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The Theory of London – van der Waals Forces and Certain Features of the Equation of State of Gases

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THE THEORY OF LONDON-VAN DER WAALS FORCES AND CERTAIN FEATURES OF THE EQUATION OF STATE OF GASES

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1. INTRODUCTION : THE NATURE OF VAN DER WAALS FORCES

The equation of state of an ideal gas is

$$pV = RT \tag{1.1}$$

where R is the gas constant. The molecules of an ideal gas are point particles which have no interaction forces between them. At low density (low pressure, p), and high temperature, T, most real gases obey the ideal gas law (1.1).

In order to explain the behavior of electrically neutral real gases at ordinary temperatures and pressures, van der Waals (1) proposed an equation of state

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{1.2}$$

where a and b are two positive constants. The constant a measures the specific strength of attractive molecular forces; b represents the fact that the molecules of the gas occupy a finite volume and that they are sources of strongly repulsive "overlap" forces of very short range. "Van der Waals force" refers to that force which gives rise to the constant a in (1.2), that is, to attractive molecular forces. These forces are also called London "dispersion forces" (2).

The knowledge of the existence of van der Waals forces goes back much further than the work of van der Waals (1). Borelli and Jurin (3) postulated the existence of attractive molecular forces between the molecules of the tube walls and of the liquid in order to explain their findings on capillary action. Clairault (4) pointed out that if these forces were the cause of surface tension, their action must be general and embrace all molecules. Laplace (5) and Gauss (6) showed that the dependence of surface tension on curvature could be derived from the assumption of short range central forces. Maxwell (7), concluding from the data on viscosity and diffusion of gases, proposed that these forces were repulsive and were proportional to R^{-5}, but the porous plug experiment of Joules and Kelvin (1853) contradicted Maxwell's conclusions even at that time. Van der Waals (1) derived his equation of state (1.2) without specifying the forces any more than to regard them as attractive. Boltzmann (8) investigated the range and space dependence of intermolecular forces following the work of Maxwell (7).

Sutherland (9) used a force law of the form

$$F = CR^{-4} \tag{1.3}$$

and he established a general correlation between the values of the constant C for various substances and their static atomic polarizabilities. He attempted an analysis of intermolecular forces in terms of molecular structure, and for the first time related these forces to electromagnetic properties, although in a qualitative manner. The equation (1.3), of course, is not valid.

Lennard-Jones (10) carried out calculations similar to Sutherland's, with some refinements and generalizations. He introduced a general force law of the form

$$F = \lambda R^{-n} - \mu R^{-m} \quad , \quad n > m \tag{1.4}$$

in which the first term represents a repulsive force of short range and the second term is the van der Waals force. Extensive use of the force law (1.4) has been made in statistical mechanics for the calculation and correlation of such diverse things as the virial coefficients and viscosities.

Reinganum (11) and Keesom (12) assumed that the molecules interact with each other by virtue of carrying dipoles and quadrupoles, being caught in attractive positions and forming alignments giving rise to Richteffekt or orientation effect.

Two particles of dipole moments q_1 and q_2, separated by a distance R, obtain a mean interaction energy proportional to $q_1{}^2\ q_2{}^2/R^6$. However, at high temperatures, the orientation effect becomes negligible because the trapping of molecules with high kinetic energy is unlikely, but van der Waals forces remain appreciable.

Debye (13) attempted to explain these forces by an induction effect not dependent on temperature, with quadrupoles as polarizing structures, and found the interaction energy to vary as R^{-8}. Falkenhagen (14) extended Debye's theory of the induction effect to dipole gases and calculated the second virial coefficient, including the effect of alignment in his calculation.

The electromagnetic nature of van der Waals forces was first clearly understood when London (15) applied second order quantum mechanical perturbation theory to the electrostatic interaction of two dipoles; the interaction energy is given by

$$\Delta U_2 = -\mu R^{-6} \tag{1.5}$$

However, such a treatment is possible only so long as particle separation (R) is small compared with the atomic wavelengths (λ).

In order to explain the stability of lyophobic colloids, Verwey and Overbeek (16) assumed that for particle separations large compared with typical atomic wavelengths the London-van der Waals forces varied more rapidly than R^{-7} as given by (1.5), and they suggested that the consideration of relativistic and retardation effects could become important. Casimir and Polder (17) used fourth-order perturbation theory in the interaction of an atom with the electromagnetic field, and obtained the retarded ($R \gg \lambda$) interaction energy between two atoms as

$$\Delta U_2(R \rightarrow \infty) = -\,23\,\hbar c\,\alpha_1(0)\,\alpha_2(0)/4\pi R^7\ , \tag{1.6}$$

where $\alpha(0)$ is the static polarizability of the atom. Casimir (18) also calculated the force between an atom and a conducting wall and reproduced the retarded law of interaction (1.6) by considering the perturbation of the quantum mechanical zeropoint energy of the radiation field within which the two interacting atoms may be thought placed. Error in Leech's (19) calculation of the retardation effects by symmetric methods led to the correct evaluation of transverse interaction terms by Aub, Power and Zienau (20).

Axilrod and Teller (21) and Muto (22) first investigated the non-additive correction in the interaction of three atoms, each for a simplified atomic model. McGinnies and Jansen (23) have examined the validity of two-body interactions in molecular physics. Podlubnyi (24), using invariant technique, has reported an expression for the interaction energy of three atoms which does not give correctly either the static limit (21, 22) or the retarded interaction.

Lifshitz (25) has considered the general problem of molecular attractive forces between solids, and Dzyaloshinski et al (26) have extended the theory of Lifshitz to bodies separated by a liquid layer.

2. STATIONARY PERTURBATION CALCULATIONS OF THE VAN DER WAALS INTERACTION ENERGY

Here we shall review the application of quantum mechanical perturbation theory to calculate the van der Waals interaction energy of spherically symmetric identical neutral atoms.

A. Two Neutral Atoms

Let $\vec{R}_1$ and $\vec{R}_2$ be the position vectors of the two atoms, and let $\vec{R}_2 - \vec{R}_1 = R\hat{r}_{12}$, where R is the interatomic distance and $\hat{r}_{12}$ is the unit vector along R. By assuming R to be large enough the overlap effects are neglected, and the force between the atoms is due to dipole-dipole interaction.

The Hamiltonian of this system may be written as

$$H = H_o + H_d \, , \tag{2.1}$$

where H_o is the unperturbed Hamiltonian of the system of two independent atoms in their groundstates, and H_d is the interaction between the atoms. H_d is treated as a small perturbation and, in the dipole approximation, it is given by

$$H_d = q(1) \ \frac{\hat{1} - 3\hat{r}_{12}\hat{r}_{12}}{R^3} \ q(2) \ , \tag{2.2}$$

where q(i) is the dipole moment of the ith atom, and $\hat{1}$ is the unit dyadic.

Now let E_n be the eigenvalues of H_o, E_o be the unperturbed energy of the groundstate. $\langle n | H_d | m \rangle$ represents the nm matrix element of H_d in the representation in which H_o is diagonal,

$$\langle n | H_o | m \rangle = E_n \, \delta_{nm} \tag{2.3}$$

The energy of the groundstate, E, up to the second order in perturbation, is given by

$$E = E_o + \Delta U_2 \quad , \tag{2.4}$$

where

$$\Delta U_2 = \sum_{n \neq 0} \frac{\langle 0 | H_d | n \rangle \ \langle n | H_d | 0 \rangle}{E_o - E_n} \ , \tag{2.5}$$

since for spherically symmetric atoms in the groundstate $\langle 0 | H_d | 0 \rangle = 0$.

The unperturbed Hamiltonian, H_o, may be written as the sum of the Hamiltonians of the individual atoms, $H_o = H(1) + H(2)$, and (2.5) may be expressed as :

$$\Delta U_2 =$$

$$-\sum_{a,b \neq 0}\sum \frac{\langle 0 | q(1) | a \rangle \cdot Q_{12} \cdot \langle 0 | q(2) | b \rangle \ \langle b | q(2) | 0 \rangle \cdot Q_{21} \cdot \langle a | q(1) | 0 \rangle}{W_a(1) + W_b(2)} \tag{2.6}$$

In (2.6), we have used:

$$Q_{12} = \frac{\hat{1} - 3\hat{r}_{12}\hat{r}_{12}}{R^3} \quad ;$$

$$E_n - E_o = W_a(1) + W_b(2) \quad ; \quad W_a(1) = w_a(1) - w_o(1) \tag{2.7}$$

and $W_b(2) = w_b(2) - w_o(2)$,

where $w_a(1)$ and $w_b(2)$ are the eigenvalues of $H(1)$ and $H(2)$ respectively, and $w_o(i)$ is the unperturbed groundstate energy of the ith atom; $n \equiv (a,b)$. The summation in (2.6) is to be taken over $a \neq 0$ and $b \neq 0$, since $\langle 0 \,|\, q \,|\, 0 \rangle = 0$.

In terms of $q_x(i)$, the x-component of $q(i)$, (2.6) becomes

$$\Delta U_2 = -\sum_{a,b\neq 0}\sum \frac{\left|\langle 0|q_x(1)|a\rangle\right|^2 \left|\langle 0|q_x(2)|b\rangle\right|^2}{W_a(1) + W_b(2)} \,\mathrm{Tr}\, Q_{12} \cdot Q_{21}$$

$$= -\mu R^{-6} \quad , \tag{2.8}$$

where

$$\mu = 6 \sum_{a,b\neq 0}\sum \frac{\left|\langle 0|q_x(1)|a\rangle\right|^2 \left|\langle 0|q_x(2)|b\rangle\right|^2}{W_a(1) + W_b(2)} \tag{2.9}$$

By an expansion of the perturbation operator to include higher powers of the coordinates, the van der Waals interaction energy is found (3) to be

$$\Delta U_2 = -\frac{6e^2 a_o^{\,5}}{R^6} - \frac{135e^2 a_o^{\,7}}{R^8} - \frac{1416e^2 a_o^{\,9}}{R^{10}} \quad , \tag{2.10}$$

where e is the electronic charge and a_o the Bohr radius. An upper limit on the value of ΔU_2 can be obtained by the variation method (27).

B. Three Neutral Atoms

The third order stationary perturbation theory has been applied (21, 22) to calculate the van der Waals interaction between three neutral atoms. In this case a specific three-body non-additive contribution to the interaction energy of the atoms is also obtained, the accuracy of which can be determined by the variation method (27) by evaluating the upper limit of the groundstate energy of the system.

Consider a system of three neutral, spherically symmetric hydrogen atoms in their groundstates, fixed in space. The interatomic distance is given by

$$\vec{R}_i - \vec{R}_j = R_{ij}\hat{r}_{ij} \tag{2.11}$$

$$|\hat{r}_{ij}| = 1 \ , \quad i,j = 1,2,3$$

The Hamiltonian of the system is

$$H = H_o + H_d \tag{2.12}$$

where H_o, the Hamiltonian of the unperturbed system, is

$$H_o = \sum_i H(i) \ , \tag{2.13}$$

$H(i)$'s being the Hamiltonians of the unperturbed atoms. The perturbation operator, H_d, is again the dipole interaction potential of the atoms, given by

$$H_d = \sum H_d^{ij} = \sum q(i) \frac{\hat{1} - 3\hat{r}_{ij}\hat{r}_{ij}}{R_{ij}^3} q(j) \tag{2.14}$$

The energy of the groundstate, E, up to the third order in perturbation, is given by

$$E = E_o + \Delta U_2(R_{12},R_{23},R_{31}) + \Delta U_3(R_{12},R_{23},R_{31}) \tag{2.15}$$

In (2.15), the second term is a sum of three two-body interactions,

$$\Delta U_2(R_{12},R_{23},R_{31}) = -\mu_{12}R_{12}^{-6} - \mu_{23}R_{23}^{-6} - \mu_{31}R_{31}^{-6} \ , \tag{2.16}$$

while the third, non-additive, term is

$$\Delta U_3 = \sum\sum_{n,m\neq 0} \frac{\langle 0|H_d|n\rangle \langle n|H_d|m\rangle \langle m|H_d|0\rangle}{(E_o - E_n)(E_o - E_m)} +$$

$$\sum_{n\neq 0} \frac{\Delta U_1 \langle 0|H_d|n\rangle \langle n|H_d|0\rangle}{(E_o - E_n)^2} \tag{2.17}$$

In (2.17), the second term is zero since $\Delta U_1 = \langle 0|H_d|0\rangle = 0$. The third order interaction energy, ΔU_3, can be expressed (21, 27) as a sum of six terms of the type

$$\sum_{a,b,c\neq 0}\sum\sum \frac{\langle 000|H_d|ab0\rangle \ \langle ab0|H_d|a0c\rangle \ \langle a0c|H_d|000\rangle}{(W_a(1) + W_b(2))(W_a(1) + W_c(3))}, \tag{2.18}$$

sincs ths matrix elements $\langle n|H_d|n'\rangle \equiv \langle abc|H_d|a'b'c'\rangle$ vanish for $a = a'$, $b = b'$, $c = c'$. The W's are defined in (2.7), (2.18) can be reduced to

$$\sum_{a,b,c\neq 0}\sum\sum \frac{|\langle 0|q_x(1)|a\rangle|^2 \ |\langle 0|Q_x(2)|b\rangle|^2 \ |\langle 0|q_x(3)|c\rangle|^2}{(W_a(1) + W_b(2))(W_a(1) + W_c(3))} .$$

$$\mathrm{Tr}\ Q_{12}\cdot Q_{23}\cdot Q_{31} \tag{2.19}$$

Let θ_1, θ_2, θ_3 be the inner angles of the triangle formed by the three atoms. Defining $\cos\theta_1 = -\hat{r}_{31}\cdot\hat{r}_{12} = (R_{31}^2+R_{12}^2-R_{23}^2)/2R_{31}R_{12}$, and using the identity $\cos^2\theta_1 + \cos^2\theta_2 + \cos^2\theta_3 = 1 - 2\cos\theta_1\cos\theta_2\cos\theta_3$, we have

$$\mathrm{Tr}\ Q_{12}\cdot Q_{23}\cdot Q_{31} = 3(R_{12}R_{23}R_{31})^{-3}(3\cos\theta_1\cos\theta_2\cos\theta_3 + 1) \tag{2.20}$$

With the help of (2.19) and (2.20), the expression for the third order perturbation energy becomes

$$\Delta U_3(R_{12},R_{23},R_{31}) = f(q_x(i),W)(R_{12}R_{23}R_{31})^{-3}(3\cos\theta_1\cos\theta_2\cos\theta_3 + 1), \tag{2.21}$$

where

$$f(q_x(i),W) = 12\sum_{a,b,c\neq 0}\sum\sum (W_a(1)+W_b(2))^{-1}(W_b(2)+W_c(3))^{-1} \cdot (W_c(3)+W_a(1))^{-1}\cdot(W_a(1)+W_b(2)+W_c(3)) \cdot |\langle 0|q_x(1)|a\rangle|^2\ |\langle 0|q_x(2)|b\rangle|^2\ |\langle 0|q_x(3)|c\rangle|^2 \tag{2.22}$$

From (2.21) one finds that when all θ_i's are smaller than 117°, the non-additive correction is positive (repulsive); when one of the θ_i's is larger than 126° the correction is negative (attractive).

In the case of a system of three harmonic oscillators (22) with angular frequencies ω_i all the matrix elements $\langle 0|q_x(i)|a\rangle$ vanish, except the element $\langle 0|q_x(i)|1\rangle$ for which $W_1(i) = \hbar\omega_i$, $2\pi\hbar$ = Planck's constant, i = 1,2,3. From (2.9) we have

$$\mu_{ij} = \frac{2}{3}\,\frac{\langle 0|q^2(i)|0\rangle\,\langle 0|q^2(j)|0\rangle}{\hbar(\omega_i + \omega_j)} \quad , \tag{2.23}$$

and, from (2.22),

$$f(q,W) = \nu_{123} = \frac{4}{9}\,\frac{\omega_1 + \omega_2 + \omega_3}{\hbar^2(\omega_1+\omega_2)(\omega_2+\omega_3)(\omega_3+\omega_1)}\,.$$

$$\langle 0|q^2(1)|0\rangle\,\langle 0|q^2(2)|0\rangle\,\langle 0|q^2(3)|0\rangle \quad , \tag{2.24}$$

using the relation $\langle 0|q^2(i)|0\rangle = 3\langle 0|q_x{}^2(i)|0\rangle$.

For three identical oscillators, one obtains the relations

$$\mu = \frac{1}{2}\,\alpha\,\langle 0|q^2|0\rangle \quad ; \quad \nu = \frac{3}{8}\,\alpha^2\,\langle 0|q^2|0\rangle \quad , \tag{2.25}$$

where α is the polarizability for an oscillator of mass m and charge e, $\alpha = \frac{2}{3}\,\langle 0|q^2|0\rangle/\hbar\omega$. The relations (2.25) give

$$4\nu = 3\alpha\mu \tag{2.26}$$

(2.25) and (2.26) hold (22, 27) for a system of spherically symmetric neutral atoms.

C. Higher Order Perturbation Contributions

The Drude oscillator model provides a means of deriving the second order dipole-dipole contribution to the London-van der Waals interaction energy in a simple way (2, 15). The oscillator model can be used (22) to derive the non-additive correction in the third order interaction energy, and can be extended to calculate the nth-order contribution to the interaction energy of a system of molecules. Higher order perturbation corrections become important (21, 23) in the interaction with dipole-dipole approximation, and all orders of perturbation have been considered (28) in the determination of the cohesive energy of a linear lattice.

Consider a system of molecules which have equal unperturbed frequencies and which are coupled only by dipole-dipole perturbing potentials. Each molecule is treated as an isotropic harmonic oscillator of vibrating mass m_i, internal potential energy $k_i\vec{r}_i^{\,2}/2$, and electric dipole moment $\epsilon_i\vec{r}_i$. The Lagrangian for the system is

$$L = \frac{1}{2}\sum_{i=1}^{N} m_i\left(\frac{d\vec{r}_i}{dt}\right)^2 - \frac{1}{2}\sum_{i=1}^{N} k_i\vec{r}_i^{\,2} - \frac{1}{2}\sum_{i=1}^{N}{}' \sum_{j=1}^{N}{}' \frac{\epsilon_i\epsilon_j}{R_{ij}^3} \times$$

$$\vec{r}_i \cdot (\hat{1} - 3\hat{r}_{ij}\hat{r}_{ij}) \cdot \vec{r}_j \tag{2.27}$$

where $\vec{R}_{ij} = R_{ij}\hat{r}_{ij}$, and primes on the summation indicate that the terms $i=j$ are omitted. (2.27) can be written in terms of normal coordinates, Q_s,

$$L = \frac{1}{2}\sum_{s=1}^{3N} \dot{Q}_s^{\,2} - \frac{1}{2}\sum_{s=1}^{3N} \omega_s^{\,2}Q_s^{\,2} \tag{2.28}$$

where the Q_s are linear combinations of the components of the $\vec{r}_i$. Q_s oscillates with the angular frequency ω_s which is given by the 3N solutions of the secular equation

$$\left|M - \omega^2 I\right| = 0 \tag{2.29}$$

where

$$M = \begin{pmatrix} (k_1/m_1)\hat{1} & G_{12} & \cdots & G_{1N} \\ G_{12} & (k_2/m_2)\hat{1} & & G_{2N} \\ \vdots & \vdots & & \vdots \\ G_{1N} & G_{2N} & & (k_N/m_N)\hat{1} \end{pmatrix} \tag{2.30}$$

and $G_{ij} = \epsilon_i \epsilon_j (m_i m_j)^{-1/2} R_{ij}^{-3} (\hat{1} - 3\hat{r}_{ij}\hat{r}_{ij})$, (2.31)

and I is a 3Nx3N identity matrix.

To treat this system quantum mechanically, one may write for the total energy of the system

$$U = \sum_{s=1}^{3N} (n_s + \frac{1}{2})\hbar\omega_s \quad , \tag{2.32}$$

where n_s is the quantum number for the sth oscillator or normal mode.

The interaction energy of the system is the difference between the groundstate energy of the system, $U = \frac{1}{2}\hbar \sum \omega_s$, and the unperturbed ground-level energy,

$$\Delta U = U - U_o = \frac{1}{2}\hbar \sum_{s=1}^{3N} \omega_s - \frac{3}{2}\hbar \sum_{i=1}^{N} (k_i/m_i)^{1/2} \tag{2.33}$$

With ω_o as the unperturbed energy of all the molecules, all the diagonal elements in (2.30) are $k_i/m_i = \omega_o^2$. The diagonalized matrix of M is M', with diagonal elements ω_s^2. Now, define a matrix

$$A \equiv \omega_o^{-2} M - I = \begin{pmatrix} 0 & Q_{12} \cdots\cdots & Q_{1N} \\ Q_{12} & 0 \cdots\cdots\cdots & Q_{2N} \\ \cdots\cdots & \cdots\cdots\cdots & \cdots\cdots \\ Q_{1N} & Q_{2N} & 0 \end{pmatrix} \tag{2.34}$$

$$\text{where } Q_{ij} = (\alpha_i \alpha_j)^{1/2} (\hat{1} - 3\hat{r}_{ij}\hat{r}_{ij}) R_{ij}^{-3} \tag{2.35}$$

and $\alpha_i = \epsilon_i^2/k_i$ = polarizability of the ith molecule. If S is a matrix which diagonalises M, then $A' \equiv S^{-1}AS = \omega_o^2 S^{-1}MS - S^{-1}IS = \omega_o^{-2}M' - I$ is diagonal, and A has the eigenvalues

$$A'_{ss} = (\omega_s^2/\omega_o^2) - 1 \tag{2.36}$$

The interaction energy of the system, from (2.33), then is

$$\Delta U = U-U_o = \frac{1}{2}\hbar\omega_o \sum_{s=1}^{3N} (1+A'_{ss})^{1/2} - \frac{3}{2}N\hbar\omega_o = \sum_{n=1}^{\infty} \Delta U_n \qquad (2.37)$$

where

$$\Delta U_n = -\frac{1}{2}\hbar\omega_o \left[(-1)^n \frac{1.1.3....(2n-3)}{2^n\, n\,!}\right] \mathrm{Tr}\, A^n \qquad (2.38)$$

In (2.37) the radical is expanded using binomial theorem, and the theorem for the invariance of a trace under a canonical transformation justifies setting $\sum_{s=1}^{3N}(A'_{ss})^n \equiv \mathrm{Tr}\,(A')^n =$ $\mathrm{Tr}\, A^n$.

ΔU_n gives the nth order contribution to the energy of the system, and it depends on the trace of the nth power of the matrix A.

$\Delta U_1 = 0$ because $\mathrm{Tr}\, A = 0$.

For the second order contribution, we have

$$\Delta U_2 = -\frac{1}{4}\hbar\omega_o\, \mathrm{Tr}\, A^2$$

$$= -\frac{1}{16}\hbar\omega_o \sum_{i=1}^{N}{}' \sum_{j=1}^{N}{}' \mathrm{Tr}\, Q_{ij}\cdot Q_{ji}$$

$$= -\frac{3}{4}\hbar\omega_o \sum_{i=1}^{N-1} \sum_{j>i}^{N} \alpha_i\,\alpha_j R_{ij}^{-6} \qquad (2.39)$$

(2.39) gives the interaction energy of the system as the sum of the second order pair terms over all pairs of molecules belonging to the system. From (2.38) the third order contribution is obtained as

$$\Delta U_3 = \frac{1}{32}\hbar\omega_o \sum_{i=1}^{N}{}' \sum_{j=1}^{N}{}' \sum_{k=1}^{N}{}' \mathrm{Tr}\, Q_{ij}\cdot Q_{kj}\cdot Q_{ki}$$

$$= \frac{9}{16}\hbar\omega_o \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \sum_{k>j}^{N} \frac{\alpha_i\,\alpha_j\,\alpha_k(1+3\cos\theta_i\cos\theta_j\cos\theta_k)}{(R_{ij}R_{jk}R_{ki})^3}, \qquad (2.40)$$

which is the sum of triple-diple (21) terms, discussed in section 2(B), for molecules of equal unperturbed frequency over all triplets of molecules belonging to the system.

In order to evaluate the general term (2.38), Tr A^n is calculated.

$$\mathrm{Tr}\, A^n = \sum_{i_1=1}^{N}{}' \cdots\cdots \sum_{i_n=1}^{N}{}' \mathrm{Tr}\, Q_{i_1 i_2} \cdot Q_{i_2 i_3} \cdots\cdots Q_{i_n i_1} \quad , \qquad (2.41)$$

where the Q_{ij}'s are defined in (2.35), and the primes on the summations indicate that $i_1=i_2$, ... $i_n \neq i_1$. (2.41) is evaluated with the help of vector-dyadic algebra.

The nth-order contribution to the energy of a system of molecules which have equal unperturbed frequencies, and which are coupled only by dipole-dipole perturbing potentials, is thus given by

$$\Delta U_n = -\frac{1}{2}\hbar\,\omega_o \left[(-1)^n \frac{1.1.3\ldots(2n-3)}{2^n n}\right] \; X$$

$$\sum_{i_1 \neq i_2}^{N} \cdots \sum_{i_n \neq i_1}^{N} \frac{\alpha_{i_1} \cdots \alpha_{i_n}}{(R_{i_1 i_2} \cdots R_{i_n i_1})^3} \; X$$

$$\Bigg\{ 3 - 3n + 9 \sum_{a=1}^{n-1} \sum_{b\ a}^{n} (\hat{r}_{i_a i_{a+1}} \cdot \hat{r}_{i_b i_{b+1}})^2$$

$$- 27 \sum_{a=1}^{n-2} \sum_{b>a}^{n-1} \sum_{c>b}^{n} (\hat{r}_{i_a i_{a+1}} \cdot \hat{r}_{i_b i_{b+1}}) \; X$$

$$(\hat{r}_{i_b i_{b+1}} \cdot \hat{r}_{i_c i_{c+1}})(\hat{r}_{i_c i_{c+1}} \cdot \hat{r}_{i_b i_{b+1}}) \Bigg\} + \cdots$$

$$+ (-1)^n 3^n (\hat{r}_{i_1 i_2} \cdot \hat{r}_{i_2 i_3}) \; X \; (\hat{r}_{i_2 i_3} \cdot \hat{r}_{i_3 i_4}) \cdots$$

$$(\hat{r}_{i_n i_1} \cdot \hat{r}_{i_1 i_2}) \qquad (2.42)$$

ΔU_n depends on the frequency ω_0, the polarizability α_i, the distances $R_{i_1 i_2}$ between the molecules, and the cosines of the angles between the lines joining the molecular centers. Each term $(R_{i_1 i_2} \ldots R_{i_n i_1})^{-3}$ .... of (2.42) corresponds to a closed graph $(i_1 i_2 \ldots i_n)$ drawn with n of the N molecules as vartices.

3. COVARIANT PERTURBATION CALCULATIONS OF THE LONDON-VAN DER WAALS INTERACTION ENERGY OF NEUTRAL ATOMS

The application of quantum electrodynamics provides a fundamental and general basis to the theory of London-van der Waals forces (17, 20, 26). The Feynman-Dyson covariant perturbation techniques (29) help to introduce relativistic and retardation effects in the calculation of the interaction energy in a natural manner.

A. Two Atoms

The unperturbed system consists of two neutral hydrogen atoms, A and B, in their groundstates, and the electromagnetic radiation field in its vacuum state, there being no interaction between the constituents of the system. The atoms are regarded as fixed in space and nuclear recoil effects are neglected. The interatomic distance, R, is given by

$$\vec{R} = \vec{R}_1 - \vec{R}_2 = R\hat{r}_{12} \tag{3.1}$$

where $\vec{R}_1$ and $\vec{R}_2$ are the positions of the two atoms with respect to the origin. The unperturbed groundstate of the system is given by

$$|G\rangle \equiv |0_F, 0_A, 0_B\rangle \tag{3.2}$$

where 0_A, 0_B refer to the atomic groundstates, and 0_F denotes the vacuum of the radiation field.

The electrons of each atom are treated as Dirac particles bound in a Coulomb field, V(r), and the electron field operators satisfy the Dirac equation

$$(H - E_n)\psi_n = (-i\vec{\alpha}\cdot\vec{\nabla} + \beta m + V(r) - E_n)\psi_n = 0 \ , \tag{3.3}$$

or, in covariant form

$$(\gamma_\mu (i\, \partial_\mu - eA_\mu) - m)\psi = 0 \tag{3.3a}$$

where the external field, $V(r)$, is contained in $A_\mu(x)$. The electrons interact with each other via the electromagnetic field in the Lorentz gauge.

Neglecting overlap effects in the interaction (by requiring that the atoms be far enough apart so that the electrons of the atoms move in different potential wells), and using the interaction representation for boundstate perturbation theory (30), the following relations are obtained for the electron current density operators of the two atoms :

$$J_\mu (x) = J_\mu^{(1)}(x) + J_\mu^{(2)}(x) \tag{3.4}$$

$$\left[J_\mu^{(1)}(x),\ J_\nu^{(2)}(x')\right] = 0 \quad ; \quad \mu,\nu = 1,2,3,4 \tag{3.5}$$

For a larger number of atoms without overlap, one can write

$$J_\mu(x) = \sum_i J^{(i)}(x) \tag{3.6}$$

$$\left[J_\mu^{(i)}(x),\ J_\nu^{(j)}(x')\right] = 0 \quad , \quad i \neq j \tag{3.7}$$

In the bound interaction representation (30) the photon variables commute with the bound electron variables

$$\left[J_\mu(x),\ A_\nu(x')\right] = 0 \quad , \tag{3.8}$$

and the current density matrix elements are given by

$$\left\langle m_i \middle| J_\mu^{(i)}(x) \middle| n_i \right\rangle = J^{(i)}_{\mu\, mn}(\vec{r})\, e^{i(E_m - E_n)t} \tag{3.9}$$

If the origin of space coordinates is placed at the center of an atom, the current density matrix elements are given by

$$\begin{aligned} J_{imn}(r) &= e\, \psi_m^+(\vec{r})\, \alpha_i\, \psi_n(\vec{r}) \ , \\ J_{4mn}(r) &= ie\, \psi_m^+(\vec{r})\, \psi_n(\vec{r}) \ , \end{aligned} \tag{3.10}$$

where the ψ's are the four-spinor solutions of (3.3).

The Interaction Energy of Two Atoms

Consider the perturbation of the groundstate (3.2) when the interaction between the atoms and the radiation field is turned on adiabatically. The lowest order perturbation anergy that contributes to the London-van der Waals interaction is of the fourth order in the electronic charge e.

The Hamiltonian density for the interaction of matter with the radiation field is

$$H(x) = - J_\mu(x)A_\mu(x), \tag{3.11}$$

and the S matrix for the system is (29)

$$S = 1 + \sum_{n=1}^{\infty} S_\epsilon^{(n)} , \tag{3.12}$$

in which the nth order term, $S_\epsilon^{(n)}$, is given by

$$S_\epsilon^{(n)} = \frac{(-i)^n}{n!} \int_{-\infty}^{+\infty} d^4x_1 \dots \int_{-\infty}^{+\infty} d^4x_n P\left[H(x_1)\dots H(x_n)\right] e^{-\epsilon(|t_1|+\dots+|t_n|)} \tag{3.13}$$

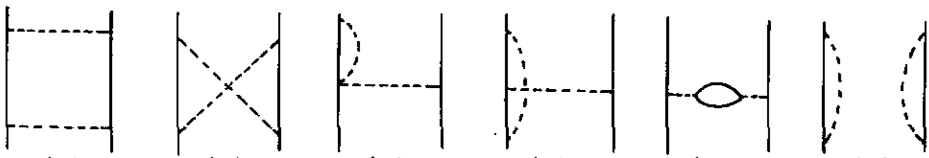
with the units $\hbar=c=1$, $e^2=1/137$.

In (3.13), P is the time-ordering operator, and the convergence factors have been introduced according to the adiabatic hypothesis (29).

The fourth order contribution to the S matrix is

$$S_\epsilon^{(4)} = \frac{1}{24} \int_{-\infty}^{+\infty} d^4x_1 \dots \int_{-\infty}^{+\infty} d^4x_4 P\left[H(x_1)\dots H(x_4)\right] e^{-\epsilon(|t_1|+\dots+|t_4|)} \tag{3.14}$$

The fourth order Feynman diagrams are shown in the figure. Of these only the diagrams (a) and (b) contribute to the London-van der Waals interaction energy; the others (being renormalization, vacuum polarization, or self-energy diagrams) are subtracted out from the fourth order contribution to the S matrix.



(a) (b) (c) (d) (e) (f)

Fourth order diagrams

The fourth order perturbation energy can be written (31) in terms of the adiabatic S matrix as

$$\Delta U_4 = \lim_{\epsilon \to 0} 2i\epsilon \left\langle G \middle| S_\epsilon^{(4)} \middle| G \right\rangle \quad , \tag{3.15}$$

where $|G\rangle$ is defined in (3.2).

With (3.11) and (3.14), S_ϵ^4 may be written as

$$S_\epsilon^4 = \frac{1}{24} \int_{-\infty}^{+\infty} d^4x_1 \ldots \int_{-\infty}^{+\infty} d^4x_4 P\left[J_\mu(x_1) J_\nu(x_2) J_\sigma(x_3) J_\tau(x_4)\right] \cdot P\left[A_\mu(x_1) A_\nu(x_2) A_\sigma(x_3) A_\tau(x_4)\right] e^{-\epsilon(|t_1| + \ldots + |t_4|)} \tag{3.16}$$

The causal photon propagator (29) is

$$D_F(x) = \frac{2i}{(2\pi)^4} \int d^3\vec{k}\, e^{i\vec{k}\cdot\vec{r}} \int_{C_F} d\omega \frac{e^{-i\omega t}}{\vec{k}^2 - \omega^2} , \tag{3.17}$$

where C_F denotes the Feynman path for the circumvention of poles.

Using Wick's theorem (32), the symmetries of the P-product, and the relations (3.4) and (3.5), one obtains

$$\left\langle G \middle| S^4 \middle| G \right\rangle' = 2\pi^2 \int d^4x_1 \ldots \int d^4x_4 \left\langle 0_A \middle| P\left[J^A_\mu(x_1) J^A_\nu(x_2)\right] \middle| 0_A \right\rangle \cdot \left\langle 0_B \middle| P\left[J^B_\mu(x_3) J^B_\nu(x_4)\right] \middle| 0_B \right\rangle \cdot D_F(x_1 - x_3) D_F(x_2 - x_4) \cdot e^{-\epsilon(|t_1| + \ldots + |t_4|)} \tag{3.18}$$

The prime on the left side of (3.18) denotes the fact that only the diagrams (a) and (b) have been used in the calculation. (3.9) and (3.17) are used in (3.18), the time integrations are performed, and then from (3.15) the interaction energy is found to be:

$$\Delta U_4 = \frac{i}{16\pi^5}\int d^3\vec{k}\, d^3\vec{k}'\, d\omega\,(\vec{k}^2-\omega^2)^{-1}(\vec{k}'^2-\omega^2)^{-1} \cdot$$

$$M^{(A)}_{\mu\nu}(\vec{k},\vec{k}',\omega)M^{(B)}_{\mu\nu}(-k,-k',-\omega) \tag{3.19}$$

where

$$M^{(i)}_{\mu\nu}(\vec{k},\vec{k}',\omega) = \int d^3\vec{r}\, d^3\vec{r}'\, e^{i(\vec{k}\,\vec{r} + \vec{k}'\vec{r}')} \cdot$$

$$\sum_n \left(\frac{J^i_{\mu 0_i n}(\vec{r})J^i_{\nu n 0_i}(\vec{r}')}{E_o - E_n - \omega + i\epsilon} + \frac{J^i_{\nu 0_i n}(\vec{r}')J^i_{\mu n 0_i}(\vec{r})}{E_o - E_n + \omega + i\epsilon} \right) \tag{3.20}$$

(3.19) gives the interaction energy of two neutral atoms and embodies relativistic and retardation effects.

If the relativistic and higher multipole effects are neglected, the interaction energy may be calculated in the non-relativistic and dipole approximations. The groundstates of the atoms are 1s-states and the only excited states which contribute to the perturbation energy are assumed to be 2p-states. The three 2p-wavefunctions are so chosen that the corresponding matrix elements, $\langle 1s|\vec{q}|2p\rangle = \vec{q}_{0n}$, of the electric dipole moment $\vec{q}$ of the atom lie along the three space axes. The non-relativistic reduction of the operators and wavefunctions in expressions like (3.20) is performed with the help of Foldy-Wouthuysen transformations (33). The non-relativistic interaction energy of two neutral hydrogen atoms is found to be

$$\Delta U_2 = \frac{i}{16\pi^5}\lim_{\gamma\to 0}\int d^3\vec{k}\, d^3\vec{k}'\, d\omega\, e^{i(\vec{k}+\vec{k}').\vec{R}-\gamma(|\vec{k}|+|\vec{k}'|)}\,\alpha_1(\omega)\alpha_2(\omega)$$

$$\cdot\,(\vec{k}^2-\omega^2)^{-1}(\vec{k}'^2-\omega^2)^{-1}\left[(\vec{k}.\vec{k}')^2-\omega^2(\vec{k}^2+\vec{k}'^2)+3\omega^4\right] \tag{3.21}$$

where $\alpha(\omega)$ is the real part of the atomic polarizability, and is given by

$$\alpha_i(\omega) = \sum_n 2\,\omega_{n0}\,|q_{0n}(i)|^2/(\omega^2_{n0}-\omega^2) \tag{3.22}$$

In (3.21) the k-integrations are divergent and they are calculated by introducing a convergence factor $e^{-\gamma k}$ and subsequently taking the limit $\gamma \rightarrow 0$. We assume that $k \ll 1/a$ in neglecting the effects of higher multipoles, where a is of the order of the size of the atom; thus as γ tends to zero, values of the order of magnitude a/R are ignored. The interaction energy is finally obtained as

$$\Delta U_2 = - \frac{4}{\pi^2} \frac{|q(1)|^2 \; |q(2)|^2 E^2}{\hbar c R^2} \int_0^\infty du \, \frac{u^4 \, e^{-2uR}}{(E^2+u^2)^2} \cdot$$

$$\left(1 + \frac{2}{uR} + \frac{5}{u^2R^2} + \frac{6}{u^3R^3} + \frac{3}{u^4R^4}\right) , \qquad (3.23)$$

which is the result of Casimir and Polder (17). In writing (3.23) an idealized spectrum is assumed for the atom, namely, one triply degenerate p-state of energy E above the groundstate $(E_n - E_o = E)$, and $\lambda = \hbar c/E$.

In the limit of very small distances, $R \ll \lambda$, the interaction energy expression (3.23) is evaluated to obtain London's stationary perturbation formula (2.8), $\Delta U_2 = -\mu R^{-6}$.

For large R (wave zone region, $R \gg \lambda$), the retarded interaction energy becomes

$$\Delta U_2 = \frac{23 \hbar c \, \alpha_1(o) \, \alpha_2(o)}{4 \pi R^7} \qquad (3.24)$$

in terms of the static atomic polarizabilities, $\alpha_i(o)$, of the atoms.

B. Three Atoms

As for two atoms in (3.2), the unperturbed groundstate of a system of three atoms A, B, and C, in their groundstates, and the radiation field in its vacuum state, can be written as

$$|G\rangle = |0_F, 0_A, 0_B, 0_C\rangle \qquad (3.25)$$

The sixth order contribution to the S matrix is

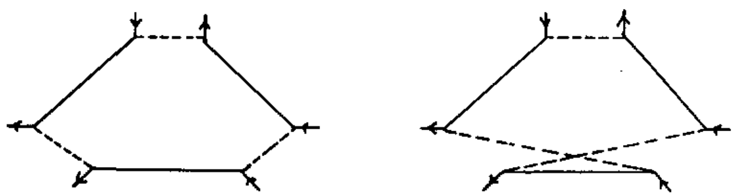
$$S_\epsilon^{(6)} = \frac{(-i)^6}{6!} \int_{-\infty}^{+\infty} d^4x_1 \ldots \int_{-\infty}^{+\infty} d^4x_6 P\left[H(x_1)\ldots H(x_6)\right] e^{-\epsilon(|t_1| + \ldots + |t_6|)} \qquad (3.26)$$

and the sixth order perturbation energy is calculated from the formula

$$\Delta U_6 = \lim_{\epsilon \to 0} 3i\epsilon \left\langle G \left| S_\epsilon^{(6)} \right| G \right\rangle \quad , \tag{3.27}$$

where $|G\rangle$ is now given by (3.25).

The diagrams of interest in the calculation of London-van der Waals interaction energy of three atoms (that is, for the specific three-body interaction) are those in which the interaction arises by an exchange of three photons between the three atoms, each atom being involved in the exchange by the absorption and emission of a photon. Thus the contributing diagrams are:



The expectation value to be used in (3.27) is

$$\begin{aligned} \left\langle G \left| S_\epsilon^{(6)} \right| G \right\rangle' = 8\pi^3 \int d^4x_1 \ldots \int d^4x_6 \left\langle 0_A \left| P\left[J^A_\mu(x_1) J^A_\rho(x_2) \right] \right| 0_A \right\rangle \cdot \\ \left\langle 0_B \left| P\left[J^B_\mu(x_3) J^B_\sigma(x_4) \right] \right| 0_B \right\rangle \cdot \left\langle 0_C \left| P\left[J^C_\sigma(x_5) J^C_\rho(x_6) \right] \right| 0_C \right\rangle \cdot \\ D_F(x_1-x_3) D_F(x_4-x_5) D_F(x_6-x_2) e^{-\epsilon(|t_1|+\ldots+|t_6|)} , \end{aligned} \tag{3.28}$$

where the prime on the left side denotes the fact that the contribution of other six order diagrams has been subtracted out. From (3.27) and (3.28), the interaction energy of three neutral atoms, including relativistic and retardation effects, is found to be

$$\begin{aligned} \Delta U_6 = \frac{i}{16\pi^7} \int d^3\vec{k}_1 d^3\vec{k}_2 d^3\vec{k}_3 d\omega \, (\vec{k}_1^2 - \omega^2)^{-1} (\vec{k}_2^2 - \omega^2)^{-1} (\vec{k}_3^2 - \omega^2)^{-1} \cdot \\ M^A_{\mu\rho}(\vec{k}_3, \vec{k}_1, \omega) M^B_{\mu\sigma}(\vec{k}_1, \vec{k}_2, \omega) M^C_{\sigma\rho}(\vec{k}_2, \vec{k}_3, \omega) , \end{aligned} \tag{3.29}$$

where the matrices M are defined in (3.20).

The non-relativistic transformation of the operators and wavefunctions in (3.29) gives, in the dipole approximation, the non-relativistic interaction energy of three neutral atoms as

$$\Delta U_3 = \frac{i}{16\,\pi^7} \lim_{\substack{\epsilon \to 0 \\ \gamma \to 0}} \int d^3\vec{k}_1 d^3\vec{k}_2 d^3\vec{k}_3 d\omega \; \left[\alpha(\omega)\right]^3 (\vec{k}_1^2 - \omega^2)^{-1} \cdot$$
$$(\vec{k}_2^2 - \omega^2)^{-1} (\vec{k}_3^2 - \omega^2)^{-1} \Big[- (\vec{k}_1.\vec{k}_2)(\vec{k}_2.\vec{k}_3)(\vec{k}_3.\vec{k}_1) +$$
$$\omega^2 \left\{ (\vec{k}_1.\vec{k}_2)^2 + (\vec{k}_2.\vec{k}_3)^2 + (\vec{k}_3.\vec{k}_1)^2 \right\} - \omega^4 (\vec{k}_1^2 + \vec{k}_2^2 + \vec{k}_3^2) + 3\,\omega^6 \Big] \cdot$$
$$e^{i(\vec{k}_1.\vec{R}_{23} + \vec{k}_2.\vec{R}_{31} + \vec{k}_3.\vec{R}_{12}) - \gamma(|\vec{k}_1| + |\vec{k}_2| + |\vec{k}_3|)} \tag{3.30}$$

where R_{ij} are the interatomic separations. In (3.30) the ω-integration is over the Feynman path. When the atoms are not identical, the $\alpha(\omega)$'s occur as the product of the polarizabilities of the individual atoms.

In the static limit ($R \ll \lambda$) the interaction energy becomes

$$\Delta U_3 = \frac{9}{16} E \left[\alpha(0)\right]^3 (R_{12}R_{23}R_{31})^{-3} (3\cos\theta_1 \cos\theta_2 \cos\theta_3 + 1), \tag{3.31}$$

which compares with (2.21) and (2.40), and is the triple-dipole interaction (21).

In the equilateral triangle configuration, the retarded interaction energy ($R \gg \lambda\!\!\!^{-}$) of three atoms becomes

$$\Delta U_3(R \to \infty) = \frac{5.2\, \alpha_1(0)\, \alpha_2(0)\, \alpha_3(0)}{\pi R^{10}}, \tag{3.32}$$

and is repulsive.

If two atoms are close together at a distance r, with the third, A, at a long distance R, making an angle θ with the axis of the first two, the energy is found to be:

$$-\frac{7}{4}(3\cos^2\theta - 1)\frac{\hbar c}{\pi R} \frac{\alpha_A(0)\, \alpha_B(0)\, \alpha_C(0)}{R^6\, r^3} \tag{3.33}$$

Here the energy follows the R^{-7} law of (3.24), and the angular dependence reflects the anisotropic change in the polarizability of the pair BC, due to their close approach.

C. N Atoms

The specific N-body energy can be calculated in a similar fashion. In the static limit this energy is given by (2.42), while in the wave zone limit ($R \gg \lambdabar$) it turns out to be of the order

$$\Delta U_N \approx -\frac{\hbar c}{\pi R}\left(\frac{\alpha(o)}{R^3}\right)^N \tag{3.34}$$

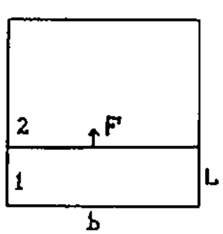
This energy is exceedingly small.

4. CASIMIR EFFECT AND TEMPERATURE CORRECTION

By considering the perturbation of the quantum mechanical zeropoint energy of the radiation field in a cavity, Casimir (18) has calculated the force between an atom and a perfectly conducting wall of the cavity as well as the retarded van der Waals law of interaction between two atoms, (3.24).

The experimental measurements (34) which confirm the existence of retardation effects in London-van der Waals forces at large distances between solids (Casimir effect) are performed at finite temperatures. It is also known that van der Waals forces persist even at high temperatures. It is, therefore, useful to calculate the contribution of temperature dependent thermal radiation to the molecular attractive forces between solids.

Consider a cubic cavity of side b. The cavity may be divided into two parts by a movable plate at distance L from one of the ends.



From statistical mechanics one has

$$A = -kT \ln Z \tag{4.1}$$

$$Z = \mathrm{Tr}\,(e^{-H/kT}) \tag{4.2}$$

where A is the free energy of the cavity and Z is the partition function; also $A=A_1+A_2$, where A_1 and A_2 are the free energies of the two parts. The Hamiltonian in (4.2) is given by

$$H = \sum_{\omega_k} \hbar\omega_k(N_k + \frac{1}{2}) \quad , \tag{4.3}$$

where ω_k are the eigenfrequencies of the electromagnetic field, and N_k are Hermitian operators with eigenvalues 0,1,2,... Thus

$$Z = \prod_{\omega_k} \sum_{N_k=o} \exp(-\frac{\hbar\omega_k}{kT}(N_k+\frac{1}{2})) = \prod_{\omega_k} \frac{\exp(-\frac{\hbar\omega_k}{2kT})}{1-\exp(-\frac{\hbar\omega_k}{kT})} \tag{4.4}$$

and

$$A_1(L,T) = \sum_{\omega_k} \frac{\hbar\omega_k}{2} + kT\ \ln(1-\exp(-\frac{\hbar\omega_k}{kT})) \tag{4.5}$$

The divergent part $\sum \frac{\hbar\omega_k}{2}$ in (4.5) is dealt with by examining the difference of free energies as in Casimir prescription (18) for the zeropoint energy. The change in free energy, if the plate moves a distance δL, is given by

$$(\delta A)_T = F\ .\ \delta L \quad , \tag{4.6}$$

where F is the force per unit area on the plate. The expression for the force between the plates, for $b \gg L$ and $b-L \gg L$, is found to be

$$F = \frac{\pi^2\hbar c}{240L^4} + \frac{\pi^2\hbar cT'}{L^3} \sum_{n=1}^{\infty} n^2\ln(1-\exp(-\frac{n}{T'L})) - \frac{\pi^6\hbar cT'^4}{45}, \tag{4.7}$$

where $T' = kT/\hbar c\pi$ and L is the distance between the plates. The first term in (4.7) is the Casimir force at T=0. The other two terms give the temperature correction to the van der Waals interaction between the two plates.

At low temperatures, $T'L \ll 1$, one obtains from (4.7)

$$F = \frac{\pi^2 \hbar c}{240}\frac{1}{L^4} - \frac{\pi^2 \hbar c}{L^3} T' \exp\left(-\frac{1}{T'L}\right) - \frac{\pi^6 \hbar c T'^4}{45} \qquad (4.8)$$

At high temperatures, $T'L \gg 1$, the sum over the logarithms in (4.7) is obtained with the help of Poisson's formula, and the force becomes

$$F = \frac{\hbar c T'}{4L^3}\zeta(3) + \pi^2 \hbar c\left(\frac{T'}{2\pi^2 L^3} + \frac{2T'^2}{L^2} + \frac{4\pi^2 T'^3}{L}\right) . \exp(-4\pi^2 T' L), \qquad (4.9)$$

where ζ is Riemann's zeta-function.

The expressions (4.8) and (4.9) compare well with the expressions obtained by Lifshitz (25) by introducing a "random" field in Maxwell's equations. However, Lifshitz does not get the exponential term in the low temperature limit given in (4.8). The temperature correction may already be considered at a distance $L > 3\times10^{-4}$ cm between the plates at room temperature (300°K).

If T=0 in the second part of the cavity, with F=-p and taking the limit $L \to \infty$, one finds from (4.8) the formula for the radiation pressure

$$p = \frac{8}{45}\frac{\pi^5 k^4 T^4}{h^3 c^3}, \qquad (4.10)$$

which, with the energy density u=3p, gives the Stefan-Boltzmann law $u = aT^4$.

5. CERTAIN FEATURES OF THE EQUATION OF STATE OF GASES

The Kamerlingh Onnes expansion for the equation of state of an imperfect dilute gas is

$$pV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2} + \ldots..\right) \qquad (5.1)$$

where B,C,.... are the second, third,...., virial coefficients respectively. These coefficients (B, C, and higher ones) have been calculated classically for a number of gases and a variety of binary potentials (2).

The thermodynamic functions of a gas of N particles contained in a volume V can be expressed in terms of the canonical or grand canonical partition functions, which are related to each other as:

$$Z_G(V,T,z) = \sum_{N=o}^{\infty} Z(V,T,N)(\lambda^3 z)^N , \qquad (5.2)$$

where z is the fugacity and λ the thermal wavelength.

$$z = \lambda^{-3} \exp \beta g \qquad (5.3)$$

$\beta = 1/kT$ and g is the chemical potential; $\lambda = h/(2\pi\, mkT)^{1/2}$.
Also

$$Z = (N!)^{-1} \lambda^{-3N} \int_V W_N(\vec{r}^N) d\vec{r}^N , \qquad (5.4)$$

$$\vec{r}^N \equiv (\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N) \equiv (1,2,\ldots N)$$

The pressure and the density of a Boltzmann gas may be expressed as expansions in the fugacity z

$$p = kT \sum_n b_n z^n \qquad (5.5)$$

$$N/V = \sum_n n b_n z^n \qquad (5.6)$$

where b_n, the Mayer cluster integrals, are defined by

$$b_n = (Vn!)^{-1} \int (1\ldots n|U_n|1\ldots n) d\vec{r}_1 \ldots d\vec{r}_n \qquad (5.7)$$

and become volume independent when one lets V become large.
If H_N is the Hamiltonian for N particles and

$$W_N \equiv \exp(-H_N/kT) , \qquad (5.8)$$

then the Ursell cluster functions, U_n, are defined by

$$(1'|W_1|1) = (1'|U_1|1)$$

$$(1',2'|W_2|1,2) = (1'|U_1|1)(2'|U_1|2) + (1',2'|U_2|1,2)$$

$$(1',2',3'|W_3|1,2,3) = (1'|U_1|1)(2'|U_1|2)(3'|U_1|3)$$
$$+ (1'|U_1|1)(2',3'|U_2|2,3) + (2'|U_1|2)(1',3'|U_2|1,3)$$
$$+ (3'|U_1|3)(1',2'|U_2|1,2) + (1',2',3'|U_3|1,2,3), \text{ etc.} \qquad (5.9)$$

Ursell and Mayer (35) first used this procedure for classical statistical mechanics and Kahn and Uhlenbeck (36) for quantum statistical mechanics. U_n is required for the n-body problem. For a Bose or Fermi gas one is interested in $b_n^{\,s}$ and $U_n^{\,s}$, and Lee and Yang (37) have shown how $U_n^{\,s}$ may be calculated in terms of U_n, and how U_n, for $n > 2$, may be written in terms of U_2.

By eliminating z from the relations (5.5) and (5.6), the equation of state may be written as a power series in either the number density $\frac{N}{V} = v^{-1}$,

$$pv = kT\left(1 + \frac{-b_2}{v} + \frac{4b_2^{\,2} - 2b_3}{v^2} + \ldots.\right) \qquad (5.10)$$

or in p,

$$pv = kT\left(1 - b_2 p\beta + (3b_2^{\,2} - 2b_3)(p\beta)^2 + \ldots.\right) \qquad (5.11)$$

$$pv = 1 - \sum_{i=1}^{\infty} \frac{i}{i+1} \beta_i \, v^{-i} \quad , \qquad (5.11a)$$

where $\beta = (kT)^{-1}$ and β_i, the irreducible cluster integrals, are various combinations of the b_n. Mayer (35) has given the general equations for β_i when the intermolecular potential, $U(r_{ij})$, is central and pairwise additive, and the virial coefficients are related to β_i as:

$$B = \frac{1}{2}N\beta_1 \quad , \qquad C = \frac{2}{3}N^2\beta_2 \quad , \qquad D = \frac{3}{4}N^3\beta_3 \qquad (5.12)$$

Otherwise, from the power series in v one has

$$B = -b_2 \quad , \qquad C = 4B^2 - 2b_3 \quad , \qquad D = 12BC - 12B^3 - 3b_4, \text{ etc.} \qquad (5.13)$$

A. Second Virial Coefficient

At high temperatures the second virial coefficient is correctly given by the classical expression

$$B = -2\pi N \int_0^\infty (e^{-U(r)/kT} - 1) r^2 dr \quad , \tag{5.14}$$

where $U(r)$ = intermolecular potential energy; at low temperatures, for Boltzmann statistics, it is found to be given by

$$B = \frac{1}{2} \lambda^3 \sum_{l=0} (2l + 1) B_l \quad , \tag{5.15}$$

where

$$B_l = \sum_n \exp(-\beta E_{nl}) + \frac{1}{\pi} \int_0^\infty \exp(-\beta E) \frac{d\eta_l}{dE} dE \quad , \tag{5.16}$$

η_l being the lth phase shift.

The generalization of B from (5.15) to Bose-Einstein or Fermi-Dirac statistics is straightforward and, taking into account an intrinsic spin s of the particles, one obtains:

$$\begin{aligned} B_{BE}^{(s)} &= f_1 B_{BE} + f_2 B_{FD} \quad , \\ B_{FD}^{(s)} &= f_1 B_{FD} + f_2 B_{BE} \quad , \end{aligned} \tag{5.17}$$

where $f_1=(s+1)/(2s+1)$ and $f_2=s/(2s+1)$, while B_{BE} and B_{FD} refer to zero spin and are given by

$$\begin{aligned} B_{BE} &= -\frac{1}{2} \lambda^3 \left(\frac{1}{8} + 2 \sum_{l \text{ even}} (2l + 1) B_l\right) \quad , \\ B_{FD} &= -\frac{1}{2} \lambda^3 \left(-\frac{1}{8} + \sum_{l \text{ odd}} (2l + 1) B_l\right) \end{aligned} \tag{5.18}$$

Considering only S states and at the most one discrete state, and $s=0$ for BE(He^4), $s=1/2$ for FD(He^3), the equations (5.18) give

$$\begin{aligned} B_{BE} &= -\frac{1}{2} \lambda^3 \left(\frac{1}{8} + 2B_0\right) \quad , \\ B_{FD}^{(1/2)} &= -\frac{1}{2} \lambda^3_{(1/2)} \left(-\frac{1}{16} + \frac{1}{2} B_0\right) \quad , \end{aligned} \tag{5.19}$$

where $B_o = e^{\beta E_{nl}} + B_o' \; ; \; B_o' = \frac{1}{\pi} \int_0^\infty \exp(-\beta E) \, \frac{d\eta_l}{dE} \, dE.$

Numerical calculations based on potentials like the Lennard-Jones (12, 6) potential show that even at 1^oK the D-state contributions in (5.15) are appreciable (38). Using a square-well potential to evaluate (5.15), it may be concluded (39) that the two-body system of He^4-He^3 has a discrete level while both the He^4-He^3 and He^3-He^3 systems have no discrete level. The validity of the expansions of η_l for various regimes of binding (40) is extremely limited in the case of B at low temperature.

Diffraction Corrections to B

In order to introduce quantum mechanical diffraction corrections, which become important at high temperatures, the second virial coefficient may be developed in a power series in the Planck's constant (Wigner-Kirkwood expansion, 36):

$$B = B^{(o)} + B^{(1)}q + B^{(2)}q^2 + B^{(3)}q^3 + \ldots\ldots, \tag{5.20}$$

where $q = \hbar^2/2m^*$; $\hbar = h/2\pi$, and m^* is the reduced mass of the two-body system. At high temperatures, the Bloch equation

$$\frac{\partial\rho}{\partial\beta} = - H\rho \tag{5.21}$$

may be solved to give

$$\lambda^{*3} \rho(\vec{r},\vec{r}) = \exp W(\vec{r},\vec{r}) \tag{5.22}$$

where the star denotes that m^* has been used in λ. W may also be developed in a series like (5.20), and since $B = 2\pi N \int_0^\infty (1 - \exp W(\vec{r},\vec{r}))r^2 dr$, the iterative solutions of the Bloch equation yield (36, 39):

$$B^{(o)} = 2\pi \int_0^\infty (1 - \exp(-u))r^2 dr \quad , \tag{5.23a}$$

$$B^{(1)} = \frac{\pi}{6}\beta^3 \int_0^\infty \exp(-u)U'^2 \; r^2 dr \quad , \tag{5.23b}$$

$$B^{(2)} = -\frac{\pi}{6}\beta^4 \int_0^\infty \exp(-u)\left(\frac{U''^2}{10} + \frac{U'^2}{5r^2} + \frac{\beta U'^3}{9r} - \frac{\beta^2 U'^4}{72}\right) r^2 dr \; , \tag{5.23c}$$

$$B^{(3)} = \pi\beta^5 \int_0^\infty \exp(-u)\left(\frac{U'''^2}{840} + \frac{U''^2}{140r^2} + \frac{\beta U''^3}{756} + \frac{\beta U' U''^2}{180r}\right.$$

$$\left. + \frac{\beta U'^3}{945r^3} - \frac{\beta^2 U'^2 U''^2}{720} - \frac{\beta^2 U'^4}{6480r^2} - \frac{\beta^3 U'^5}{2160r} + \frac{\beta^4 U'^6}{25920}\right) r^2 dr \; , \tag{5.23d}$$

where $u=\beta U(r)$, $\beta = 1/kT$, and the primes denote derivatives with respect to r.

The usefulness of such results is somewhat limited by the fact that little is known about the convergence of the Wigner-Kirkwood expansion like (5.20). The convergence problems in such an expansion are analogous to those in the perturbation expansion of the S matrix in quantum field theory. Such types of series are characterized by the fact that the expansion coefficients are functionals of the interaction potentials (fields), and the convergence (if any) of the series depends on the type of the interaction potential (field).

The partition function is

$$Z = \mathrm{Tr}\, \exp(-\beta H) \tag{5.24}$$

where $H = \sum_i (-\hbar^2/2m_i)\nabla_i^2 + \sum_{i<j} U(r_{ij})$ (5.25)

The WK expansion is obtained by considering the kinetic energy small compared with the potential energy, and the partition function for one particle in terms of this expansion becomes

$$\mathrm{Tr}\, \exp(-\beta H) = \lambda^{-3}\int d^3r\, \exp(-u)\Big[1 - \frac{\lambda^2}{12}(\nabla u)^2 + \frac{\lambda^4}{1440}\cdot((\nabla u)^2)^2$$

$$- 8(\nabla u)^2\, \nabla^2 u + 12(\nabla^2 u)^2 - \ldots\Big] \; , \tag{5.26}$$

where $\lambda = \hbar/(2mkT)^{1/2}$. It might appear from (5.26) that the partition function is an analytic function of λ^2. However, it need not be so for all interaction potentials and, for example, the coefficients of λ^6 and higher terms with $U(r)=g_0\exp(-r/r_0)$

are divergent. For the potentials for which the Mayer cluster integrals exist, the pressure can be expressed as a power series in the number density, v^{-1}, and is an analytic function of v^{-1}.

The second virial coefficient may be written as:

$$B = -\frac{(4\pi\lambda)^{3/2}}{2\,!}\left[\mathrm{Tr}\,\exp(-\beta(H_o+U)) - \mathrm{Tr}\,\exp(-\beta H_o)\right] \quad (5.27a)$$

$$\xrightarrow[\hbar\to 0]{} -\frac{1}{2!}\int d^3r(\exp(-u)-1) \quad , \quad (5.27b)$$

where $H_o = -(\hbar^2/2m^*)\nabla^2$. Using the resolvent formalism

$$\exp(-\beta H) = \frac{1}{2\pi i}\int_C \frac{dz\,\exp(-\beta H)}{z-H} \quad , \quad (5.28)$$

the expansion for B can also be obtained from a perturbation expansion of U as

$$B = -\frac{(4\pi\lambda^2)^{3/2}}{2!}\sum_{n=1}\frac{d^3p\,\exp(-\beta E_o)}{(2\pi\hbar)^3}\cdot\frac{1}{2\pi i}\int_C\frac{dz\,\exp(-\beta z)}{z}\,\cdot$$

$$\left\langle p\left|\left(\frac{1}{z-(H_o-E_o)}U\right)^n\right|p\right\rangle \quad , \quad (5.29)$$

where $E_o=p^2/2m^*$ and $|p\rangle$ are the eigenfunctions of H_o.

(5.29) is evaluated with the help of the ordered exponential method (41), and the nth order of B is found to be

$$B_n = -\frac{(\beta)^n}{2!}\int\frac{V^n d^3k_1\ldots d^3k_n}{(2\pi)^{3(n-1)}}\cdot\delta(\vec{k}_n-\vec{k}_1-\ldots-\vec{k}_{n-1})\,\cdot$$

$$U(k_1)\ldots U(k_n)S_n(\lambda k_1,\ldots,\lambda k_{n-1}) \quad , \quad (5.30)$$

where U(k) is the Fourier transform of the potential, and the S_n contain all the quantum mechanical diffraction effects. On evaluating B_n, the WK expansion of the second virial coefficient is found to be

$$B = \sum_n B_n = -\frac{1}{2}\int d^3r\left[(e^{-u}-1) - \frac{\chi^2}{12}(\nabla u)^2 e^{-u} + O(\chi^4) + \dots\right] \quad (5.31)$$

Here the expansion like (5.20) has been obtained from a perturbation expansion. The quantum mechanical corrections to higher virial coefficients can be discussed analogously.

B. Third Virial Coefficient

The third virial coefficient is related to the potential energy, U_{ij}, of a pair of molecules i and j separated by a distance r_{ij} by the equation

$$C = -\frac{8\pi^2 N^2}{3}\iiint f_{12}f_{13}f_{23}r_{12}r_{13}r_{23}dr_{12}dr_{13}dr_{23} \quad (5.32)$$

where $f_{ij} = \exp(-U_{ij}/kT) - 1$ (5.33)

In terms of the cluster integrals b_2 and b_3, C is given by

$$C = (4b_2{}^2 - 2b_3)N^2 \quad (5.34)$$

Potential Non-Additivity

If the three-body potential, $U(r_{12}, r_{23}, r_{31})$ is not pairwise additive then we assume it to be given by

$$U_{123} = \sum_{1,2,3} U_{ij} + u_{123} \quad (5.35)$$

where $u_{123} = \Delta U_3$ represents the specific three-body effect and is given by (2.21) or (3.31). The third cluster integral may be written as

$$\overline{b}_3 = b_3 + b_3^{(1)}, \quad (5.36)$$

where b_3 is used in (5.34) with $u_{123}=0$; and $b_3^{(1)}$, the contribution due to potential non-additivity, is given by

$$b_3^{(1)} = \frac{4\pi^2}{3}\iiint \exp\left(\frac{-\sum U_{ij}}{kT}\right)\left(\left(\exp\left(-\frac{u_{123}}{kT}\right)-1\right)\right)r_{12}r_{23}r_{31}dr_{12}dr_{23}dr_{31}, \quad (5.37)$$

the integration being over those r_{ij} which form a triangle.

The third virial coefficient with non-additive effects is

$$\bar{C} = C + C^{(1)} , \tag{5.38}$$

where C is given by (5.34) and

$$C^{(1)} = - 2N^2 b_3^{(1)} , \tag{5.39}$$

with $b_3^{(1)}$ given by (5.37). For the van der Waals potential with a hard core:

$$\begin{aligned} U_{ij} &= + \infty , \quad r_{ij} < r_o \\ &= - 4U_o (r_o/r_{ij})^6 , \quad r_{ij} > r_o \end{aligned} \tag{5.40}$$

and $$\exp\left(\frac{-\sum U_{ij}}{kT}\right) = 0 , \quad r_{ij} < r_o ,$$

one obtains

$$u_{123}/kT = 3(\alpha/r_o^{\ 3})(U_o/kT)(r_{12}r_{23}r_{31}/r_o^{\ 3})^{-3} G , \tag{5.41}$$

where $G = (3\cos\theta_1 \cos\theta_2 \cos\theta_3 + 1)$, and U_o is the potential minimum. In terms of reduced quantities, with r_{ij} changed into dimensionless variables, the non-additive correction upto the terms in $(T^*)^{-2}$ is:

$$C^{(1)*} = C^{(1)}/b_o^{\ 2} = \frac{18\alpha^*}{T^*} \iiint \left[\left(\left(1 + \frac{4}{T^*}(x^{-6} + y^{-6} + z^{-6})\right) \frac{G}{(xyz)^2} - \frac{3}{2}\left(\frac{\alpha^*}{T^*}\right) \frac{G^2}{(xyz)^5} \right] dxdydz \tag{5.42}$$

The integrations in (5.40) are elementary and can be reduced to forms which are evaluated (42) numerically.

The non-additive correction to C may also be obtained by expanding b_3 into a Taylor series about h=0, h being the measure of potential non-additivity.

$$b_3 = (b_3)_{h=o} + h(b_3')_{h=o} + \ldots\ldots , \tag{5.43}$$

where in b_3, U_{123} is pairwise additive, and prime denotes partial derivative with respect to h.

$$(b_3')_{h=o} = -\frac{4\pi^2}{3kT}\iiint \exp\left(\frac{-\sum U_{ij}}{kT}\right).G.(r_{12}r_{23}r_{31})^{-3}dr_{12}dr_{23}dr_{31} \tag{5.44}$$

For the Lennard-Jones potential, $fr^{-12}-gr^{-6}$, one obtains:

$$(b_3')_{h=o} = -\frac{1}{kT}\left(\frac{kT}{f}\right)^{1/4}\sum_{p=o}^{\infty} M_p y^p \tag{5.45}$$

where

$$M_p = \frac{\pi^2}{3}\frac{1}{p!}\Gamma\left(\frac{2p+1}{4}\right)\int_o^1\int_{1-t}^1 \langle 6\rangle^p \langle 12\rangle^{-(2t+1)/4} . \frac{G}{s^2t^2}dsdt \tag{5.46}$$

and $y = \left(\frac{g}{kT}\right)\left(\frac{kT}{f}\right)^{1/2}$

Instead of $b_3^{(1)}$, the correction $(b_3')_{h=o}$ may be substituted in (5.39) in order to obtain the specific three-body interaction contribution to C for the Lennard-Jones (12, 6) potential. The theoretical curves for C, corrected for the non-additive effect, compare favorably with measured values and point to the reality of three-body forces in the equation of state of gases.

Low and High Temperature Expressions of C

C can be written in the form

$$C/b_o^2 = -6\int_o^{\infty}\int_o^{\infty}\int_{|r_{12}-r_{13}|}^{(r_{12}+r_{13})} f_{12}f_{13}f_{23}r_{12}r_{13}r_{23}dr_{12}dr_{13}dr_{23} \tag{5.47}$$

where $f_{ij} = \exp(-xr^{-n}+2xr^{-n/2})-1$, $x = U_o/kT$,

$$b_o^2 = (4/9)\pi^2N^2r_o^6 \tag{5.48}$$

The integration is over that part of the positive octant of r_{ij} space which lies between the planes $r_{12}=r_{13}+r_{23}$, $r_{13}=r_{12}+r_{23}$, and $r_{23}=r_{12}+r_{23}$. Writing (5.47) as

$$\int_o^{\infty}\int_o^{\infty}\int_o^{\infty} - \frac{3}{2}\int_o^{\infty}\int_o^{\infty}\int_o^{|r_{12}-r_{13}|} , \tag{5.49}$$

the integrations give

$$\left(\int_0^\infty f(r)dr\right)^3 = x^{6n}\left(I_{2/n}^{n}(x)\right)^3 , \quad (5.50)$$

$$-\frac{3}{2}\int_0^\infty\int_0^\infty\int_0^{|r_{12}-r_{13}|} f_{12}f_{13}(-1)r_{12}r_{13}r_{23}dr_{12}dr_{13}dr_{23}$$

$$= -\frac{3}{2}x^{6/n}\left[(I_{2/n}^{n}(x)(I_{4/n}^{n}(x)) - (I_{3/n}^{n}(x))^2\right] , \quad (5.51)$$

with $f_{23} = (-1)+(1+f_{23})$, the remaining part of the integral being

$$-3\int_0^\infty\int_0^{r_{12}}\int_0^{(r_{12}-r_{13})} f_{12}f_{13}(1+f_{23})r_{12}r_{13}r_{23}dr_{12}dr_{13}dr_{23} \quad (5.52)$$

$I_p^{\,n}$ satisfies the confluent hypergeometric equation

$$xd^2I_p^{\,n}/dx^2 + \left(\frac{1}{2} - x\right)dI_p^{\,n}/dx + pI_p^{\,n} = 0 , \quad (5.53)$$

and in the asymptotic limit

$$nI_p^{\,n}(x) = 2\pi^{1/2}\,x^{-1/2-p}\,e^x\sum_{j=o}\frac{(p+1+j)!(p+\frac{1}{2}+j)!x^{-j}}{(p+1)!(p+\frac{1}{2})!\;j!} \quad (5.54)$$

The asymptotic limit of C at low temperatures is given by

$$2^{-12/n}\,C/b_o^{\,2} = -\,6x^{6/n}\left(I_{2/n}^{n}(x)\right)^3 \quad (5.55)$$

At high temperatures C is proportional to $(kT)^{-6/n}$ and is independent of the index m of a Lennard-Jones (n,m) potential. On calculating the contribution of the integrals (5.51) and (5.52), C for $(n,\frac{1}{2}n)$ potential is given by

$$C = c_o\,b_o^{\,2}\,2^{12/n}\,x^{6/n} , \quad (5.56)$$

where $$c_o = \frac{5}{8}\left(1 + \frac{6\gamma}{n} + O\left(\frac{1}{n^2}\right)\right) , \quad (5.57)$$

being Euler's constant.

The application of disperaion relations to connect the low and high temperature behavior of virial coefficients will be discussed elsewhere.

C. Ordered Exponential and Virial Coefficients

Let H_o be the Hamiltonian of the unperturbed syatem, and let U be the interaction potential. In the interaction representation

$$U(s) = \exp(sH_o)U\exp(-sH_o) \tag{5.58}$$

U may be divided into arbitrary parts,

$$U = \sum_a U_a \tag{5.59}$$

In terms of the ordered exponential (41), we have:

$$\exp(-\beta(H_o+U)) = \exp(-\beta H_o)\exp_P\left(-\int_0^\beta U(s)ds\right), \tag{5.60}$$

and
$$\exp_P\left(-\int_0^\beta U(s)ds\right) = \left(\exp\left(-\sum_a \int_0^\beta U_a(s)ds\right)\right)_P, \tag{5.61}$$

where $(\ )_P$ denotes chronological ordering. The right side of (5.61) may be written as

$$\left(\exp\left(-\sum_a \int_0^\beta U_a(s)ds\right)\right)_P = \left(\prod_a(1+f_a)\right)_P \tag{5.62}$$

where
$$f_a = \exp\left(-\int_0^\beta U_a(s)ds\right) - 1 \tag{5.63}$$

(5.61) with (5.62) may be developed as a Mayer expansion:

$$\exp_P\left(-\int_0^\beta U(s)ds\right) = \left(1 + \sum_a f_a + \sum_{a<b} f_a f_b + \sum_{a<b<c} f_a f_b f_c + \dots\right)_P$$

$$= 1 + \sum_a (f_a)_P + \sum_{a<b}(f_a f_b)_P + \sum_{a<b<c}(f_a f_b f_c)_P + \dots \tag{5.64}$$

(5.64) gives the ordered exponential expansion of U(s), and with (5.60) and (5.62) one obtains:

$$\exp(-\beta(H_o+U)) = \exp(-\beta H_o) + \sum_a \Big[\exp(-\beta(H_o+U_a)) - \exp(-\beta H_o)$$

$$+ \sum_{a<b} \exp(-\beta(H_o+U_a+U_b)) - \exp(-\beta(H_o+U_a))$$

$$- \exp(-\beta(H_o+U_b)) + \exp(-\beta H_o)\Big] + \ldots\ldots \qquad (5.65)$$

Consider a gas of N identical molecules for which

$$H_o = \sum_{i=1}^{N} K_i = \sum_i (\hbar^2/2m)\nabla_i \cdot \nabla_i \qquad (5.66)$$

and the interaction potential is given by

$$U = \sum_{i<j} U_{ij}^{(2)} + \sum_{i<j<k} U_{ijk}^{(3)} + \ldots\ldots \qquad (5.67)$$

where $U_{ij}^{(2)}$ is the two-body potential, $U_{ijk}^{(3)}$ the three-body potential, etc. (5.66) and (5.67) are used in (5.65) and the series is arranged as a sum of no-interaction terms, two-particle interactions, three-particle interactions, etc.

$$\exp(-\beta(H_o+U)) = \prod_{h=1}^{N} S^{(1)}(h) + \sum_{i<j} S^{(2)}(ij) \prod_{h\neq i,j} S^{(1)}(h) +$$

$$\sum_{(i<j)\neq(k<l)} S^{(2)}(ij) S^{(2)}(kl) \prod_{h\neq i,j,k,l} S^{(1)}(h) + \ldots\ldots$$

$$\sum_{i<j<k} S^{(3)}(ijk) \prod_{h\neq i,j,k} S^{(1)}(h) + \ldots\ldots + \ldots\ldots , \qquad (5.68)$$

where $S^{(2)}(ij)$ denotes double collision between ith and jth molecules, $S^{(3)}(ijk)$ denotes triple collision, and so on.

The free energy, A, is given by the relation

$$\exp(-\beta A) = \mathrm{Tr}\Big[\exp(-\beta(H_o+U))\, \delta_{q,\pm}^{(N)}\Big]/N! \quad , \qquad (5.69)$$

where $\delta_{q,\pm}^{(N)}$ is the determinant of N δ-functions according to BE(+) or FD(-) statistics. The expansions for S, $\delta_q^{(N)}$, are obtained by Ursell's method, and one finds

$$\exp(-\beta A) = \frac{V^N}{N!q^N}\Big[1 + \sum_{i<j}\frac{q^2}{V^2}H^{(2)}(ij) +$$

$$\sum_{(i<j)\neq(k<l)}\frac{q^4}{V^4}\,\mathrm{Tr}\,H^{(2)}(ij)H^{(2)}(kl) + \dots +$$

$$\sum_{i<j<k}\frac{q^3}{V^3}\,\mathrm{Tr}\,H^{(3)}(ijk)+\dots+\sum_{i<j<k<l}\frac{q^4}{V^4}\,\mathrm{Tr}\,H^{(4)}(ijkl) + \dots\Big], \tag{5.70}$$

where $q=\lambda^3$, and H are Ursell functions determined by the combinations of S and δ. The cluster integrals are given by

$$b_n = (q^n/n!V)\,\mathrm{Tr}\,H^{(n)}(12\dots n) , \tag{5.71}$$

and the virial coefficients are

$$B = -b_2 , \; C = 4B^2 - 2b_3 , \quad D = 12BC - 12B^3 - 3b_4 , \text{ etc.} \tag{5.72}$$

The coefficients in the Wigner-Kirkwood expansion formulas (like 5.20), that is the diffraction corrections, for B and C are given by

$$B_o = -\frac{1}{2}\int d^3\mathbf{r}(e^{-u}-1) ; \quad B_1 = \frac{\beta^2}{12}\cdot\frac{1}{2}\int d^3\mathbf{r}\; e^{-u}(KUU) , \tag{5.73}$$

$$B_2 = \frac{\beta^2}{120}\cdot\frac{1}{2}\int d^3r\; e^{-u}\Big[(KU(LU)) + \frac{\beta}{3}(KU(KUU)) - \frac{5\beta^2}{12}(KUU)^2\Big],$$

etc., where $u=\beta U$, $U = U^{(2)}(r)$, and the operators K and L are such that

$$(KFG) = \nabla_r F \cdot \nabla_r G , \quad (LF) = \nabla_{\mathbf{r}}\cdot\nabla_r F , \tag{5.74}$$

F and G being arbitrary functions.

$$C_o = 4B_o^2 - 2VB_o - \frac{1}{3}\iint d^3r_1 d^3r_2(e^{-u}-1) ,$$

$$C_1 = 8B_1B_o - 2VB_1 + \frac{\beta^3}{12}\,\frac{1}{3}\iint d^3r_1 d^3r_2\; e^{-u}(KUU) ,$$

$$C_2 = 4(2B_2B_o + B_1^2) - 2VB_2 + \frac{\beta^2}{120} \cdot \frac{1}{3}\iint d^3r_1 d^3r_2 \cdot$$

$$e^{-u}\left[(KU(LU)) + \frac{\beta}{3}(KU(KUU)) - \frac{5\beta^2}{12}(KUU)^2\right], \qquad (5.75)$$

etc., where r_1 and r_2 are relative coordinates, $u = \beta U$, and

$$U = U^{(2)}(\vec{r}_1) + U^{(2)}(\vec{r}_2) + U^{(2)}(\vec{r}_1 - \vec{r}_2) + U^{(3)}(\vec{r}_1, \vec{r}_2) \qquad (5.76)$$

$$(KFG) = \nabla_{r_1}F \cdot \nabla_{r_1}G + \nabla_{r_2}F \cdot \nabla_{r_2}G + \frac{1}{2}(\nabla_{r_1}F \cdot \nabla_{r_2}G + \nabla_{r_2}F \cdot \nabla_{r_1}G)$$

$$(LF) = \nabla_{r_1} \cdot \nabla_{r_1}F + \nabla_{r_2} \cdot \nabla_{r_2}F + \nabla_{r_1} \cdot \nabla_{r_2}F$$

These analogies can be extended to higher virial coefficients.

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NOTE : This article is based on another rather comprehensive account of London-van der Waals forces (between neutral atoms and between macroscopic bodies) and certain features of the equation of state of gases. Some of the problems treated here briefly will be discussed in greater detail elsewhere.

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