^{-\beta E_{n_in_j}}\left(\frac{SS^*}{A}-\frac{ss^*}{B}\right).$$

The factor $N(N-1)/2$ enters from the sum over (ij).

In S and s we separate into relative and center of gravity wave functions. The symmetry or antisymmetry will then enter only in the wave function for the relative motion. Summing and integrating over the center of gravity wave functions we reduce to

$$\frac{4V^{N-1}}{N!}\left(\frac{1}{2\pi\lambda^2}\right)^{3N/2}(\pi\lambda^2)^{\frac{3}{2}}\frac{N(N-1)}{2}\int\int\int\sum e^{-\beta E_r}\left(\frac{\psi_r\psi_r{}^*}{A}-\frac{\varphi_r\varphi_r{}^*}{B}\right)d\tau, \tag{6}$$

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[18] *Not* the symmetric or antisymmetric combinations.

where ψ_r and φ_r, are the symmetric or antisymmetric wave functions[19] for the relative motion, and E_r the relative energy.

Coming to the third bracket in f, one can verify that all terms there will contribute powers of V lower than V^{N-1}. And similarly for all the other brackets

Let
$$t=\int\int\int\Sigma e^{-\beta E_r}\left(\frac{\psi_r\psi_r^*}{A}-\frac{\varphi_r\varphi_r^*}{B}\right)d\tau.$$

Collecting the terms from (5) and (6) we have finally for (1)

$$e^{-\beta\psi}=\frac{V^N}{N!}\left(\frac{1}{2\pi\lambda^2}\right)^{3N/2}\left[1+\frac{N(N-1)}{2}\cdot\frac{\pi^{\frac{3}{2}}\lambda^3}{V}(\pm1+4t)+O'\left(\frac{1}{V^2},\frac{1}{V^3},\cdots\right)\right],\tag{7}$$

where the factor $O'(1/V^2, 1/V^3, \cdots)$ includes all those terms in lower powers of V, which we have not given explicitly. The second term in the bracket will give the second virial coefficient, but one cannot now, as is sometimes done, take the logarithm and assume the second term of the bracket small with respect to the first, since their ratio is $(N(N-1)/2)\times(\pi^{\frac{3}{2}}\lambda^3/V)(\pm1+4t)$ and it is only $(N\pi^{\frac{3}{2}}\lambda^3/2V)(\pm1+4t)$ which we are entitled to assume small. To proceed correctly, let $y_1=(N(N-1)/2)\pi^{\frac{3}{2}}\lambda^3(\pm1+4t)$, and rewrite (7) in the form

$$e^{-\beta\psi}=\frac{V^N}{N!}\left(\frac{1}{2\pi\lambda^2}\right)^{3N/2}\left[1+\frac{y_1}{V}+\frac{y_2}{V^2}+\frac{y_3}{V^3}+\cdots\right].\tag{8}$$

The coefficients $y_2, y_3\cdots y_N$ could laboriously be calculated following the method above. But it is simpler to arrive at them by the correspondence principle. For it has been shown[16] that when we go from the quantum region to the classical region of high temperatures y_1 reduces to the classical coefficient

$$\frac{N(N-1)}{2}\int\int\int(e^{-\beta V}-1)d\tau=(N-1)x,$$

where we have let $x=\frac{N}{2}\int\int\int(e^{-\beta V}-1)d\tau.$

But the classical formula is given by[2]

$$\frac{V^N}{(2\pi\lambda^2)^{3N/2}}\left[1+\frac{(N-1)x}{V}+\frac{(N-1)(N-2)(N-3)}{2!}\frac{x^2}{V^2N^2}+\cdots\right].$$

If now in place of x we write $z=(N/2)\pi^{\frac{3}{2}}\lambda^3(\pm1+4t)$, so as to get the expression

$$\frac{V^N}{(2\pi\lambda^2)^{3N/2}}\left[1+(N-1)\frac{z}{V}+\frac{(N-1)(N-2)(N-3)}{2!}\frac{z^2}{V^2N^2}+\cdots\right],$$

we see that the first two terms agree with the formula (8) we have derived, and the whole expression agrees with the classical expression in the classical region of high temperature since, as previously stated, $z\rightarrow x$. We therefore take this to be the correct quantum expression, although this provides only a sufficient but not necessary condition for determining the coefficients, y_2, y_3, etc.

Now, as shown by Fowler,[2]

$$1+(N-1)\frac{z}{V}+\frac{(N-1)(N-2)(N-3)}{2!}\frac{z^2}{N^2V^2}+\cdots=\left(1+\frac{z}{V}+O\left(\frac{z^2}{V^2}\right)\right]^N.$$

And this is an approximation of the desired order, since $(z/V)\ll1$.

Using this in Eq. (7), taking the logarithm, and differentiating with respect to the volume we get

$$\frac{pV}{RT}=1-\frac{z}{V}=1-\frac{N}{2V}\pi^{\frac{3}{2}}\lambda^3(\pm1+4t),\tag{9}$$

where in the left side we have replaced β by $1/kT$, and let $R=NK$.

We can reduce the quantities

$$t=\int\int\int_V d\tau\sum e^{-\beta E_r}\left(\frac{\psi_r\psi_r^*}{A}-\frac{\varphi_r\varphi_r^*}{B}\right),\qquad A=\int\int\int_V d\tau\psi_R\psi_R^*,\qquad B=\int\int\int_V d\tau\varphi_R\varphi_R^*.$$

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[19] ψ_r and φ_r are to be distinguished from ψ_R and φ_R which occur in A and B.

As before, we showed

$$A=\frac{2\pi}{(l+\frac{1}{2})}\frac{(l+m)!}{(l-m)!}\frac{R}{2},\qquad B=\frac{2\pi}{(l+\frac{1}{2})}\frac{(l+m)!}{(l-m)!}\frac{R}{\pi k^2}.$$

Now in polar coordinates the symmetric or antisymmetric relative wave function, ψ_r is

$$\psi_r=\frac{v(r)}{r}(P_l^m(\cos\theta)e^{im\varphi}\pm P_l^m(\cos\theta')e^{im\varphi'}),$$

where

$$\theta'=\pi-\theta,\qquad \varphi'=\varphi+\pi.$$

This is so because the interchange of the two molecules sends φ into $\varphi+\pi$, and θ into $\pi-\theta$. One has the corresponding expressions for φ_r. As before instead of summing over the three quantum numbers, we now sum over the radial quantum numbers and the degenerate states. Going to polar coordinates, inserting the above functions and the values of A and B into t, using the addition theorem,[16]

$$P_l(\cos\alpha)=\sum_{m=-l}^{+l}\frac{(l-m)!}{(l+m)!}P_l^m(\cos\theta)P_l^m(\cos\theta')e^{im(\varphi-\varphi')},$$

where

$$\cos\alpha=\cos\theta\cos\theta'+\sin\theta\sin\theta'\cos(\varphi-\varphi'),$$

and integrating over the angles, t becomes

$$t=\frac{8}{R}\int_0^R dr\sum_N e^{-\lambda^2k_n^2}\sum_l(l+\tfrac{1}{2})(1\pm(1-)^l)\left(v^2-\frac{\pi kr}{2}J_{l+\frac{1}{2}}{}^2\right),$$

where $k_n{}^2=(m/\hbar^2)E_r$. The sum is over all l. For Einstein-Bose statistics the odd ones vanish, for Fermi-Dirac the even ones vanish, thus

$$t=\frac{16}{R}\int_0^R dr\sum_n e^{-\lambda^2k_n^2}\sum_l(l+\tfrac{1}{2})\left(v^2-\frac{\pi kr}{2}J^2\right),$$

where for Einstein-Bose statistics the sum is over even l, and for Fermi-Dirac statistics the sum is over odd l. Again, since the discreteness due to the finite size of the box is negligible, the sum over n may be converted into an integral, the conversion factor, as before, being given from $dn=(R/\pi)dk$. Thus

$$t=\frac{16}{\pi}\int_0^R dr\int_0^\infty dk\sum_l(l+\tfrac{1}{2})\left(v^2-\frac{\pi kr}{2}J_{l+\frac{1}{2}}{}^2\right).$$

Inserting this in (6), we have finally

$$\frac{pV}{RT}=1+\frac{1}{V}\left\{\mp\frac{N\pi^{\frac{3}{2}}\lambda^3}{2}+32\pi\lambda^3N\int_0^\infty dkl^{-\lambda^2k^2}\sum_l(l+\tfrac{1}{2})\int_0^\infty dr\left(\frac{\pi kr}{2}J_{l+\frac{1}{2}}{}^2-v^2\right)\right\},$$

where the integral over r has been extended to infinity for the reasons previously given.

APPENDIX 2.

Since we are going to the actual lim $k=0$, we may use the formula for η in the neighborhood $k=0$,[20] namely,

$$\eta=-\frac{\pi}{2}\frac{m}{\hbar^2}\int_0^\infty rVJ_{l+\frac{1}{2}}{}^2(kr)dr.$$

Thus in the neighborhood $k=0$[21]

$$f=\sum_{\text{even } l}(-1)^l(l+\tfrac{1}{2})\frac{\sin 2}{k}\eta_l\sim 2\sum_{\text{even } l}(-1)^l(l+\tfrac{1}{2})\frac{\eta_l}{k}=-\frac{\pi m}{\hbar^2}\sum_{\text{even } l}(-1)^l(l+\tfrac{1}{2})\int_0^\infty\frac{rV}{k}J_{l+\frac{1}{2}}{}^2(kr)=\frac{-m}{2\hbar^2}\int_0^\infty rV\left(r+\frac{\sin 2kr}{2k}\right).$$

From this one sees immediately that $f'(0)$, $f'''(0)$, etc. vanish.

This also gives $f(0)=-\frac{m}{\hbar^2}\int_0^\infty Vr^2dr$. One cannot, however, calculate $f''(0)$, $f''''(0)$, etc. from this formula, since to do so accurately one must know η to higher approximations.

Nor can one be sure that this proof is correct, since it is questionable if the above formula for η is the proper one to apply as $k\to 0$. However, detailed calculations for the rigid sphere, the potential well, and the noise potential models, all confirm the fact that as $k\to 0$, the expression for η contains only odd powers of k.

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[20] Mott and Massey, *Theory of Atomic Collisions.*

[21] Watson, *Bessel Functions,* p. 152.