Statistical Theory of Low Frequency Intermolecular Forces

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The sum of states of a gas consisting of optically aniso-tropic polar molecules is shown to be substantially equal to the classical Gibbs phase integral at ordinary tempera-tures. A general method of obtaining the quantum cor-rection to be applied at low temperatures is developed. The intermolecular potential energy appearing in the phase integral is semi-classical in form. The low frequency contribution arising from the permanent dipole moments of the molecules is exactly equal to their mutual electro-static energy. The high frequency contribution is given by a modification of London's formula in which continuous functions of the molecular orientations occur instead of spatial quantum numbers.

I.

EXPERIMENTAL evidence seems to sup-port the conclusion that the permanent dipole interaction makes an important contribu-tion to the van der Waals force between polar molecules. For example, the common properties of simple polar substances, such as their higher boiling points and greater tendency for aggrega-tion, give indication of greater cohesive forces than in simple nonpolar substances. Further, a study of the equation of state shows that the virial coefficients of polar gases are much more sensitive to temperature variation than those of nonpolar gases.

In the older theories of van der Waals forces,[1] the rôle of permanent dipoles was comparatively easy to treat. However, in the quantum me-chanical theory,[2] several difficulties are en-countered. Thus an unambiguous application of perturbation theory is complicated by unsharp degeneracy, arising from the close spacing of the rotational energy levels of the molecules. Fur-ther, it seems questionable to treat the approach of the molecules as adiabatic. From the observed specific heats of polyatomic molecules at ordinary temperatures, it is known that there is equi-partition of energy between the rotational and translational degrees of freedom. This fact

suggests the occurrence of many inelastic colli-sions involving the interchange of energy be-tween the rotational and translational motion of the molecules. It is likely that the low fre-quency quantization of two interacting polar molecules is very complicated and does not bear any simple relation to the rotational and trans-lational quantization of two independent mole-cules.

In the present article no attempt is made to analyze the intermolecular energy states in detail. Instead, the sum of states is calculated directly with the aid of the principle of spectroscopic stability, which permits a calculation of the diagonal sum of a matrix without reference to the actual mode of quantization. If one is interested only in the equilibrium properties of the system, the sum of states furnishes all the information that is required. The general ap-proach to the present problem has many points in common with Van Vleck's treatment of the electric susceptibility of polar molecules. The method developed here may be applied equally well to the latter problem.[3]

Margenau[4] has already shown that the second virial coefficient of a gas consisting of rigid polar molecules without axial spin is closely approximated by the classical expression. The correctness of his conclusion depends upon implicit use of the invariance of the diagonal sum and not upon the type of rotational quanti-

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[1] P. Debye, Phys. Zeits. **22**, 178 (1921); W. H. Keesom, Phys. Zeits. **22**, 129, 643 (1921); H. Falkenhagen, Phys. Zeits. **23**, 87 (1922).

[2] F. London, Zeits. f. Physik **63**, 245 (1930).

[3] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Cambridge University Press (1932).

[4] H. Margenau, Zeits. f. Physik **64**, 584 (1930).

zation which he assumes. The present method seems to have certain advantages over that of Margenau. The calculations are made simpler by the use of integrals in momentum space instead of discrete sums over rotational quantum numbers. Further, a general method of obtaining the quantum correction to be applied to the classical result is provided. It is found that Margenau's estimate of the first quantum correction was about fifty percent too high.

II.

In a recent article, using methods developed by v. Neumann, Wigner and Bloch,[5] we have shown how the sum of states of a gas, consisting of point masses surrounded by conservative fields of force, could be transformed into a phase integral and finally evaluated by expansion in powers of Planck's constant. In the present article, we wish to fix our attention on the relation of the intermolecular force field to the structure and internal motion of the molecules. Therefore, for simplicity, we confine ourselves to a calculation of the sum of states of a single pair of molecules. The sum of states of the entire gas may be constructed to a sufficient degree of approximation for the calculation of the second virial coefficient from those of individual pairs. Further, we neglect corrections introduced by the Bose-Einstein or the Fermi-Dirac statistics, included in the previous article. These have been shown by Uhlenbeck and Gropper[6] to be extremely small even at quite low temperatures.

We take for consideration a pair of molecules confined in a vessel of volume v at the temperature T. The first step in the construction of the sum of states of the pair consists in an analysis of the motion to determine the allowed energy states. For the present purposes, it is convenient to speak of two types of motion, the high frequency type and the low frequency type. For the high frequency type, it is assumed that the energy differences $E_n' - E_n$ between excited states n' and the ground state n are very large relative to kT, while for the low frequency type

it is supposed that the energy difference $E_j' - E_j$ between any two neighboring states j' and j is small relative to kT. Further in order that the methods of perturbation theory may be used, it is assumed that the intermolecular perturbation energy is small relative to the high frequency term differences $E_n' - E_n$. This restriction is unnecessary in the case of the low frequency term differences $E_j' - E_j$. At ordinary temperatures the internal motion of the electrons and the vibrational motion of the nuclei in the individual molecules are of the high frequency type. The rotational and translational motion of the molecules belong, on the other hand, to the low frequency type.[7]

The positions of the electrons and nuclei in each molecule of the pair under consideration may be referred to a coordinate system fixed in that molecule with origin at the mean position of its center of gravity. The ensemble of these coordinates will be denoted by x, and the Hamiltonian operator associated with the unperturbed electronic and nuclear motion in both molecules by $H(x)$. Additional coordinates are required to specify the orientations of the molecular coordinate systems, the relative position of the centers of gravity of the two molecules and that of their common center of gravity with respect to a reference system fixed in space. Since the motion of the common center of gravity of the pair cannot be influenced by the intermolecular forces, we ignore it in the present calculations. The coordinates specifying the orientations and the relative position of the centers of gravity of the molecules may be denoted by q, and the kinetic energy operator associated with their free rotation and translation by $H^0(q)$. The intermolecular potential energy will be a function both of the coordinates

[5] J. v. Neumann, Gött. Nachr. p. 273 (1927); F. Bloch, Zeits. f. Physik **74**, 295 (1932); E. Wigner, Phys. Rev. **40**, 749 (1932); J. G. Kirkwood, Phys. Rev. **44**, 31 (1933).

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

[7] We treat here only chemically saturated molecules, the ground states of which are singlet Σ-states. If spin multiplets are allowed, the problem is complicated by a splitting of the intermolecular energy levels. In the case of soft molecules, the energy spacing of vibrational states may not be large relative to kT. However, since the dispersion f values associated with vibrational frequencies are usually small, one may assume that their contribution to the van der Waals force is negligible. Thus temperature excitation of vibrational states, while it would influence the internal specific heat, can reasonably be expected to have little influence on the intermolecular energy.

x and the coordinates q and may be represented by $V(x, q)$. An approximate solution of the dynamical problem may be obtained by treating the low frequency rotation and translation of the molecules in much the same way that the nuclear motion in a polyatomic molecule is treated. One assumes the coordinates q to be fixed and solves the following Schrödinger equation

$$[H(x) + V(x, q) - E]\psi = 0. \tag{1}$$

Suppose that the wave functions and energy levels for the unperturbed internal motion are ψ_n^0 and E_n^0, where n symbolizes the electronic and vibrational quantum numbers of both molecules. The application of perturbation theory then gives:

$$E_n(q) = E_n^0 + V_n(q),$$

$$V_n(q) = V_{nn} - \sum'_{n'} \frac{|V_{n'n}|^2}{E_{n'}^0 - E_n^0} + \cdots, \tag{2}$$

$$V_{n'n} = \int \psi_{n'}^{0*} V(x, q) \psi_n^0 dx.$$

For every value of the high frequency quantum number n, sub-energy levels and wave functions associated with molecular rotation and translation are determined by the equation:

$$\{H^0(q) + V_n(q) - E_{nj}\}\Phi_j = 0, \tag{3}$$

where j symbolizes all rotational and translational quantum numbers. The total energy of the system is then $E_n^0 + E_{nj}$ and the sum of states may be written:

$$\sigma = \sum_{n', j} e^{-\beta(E_{n'}^0 + E_{n'j})}, \tag{4}$$

where β is equal to $1/kT$.

However, if, as we have postulated, the energy difference $E_{n'}^0 - E_n^0$ between an excited state n' and the ground state n is always large relative to kT, the contribution of excited electronic and vibrational states to σ will be negligible compared with that of the ground state. Thus the sum of states will be very closely approximated by

$$\sigma = e^{-\beta E_n^0} \sum_j e^{-\beta E_{nj}}. \tag{5}$$

Since the factor $e^{-\beta E_n^0}$ can contribute only pure heat terms to the free energy function, it does not influence the equation of state and we need concern ourselves only with the factor

$$\sigma_n = \sum_j e^{-\beta E_{nj}}. \tag{6}$$

III.

Let us suppose that the motion of a dynamical system of M degrees of freedom is described in terms of $2M$ canonically conjugate momentum coordinates p and configuration coordinates q. We may assume that the wave functions $\Phi_j(q)$ form a complete normal orthogonal set in a restricted portion Ω of the entire configuration space Ω_0, generated by allowing all of the q's to range from $-\infty$ to $+\infty$. Outside of Ω, we define Φ_j to be zero. It has been shown[5] that the sum of states is identical with the diagonal sum of the matrix $[e^{-\beta H}]$ where H is the Hamiltonian operator.

$$\sigma = \sum_i [e^{-\beta H}]_{ii} = \sum_i \int_{-\infty}^{+\infty} \Delta_0(q) \Phi_i^*(q) e^{-\beta H} \Phi_i(q) dq, \tag{7}$$

$$dq = \prod_{k=1}^{M} dq_k.$$

Here $\Delta_0(q)$ is the transformation determinant of the q's. Because of the invariance of the diagonal sum, not only the characteristic functions Φ_j of the operator H, but any other convenient set of orthogonal functions may be used to evaluate σ. For this purpose we choose the following orthogonal set with continuous characteristic values p.

$$U_p(q) = \Delta_0(q)^{-\frac{1}{2}} e^{i\mathbf{p}\cdot\mathbf{q}/h}, \qquad \mathbf{p} = \sum_{k=1}^{M} p_k \mathbf{s}_k; \qquad \mathbf{p}\cdot\mathbf{q} = \sum_{k=1}^{M} p_k q_k; \qquad \mathbf{q} = \sum_{k=1}^{M} q_k \mathbf{s}_k, \tag{8}$$

where the s_k are M mutually orthogonal unit vectors. In the region Ω, $U_p(q)$ may be expanded in terms of the functions Φ_j

$$\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h} = \sum_j F_j(p)\Phi_j(q), \quad (a) \qquad F_j(p) = \int_{-\infty}^{+\infty} \Delta_0(q')^{\frac{1}{2}}\Phi_j{}^*(q')e^{i\mathbf{p}\cdot\mathbf{q}'/h}dq'. \quad (b) \tag{9}$$

The Fourier integral (9b) may be inverted to give

$$\Phi_j(q) = (2\pi h)^{-M}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\Delta_0(q')^{\frac{1}{2}}\Phi_j(q')\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot(\mathbf{q}-\mathbf{q}')}dq'dp, \qquad dp = \prod_{k=1}^{M}dpk. \tag{10}$$

When relation (10) is substituted in the integral (7), one obtains

$$\sigma = (2\pi h)^{-M}\int_{-\infty}^{+\infty}\int\int\left[\sum_j\Phi_j{}^*(q)\Phi_j(q')\right]\Delta_0(q)\Delta_0(q')^{\frac{1}{2}}e^{-i\mathbf{pq}'}e^{-\beta H}\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h}dpdq'dq. \tag{11}$$

The summation over the quantum numbers j may be carried out by means of the completeness relation

$$\sum_j\Delta_0(q)\Phi_j{}^*(q)\Phi_j(q') = \prod_{k=1}^{M}\delta(q_k-q_k') \qquad \text{when } q \text{ lies in } \Omega$$

$$= 0 \quad \text{otherwise} \tag{12}$$

$$\delta(q-q') = \delta(q'-q)$$

where $\delta(q'-q)$ is the Dirac delta-function. When Eq. (12) is introduced into the integral (11) and the integration over q' is carried out, there results

$$\sigma = (2\pi h)^{-M}\int_{-\infty}^{+\infty}\int_{\Omega}\{\Delta_0(q)^{\frac{1}{2}}e^{-i\mathbf{p}\cdot\mathbf{q}/h}e^{-\beta H}\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h}\}dpdq. \tag{13}$$

The procedure which has been followed in obtaining Eq. (13) is a generalization of the usual treatment of Fourier integral transformations in a finite one dimensional interval.[8] Because of singularities in the derivatives and possible vanishing of the transformation determinant on the boundary of the region Ω, convergence questions may arise. However, in the present problem, they do not appear to give difficulty.

Before Eq. (13) may be used to evaluate the sum of states, σ_n, of the pair of molecules considered in the previous section, a more complete specification of the low frequency coordinates q is required. For simplicity the molecules are assumed to be symmetrical rotators with no axial spin. The orientations of their respective axes of symmetry relative to a reference system fixed in space may be described by spherical coordinates ϑ_1, φ_1 and ϑ_2, φ_2. The relative coordinates of the molecular centers of gravity may be denoted by x, y, z, with the Laplacian operator Δ. The Hamiltonian operator is given by

$$H = -h^2\{(1/2m)\Delta + \sum_{k=1}^{2}(1/2J_k)L_k{}^2\} + V_n(q), \qquad L_k = s_{\vartheta_k}\frac{\partial}{\partial\vartheta_k} + \frac{s_{\varphi_k}}{\sin\vartheta_k}\frac{\partial}{\partial\varphi_k}, \tag{14a}$$

$$L_k{}^2 = \frac{1}{\sin\vartheta_k}\frac{\partial}{\partial\vartheta_k}\left(\sin\vartheta_k\frac{\partial}{\partial\vartheta_k}\right) + \frac{1}{\sin^2\vartheta_k}\frac{\partial^2}{\partial\varphi_k{}^2},$$

[8] See for example N. Wiener, *Generalized Harmonic Analysis* (8), Acta Mathematica 55 (1930).

where h is Planck's constant divided by 2π, m is the reduced mass of the pair, J_1 and J_2 the moments of inertia of the respective molecules and s_ϑ and s_φ are unit vectors. The transformation determinant is

$$\Delta_0(q) = \sin \vartheta_1 \sin \vartheta_2 \tag{14b}$$

and the region Ω is given by

$$\Omega \begin{cases} -\infty \leq x, y, z \leq +\infty \\ 0 \leq \vartheta_1, \vartheta_2 \leq \pi \\ 0 \leq \varphi_1, \varphi_2 \leq 2\pi. \end{cases} \tag{14c}$$

The sum of states σ_n of the pair of molecules is given by Eq. (13), when H, $\Delta_0(q)$ and Ω are taken from Eqs. (14a), (14b) and (14c).

The evaluation of the integral on the right-hand side of Eq. (13) depends upon a determination of the following functions,

$$w = e^{-\beta H}\Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h}, \tag{15}$$

which satisfy the Bloch equation

$$Hw + \partial w/\partial\beta = 0; \qquad \lim_{\beta=0} w = \Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h}. \tag{16}$$

In order to obtain an approximate solution of this equation we let

$$w = \Delta_0(q)^{-\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{q}/h}e^{-\beta(T+V_n)}g, \tag{17}$$

where T is the classical kinetic energy

$$T = \mathbf{p}_0^2/2m + \sum_{k=1}^{2} \frac{1}{2J_k}\left[p_{\vartheta k}^2 + \frac{p_{\varphi k}^2}{\sin^2 \vartheta_k}\right], \qquad p_0 = p_x s_x + p_y s_y + p_z s_z. \tag{18}$$

Substitution of (18) into the differential Eq. (16) and transformation into an integral equation with the aid of the boundary condition for $\beta = 0$, gives

$$g = 1 + ih\int_0^\beta e^{E\xi}K_1(ge^{-E\xi})d\xi + h^2\int_0^\beta e^{E\xi}K_2(ge^{-E\xi})d\xi, \tag{19}$$

$$E = T + V_n,$$

$$K_1 = -\frac{1}{m}\mathbf{p}_0\cdot\Delta + \sum_{k=1}^{2} \mathbf{p}_k'\cdot L_k/J_k$$

$$K_2 = \frac{1}{2m}\Delta + \sum_{k=1}^{2} \frac{1}{2J_k}\left[L_k^2 - \cot \vartheta_k \frac{\partial}{\partial\vartheta_k} + \frac{1+cs\,c^2\vartheta_k}{4}\right],$$

$$\mathbf{p}_k' = p_{\vartheta k}s_{\vartheta k} + p_{\varphi k}s_{\varphi k}/\sin \vartheta_k.$$

Solution by successive approximations gives

$$g = \sum_{l=0}^{\infty} g_l h^l, \qquad g_0 = 1, \qquad g_1 = i\int_0^\beta e^{E\xi}K_1(e^{-E\xi})d\xi, \tag{20}$$

$$g_l = \int_0^\beta e^{E\xi}\{K_1(e^{-E\xi}g_{l-1}) + K_2(e^{-E\xi}g_{l-2})\}d\xi.$$

The chief difference between Eq. (19) and a similar equation for translational motion alone, which

was obtained in a previous article, lies in the fact that the kinetic energy T is a function of the coordinates and therefore is not a characteristic value of the kinetic energy operator.

The first three terms of the series (20) may be calculated without a great amount of labor. When they are inserted in Eqs. (18) and (15) and the indicated momentum integrations are carried out, the term proportional to h vanishes and one obtains

$$\sigma_n = \left(\frac{m}{2\pi\beta h^2}\right)^{\frac{3}{2}} \frac{J_1 J_2}{(2\pi\beta h^2)^2} \int_v \int_0^{2\pi} \cdots \int_0^{\pi} e^{-\beta V_n}\left[1+\sum_{k=1}^{2}\frac{\beta h^2}{6J_k}+\chi(V_n)+\cdots\right] \sin\vartheta_1 \sin\vartheta_2 d\vartheta_1 d\vartheta_2 d\varphi_1 d\varphi_2 dx dy dz,$$

$$\chi = -\frac{\beta^2 h^2}{12}\left\{\sum_{k=1}^{2}\frac{1}{J_k}\left[L_k^2(V_n)-\frac{\beta}{2}(L_k(V_n))^2\right]+\frac{1}{m}\left[\Delta V_n-\frac{\beta}{2}(\nabla V_n)^2\right]\right\}. \tag{21}$$

To this approximation the quantum corrections for the rotational and translational parts of the motion are additive. It should perhaps be mentioned here that the integration over the relative coordinates is effectively limited to the volume of the containing vessel v, by replacing the walls by high potential barriers which cause $e^{-\beta V}$ to vanish. The kinetic part of the sum of states for free rotation and translation may be written

$$\sigma_p = \left(\frac{m}{2\pi\beta h^2}\right)^{\frac{3}{2}} \prod_{k=1}^{2}\frac{2J_k}{\beta h^2}\left(1+\frac{\beta h^2}{6J_k}+\cdots\right). \tag{22}$$

If we let $\sigma_n = \sigma_p \sigma_q$ and neglect terms of the order h^4, we find

$$\sigma_q = \frac{1}{16\pi^2}\int_v \int_0^{2\pi} \cdots \int_0^{\pi} e^{-\beta V_n}[1+\chi(V_n)] \sin\vartheta_1 \sin\vartheta_2 d\vartheta_1 \cdots d\varphi_2 dv. \tag{23}$$

The factor σ_p makes a contribution to the heat content but not to the pressure of the system. If the gas is made up of identical molecules and the equation of state is written in the virial form

$$pv/RT = 1+(B/v)+\cdots, \tag{24}$$

where p is the pressure and R is the gas constant per mol, one can show by the usual arguments that

$$B = \frac{N}{32\pi^2}\int_v \int_0^{2\pi} \cdots \int_0^{\pi} [1-e^{-\beta V_n}(1+\chi(V_n))] \sin\vartheta_1 \sin\vartheta_2 d\vartheta_1 \cdots d\varphi_2 dv, \tag{24a}$$

where N is Avogadro's number. If the quantum correction is small, as it usually is except at very low temperatures, Eq. (24) reduces effectively to the familiar classical expression for the second virial coefficient, containing the intermolecular potential V_n from Eq. (2).

IV.

We now return to a more detailed discussion of the intermolecular potential V_n given by Eq. (2). Let us suppose that ψ_n^0 and ψ_k^0 are the unperturbed high frequency wave functions of the two molecules, referred to their respective principal axes. For fixed orientations of the molecular axes and fixed positions of their centers of gravity, the unperturbed wave function of the system with neglect of exchange degeneracy is $\psi_n^0\psi_k^0$. Properly, one should build up the wave function by linear combination of the products of the individual electron wave functions of the two molecules. Partially to remedy this defect we assume that a short range repulsive potential, arising from electron exchange and interpenetration, may be added to the van der Waals potential V_{nk} calculated with

the aid of the product wave function $\psi_n{}^0\psi_k{}^0$ and we concern ourselves here only with this latter part.

The mutual electrostatic energy of the two molecules may be expanded in spherical harmonics. We assume that the molecules are neutral and that the electric center and mass center of each coincide. If R is the length and $\mathbf{s}$ is a unit vector parallel to the line joining the centers of gravity of the molecules, one obtains, neglecting multipoles of higher order than the dipole

$$V(x, q) = 1/R^3[\mu_1 \cdot \mu_2 - 3(\mu_1 \cdot \mathbf{s})(\mu_2 \cdot \mathbf{s})], \quad (25)$$

where μ_1 and μ_2 are the electric moments of the molecules. Suppose that $\gamma_1{}^{(l)}$ and $\gamma_2{}^{(r)}$ are unit vectors in the direction of the principal optical axes and $\mu_1{}^{(l)}$ and $\mu_2{}^{(r)}$ are the components of the electric moments of the respective molecules along these axes. Then from Eqs. (2) and (25), one may write

$$V_{nk}(q) = \sum_{\substack{l, r \\ =1}}^{3} V_{nk}{}^{(lr)}$$

$$V_{nk}{}^{(lr)} = \frac{\mu_{nn}{}^{(l)}\mu_{kk}{}^{(r)}}{R^3}F_{lr}(s) - \frac{1}{R^6}\left\{ \frac{\alpha_n{}^{(l)}\mu_{kk}{}^{(r)2} + \alpha_k{}^{(r)}\mu_{nn}{}^{(l)2}}{2} + \sum_{\substack{n' \neq n \\ k' \neq k}} \frac{|\mu_{n'n}{}^{(l)}|^2|\mu_{k'k}{}^{(r)}|^2}{(E_{n'}{}^0 + E_{k'}{}^0) - (E_n{}^0 + E_k{}^0)} \right\}F_{lr}(s)^2, \quad (26)$$

$$F_{lr}(s) = \gamma_1{}^{(l)} \cdot \gamma_2{}^{(r)} - 3(\gamma_1{}^{(l)} \cdot \mathbf{s})(\gamma_2{}^{(r)} \cdot \mathbf{s}).$$

Since the diagonal matrix elements μ_{nn} and μ_{kk} are merely the average values of the dipole moments, the first term of Eq. (26) is the mutual electrostatic energy of the permanent electric moments of the two molecules. The second term, arising from states $(n'k)$ and (nk'), corresponds to an interaction of the low frequencies of the one molecule with the high frequencies of the other. For these terms the summations in Eq. (2) may be carried out to give one-half the electrostatic polarizabilities $\alpha_n{}^{(l)}$ and $\alpha_k{}^{(r)}$ of the ground states of the respective molecules. Since we have chosen the principal axes, the polarizability tensor of each molecule is diagonal. The third part of Eq. (26) involves only the high frequency terms $(n'k')$. For molecules without permanent dipoles, Eq. (26), when averaged over molecular orientations by means of the formula

$$\overline{F_{lr}{}^2(s)} = 2/3 \quad (27)$$

reduces to London's formula for the van der Waals energy, averaged over all values of the space quantum numbers.

The usefulness of the semiclassical potential (26) in statistical calculations depends upon whether the quantum correction $\chi(V)$ which must be applied to the sum of states, Eqs. (21) and (23), is small. To obtain an estimate of the quantum correction, we consider two identical diatomic molecules with permanent dipole moments μ directed along their respective axes of symmetry. The first term of Eq. (26) becomes in this case

$$V = (\mu^2/R^3)[\gamma_1 \cdot \gamma_2 - 3(\gamma_1 \cdot s)(\gamma_2 \cdot s)], \quad (28)$$

where γ_1 and γ_2 are unit vectors in the direction of the symmetry axes. The remaining terms may be expressed as functions of γ_1, γ_2, $\mathbf{s}$ by means of the following relations, which may be easily verified from the orthogonality conditions for direction cosines.

$$\sum_{l=1}^{3} F_{lr}(s)^2 = 1 + 3(\gamma_2{}^{(r)} \cdot \mathbf{s})^2; \quad \sum_{l, r=1}^{3} F_{lr}(s)^2 = 6. \quad (29)$$

The expressions are rather cumbersome and will not be written down here. The translational quantum correction and the rotational quantum correction arising from the optical anisotropy will usually be small relative to the dipole-dipole quantum correction associated with the potential (28). We therefore calculate only this latter correction by means of Eq. (21). The Laplacian and gradient operators are of course independent of the orientation of the reference system. Making use of Eq. (21) and the relations

$$L_k^2(\mathbf{a} \cdot \boldsymbol{\gamma}_k) = -2(\mathbf{a} \cdot \boldsymbol{\gamma}_k),$$
$$L_k(\mathbf{a} \cdot \boldsymbol{\gamma}_k) = \mathbf{a} - \boldsymbol{\gamma}_k(\mathbf{a} \cdot \boldsymbol{\gamma}_k),$$
(30)

where $\mathbf{a}$ and $\boldsymbol{\gamma}_k$ are any two independent unit vectors, one obtains for the quantum correction

$$\chi = \frac{\beta^2 \mu^2 h^2}{3R^3} \left\{ \frac{A_1}{J} + \frac{\beta \mu^2}{R^3} \left[\frac{A_2}{J} + \frac{A_3}{mR^2} \right] \right\},$$

$$A_1 = \boldsymbol{\gamma}_1 \cdot \boldsymbol{\gamma}_2 - 3(\boldsymbol{\gamma}_1 \cdot \mathbf{s})(\boldsymbol{\gamma}_2 \cdot \mathbf{s}),$$

$$A_2 = \tfrac{1}{4}[1 + (3/2)[(\boldsymbol{\gamma}_1 \cdot \mathbf{s})^2 + (\boldsymbol{\gamma}_2 \cdot \mathbf{s})^2] - A_1^2],$$
(31)

$$A_3 = (9/8)\{A_1[A_1 - 2(\boldsymbol{\gamma}_1 \cdot \mathbf{s})(\boldsymbol{\gamma}_2 \cdot \mathbf{s})] + (\boldsymbol{\gamma}_1 \cdot \mathbf{s})^2$$
$$+ (\boldsymbol{\gamma}_2 \cdot \mathbf{s})^2 + 2(\boldsymbol{\gamma}_1 \cdot \boldsymbol{\gamma}_2)(\boldsymbol{\gamma}_1 \cdot \mathbf{s})(\boldsymbol{\gamma}_2 \cdot \mathbf{s})\}.$$

The third term of (31) may be ignored for the present, since mR^2 is usually much larger than J. Maximum interaction occurs when the two dipoles are oriented parallel to s. Here we find

$$|\chi| = \tfrac{2}{3}(\beta^2 \mu^2 h^2/R^3 J).$$
(32)

For a typical polar molecule, HCl, $\mu = 1.03 \times 10^{-18}$ e.s.u. and $J = 2.65 \times 10^{-40}$ g cm^2. In this case $\chi = 1.56 \times 10^4/R^3 T^2$ where R is expressed in Angstrom units. Thus at 300° Kelvin with a separation of 3A, a reasonable value for the distance of closest approach of two HCl molecules in thermal collisions, $\chi = 0.06$. Since this is still fairly small relative to unity, it seems possible to conclude that the classical phase integral remains a good approximation at ordinary temperatures.

It will be recalled that the integrand in the expression (23) for σ_q is also the configuration probability (Kirkwood, reference 5). The average energy may be calculated by means of the formula

$$\bar{V} = (\int V e^{-\beta V}(1+\chi)dq)/(\int e^{-\beta V}(1+\chi)dq).$$
(33)

If $e^{-\beta V}$ is expanded and the average taken over all molecular orientations, one obtains, neglecting inverse powers of R higher than the sixth:

$$\bar{V} = -\frac{2}{3}\frac{\beta \mu^4}{R^6}\left(1 - \frac{\beta h^2}{3J}\right) - \frac{2\bar{\alpha}\mu^2}{R^6}$$

$$-\frac{6}{R^6}\sum_{\substack{n \neq n \\ k, n}} \frac{\overline{|\mu_{n'n}|^2}\,\overline{|\mu_{n''n}|^2}}{E_{n'}^0 + E_{n''}^0 - 2E_n^0},$$

$$\bar{\alpha} = (\alpha_x + \alpha_y + \alpha_z)/3,$$

$$\overline{|\mu_{n'n}|^2} = [|\mu_{n'n}^{(x)}|^2 + |\mu_{n'n}^{(y)}|^2 + |\mu_{n'n}^{(z)}|^2]/3.$$
(34)

It should be remarked that this expansion is not a particularly good approximation for equation of state calculations, since $\beta\mu^2/R^3$ may not be small. However, it serves to illustrate the relative magnitudes of different contributions to the intermolecular energy. The first term corresponds to the Richt effect of Keesom.[9] Except for the small quantum correction, it has its classical value. The quantum correction $\beta h^2/3J$ is exactly twice that which must be applied to the electric susceptibility of a molecule. Thus, if terms of the order h^4 are neglected, it is seen that a dipole molecule at high temperatures has the same effective mean square moment whether interacting with the field of another dipole molecule or with an external electric field. The second term of Eq. (34) corresponds to the induction effect of Falkenhagen[1] and the third to the high frequency dispersion effect of London.[2] At ordinary temperatures, the first and third terms of Eq. (34) are of the same order of magnitude for typical polar molecules, while the second term is relatively small. At very high temperatures the influence of the first term becomes small but at low temperatures it becomes predominant.

At a later time, an attempt will be made to apply the present considerations to a calculation of the equations of state of polar molecules. It should be remarked that a calculation of the

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[9] W. H. Keesom, Phys. Zeits. **22**, 129, 643 (1921).

van der Waals A constant is not sufficient. Thus it is impossible to represent the second virial coefficient of a polar gas by $b_0 - A/RT$, except over a very short temperature range. The experimental A constants have, therefore, no clear cut theoretical significance.

From the foregoing discussion it seems possible to conclude that the sum of states of a gas at ordinary temperatures is closely approximated by the classical Gibbs phase integral. The approximation may be improved by including a quantum correction, Eq. (21), which is usually very small except at quite low temperatures. The semiclassical potential Eq. (26), from which all low frequency quantum numbers have been eliminated, is to be employed in the calculation of the phase integral. The low frequency contributions to the intermolecular energy have essentially their classical values and the high frequency contribution is given by a modification of London's formula, in which continuous functions of the molecular orientations appear in the place of space quantum numbers.

Note added in Proof: If rectangular coordinates are employed the sum of states of a particle is given by[5]

$$\sigma = (2\pi h)^{-1} \int \cdots \int e^{-i\mathbf{p}\cdot\mathbf{r}/h} e^{-\beta H}$$
$$\times e^{i\mathbf{p}\cdot\mathbf{r}/h} dx\, dy\, dz\, dp_x\, dp_y\, dp_z \quad \text{(a)}$$

where $\mathbf{p}$ is the momentum and $\mathbf{r}$ is the radius vector of the particle. To express this integral in terms of generalized coordinates, one would most simply express $\mathbf{p}\cdot\mathbf{r}$ and H in terms of the new p's and q's and replace $dx \cdots dp_z$ by the product of the differentials of the new p's and q's, since the transformation determinant in phase space is unity. However, this procedure is not convenient in the case of rigid rotor. If the rotor is represented by a mass point moving on the surface of a sphere, one sees that $\mathbf{p}\cdot\mathbf{r}$ vanishes and the integrand of (a) becomes indeterminate. For this reason it is necessary to resort to the method of Section III, in which the transformation determinate of the q's appears. Due to the uncertainty principle, quantum mechanics does not uniquely determine a probability distribution function in phase space, $P(p, q)$, but only integrated distribution functions $\overline{P}(q)$ and $\overline{P}(p)$ in configuration or in momentum space. Thus there is a certain amount of flexibility in the choice of the integrand employed in the representation of σ.