

CONTRIBUTION OF BOUND DOUBLE MOLECULES TO THE SECOND VIRIAL COEFFICIENT OF POLAR GASES

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ABSTRACT. The contribution of the bound double molecules to the second virial coefficient $B(T)$ has been calculated for the polar gases. The calculation is valid for any 'effective' relative orientation between the dipoles of the two interacting molecules and is an improvement over the one made previously by Barua, Chakraborti and Saran.

I N T R O D U C T I O N

Due to the presence of long-range, angle-dependent, dipole-dipole forces, it is difficult to represent the intermolecular potential between two polar molecules in a suitable functional form. At present, the most commonly used potential energy function, the Stockmayer potential can be represented as :

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] - \frac{\mu^2}{r^3} g(\theta_1, \theta_2, \phi), \quad \dots (1)$$

$$g(\theta_1, \theta_2, \phi) = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi, \quad \dots (2)$$

where μ is the dipole moment, θ_1 and θ_2 are the angles of inclination of the axes of the two dipoles to the line joining the centres of the molecules and ϕ is the azimuthal angle. When $\mu \rightarrow 0$, $\phi(r)$ is the commonly used Lennard-Jones (12 : 6) potential (Hirschfelder, Curtiss and Bird 1954) for nonpolar molecules.

The classical statistical expression for the second virial coefficient can be written as :

$$B(T) = \frac{N}{4} \int_0^\infty \int_\Omega (1 - e^{-\phi(r)/kT}) r^2 dr d\Omega \quad \dots (3)$$

where

$$\int_\Omega = \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2 d\phi \quad \dots (4)$$

Stockmayer (1941) and Rowlinson (1949) evaluated $B(T)$ for the polar gases from eqs. (1) and (3) by assuming equal probability for all the relative orientations of the dipoles of the interacting molecules.

Fortunately, physically more understandable and rigorous approach to the problem of calculating $B(T)$ can be achieved by breaking up $B(T)$ into three parts (Stogryn and Hirschfelder 1959) :

$$B(T) = B_f(T) + B_b(T) + B_m(T), \quad \dots (5)$$

where $B_f(T)$, $B_b(T)$ and $B_m(T)$ are respectively, the contributions of the free, bound and metastably bound double molecules to the second virial coefficient $B(T)$.

$B_b(T)$ and $B_m(T)$ are related to the equilibrium constant for dimerization. Recently Barua, Chakraborti and Saran (1965) have evaluated $B_b(T)$ mainly with the purpose of calculating the percentage of dimers in polar gases. In order to simplify the calculations, they have made certain approximations in evaluating the integrals. However, to calculate $B(T)$ accurately from eq. (5), all the parts should be calculated precisely. In the present paper we have made a refined calculation of $B_b(T)$.

O U T L I N E O F F O R M U L A T I O N

It has been recently pointed out by Semenov (1966) that the classical mechanics is not strictly valid in the range of states corresponding to bound particles where the Schrödinger equation allows only a number of discrete energy levels. Following his treatment the contribution of bound states to the second virial coefficient may be written as :

$$B_{q \text{ bound}} = -2^{3/2} N \lambda^{3/2} Z_q, \quad \dots (6)$$

where $B_{q \text{ bound}}$ includes the contribution of stable double molecules and

$$Z_q = \sum_{\rho} e^{-E_{\rho}^- / kT} = \sum_l (2l+1) \sum_n e^{-E_{nl} / kT}, \quad \dots (7)$$

where E_{ρ}^- is the energy of the bound particles, n and l are respectively the vibrational and rotational quantum numbers.

It is well known that the methods of classical statistical mechanics are applicable to the evaluation of the partitions function provided $\Delta E \ll kT$, where ΔE is the energy difference between two neighbouring quantum states of a system. The extensive study made by Stogryn and Hirschfelder (1959) and their evaluation of the maximum number of vibrational levels lead us to conclude that for heavy molecules (i.e. molecules except H_2 , He and Ne) and at not too low temperatures the difference between the classical and the quantum methods is insignificant. In the present paper we have followed the method of Hill (1955) applying classical statistical mechanics for obtaining the partition function for the bound double molecules.

For spherically symmetric potentials :

$$B_b(T) = -N\Lambda^3 Q_{2b}/V, \quad \dots (8)$$

where N is Avogadro's number, V is the volume, $\Lambda^3 = \frac{h^3}{2\pi m kT}$ and Q_{2b} is the partition function for bound double molecules. Following Hill (1955)

$$Q_{2b} = \frac{V}{2\Lambda^6} \int_{\phi(r) \leq 0}^{\infty} \exp [-\phi(r)/kT] 4\pi r^2 F(r) dr, \quad \dots (9)$$

where

$$F(r) = \frac{\Gamma \left\{ \frac{3}{2}, -\frac{\phi(r)}{kT} \right\}}{\Gamma \left(\frac{3}{2} \right)}$$

From eqs. (9) and (10) one gets :

$$B_b(T) = -2\pi N \int_d^{\infty} r^2 \exp [-\phi(r)/kT] \left[\frac{\Gamma \left(\frac{3}{2}, -\frac{\phi(r)}{kT} \right)}{\Gamma \left(\frac{3}{2} \right)} \right] dr, \quad \dots (10)$$

where $\Gamma \left\{ \frac{3}{2}, -\frac{\phi(r)}{kT} \right\}$ is incomplete gamma function and d is the value of r for which $\phi(r) = 0$.

The potential energy function given by eq. (1) can be written as :

$$\phi(r) = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6 - A(\sigma/r)^3], \quad \dots (11)$$

where

$$A = \frac{\mu^2}{4\epsilon\sigma^3 g}. \quad \dots (11a)$$

Let us define the following reduced quantities :

$$\phi^* = \phi/\epsilon, \quad r^* = r/\sigma, \quad T^* = kT/\epsilon,$$

$$d^* = d/\sigma, \quad B_b^* = B_b/b_0; \quad b_0 = \frac{z}{3} \pi N \sigma^3 \quad \dots (12)$$

In terms of the reduced quantities eq. (10) becomes :

$$B_b^*(T^*) = -3 \int_{d^*}^{\infty} r^{*2} \exp[-\phi^*/T^*] \left[\frac{\Gamma\left\{\frac{3}{2}, -\frac{\phi^*}{T^*}\right\}}{\Gamma\{3/2\}} \right] dr^* \quad \dots (13)$$

By applying certain mathematical transformations (Barua, Chakraborti and Saran 1965), we can obtain :

$$B_b^*(T^*) = -\frac{2}{\Gamma(3/2)} \sum_{n=0}^{\infty} \frac{\Gamma(1+n) \Gamma(5/2)}{\Gamma(1) \Gamma(\frac{5}{2}+n)} \cdot \frac{1}{n!} \int_{d^*}^{\infty} r^{*2} (-\phi^*/T^*)^{n+3/2} dr^* \quad (14)$$

Substituting the value of $\phi^*(r^*)$ from eq. (11) and putting $y = r^{*-3/2}$, the integral in eq. (14) reduces to :

$$\int_{d^*}^{\infty} r^{*2} (-\phi^*/T^*)^{n+3/2} dr^* = \left(\frac{4}{T^*}\right)^{n+3/2} \frac{y'}{0} \int_0^2 y^{2n} [A+y^2-y^6]^{n+3/2} dy, \quad \dots (15)$$

where

$$y' = d^{*-3/2}.$$

Thus, finally we get :

$$B_b^*(T^*, A) = -\frac{16}{\pi^{1/2}} \sum_{n=0}^{\infty} \frac{4^{2n+3/2} \cdot (n+1)!}{(2n+3)!} \left(\frac{1}{T^*}\right)^{n+3/2} \times \int_0^{y'} y^{2n} [A+y^2-y^6]^{n+3/2} dy. \quad \dots (16)$$

TABLE I

A	0.00	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
y'	1.000	1.043	1.077	1.105	1.129	1.151	1.170	1.188	1.204

TABLE II
Calculated values of $-B_b^*(T^*)$ for polar gases

T^* / A	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6
0.4	10.7306	47.23870							
0.5	6.3247	23.38052	71.15254						
0.6	4.2679	14.37019	38.25175	96.16479					
0.7	3.1223	9.92758	24.32324	54.55975	124.03463				
0.8	2.4100	7.37405	17.09987	35.57824	73.54680				
0.9	1.9325	5.75356	12.83463	25.35370	47.99361	91.08378			
1.0	1.5940	4.65067	10.08723	19.18720	35.28832	61.82270	111.32201	198.62868	
1.25	1.0738	3.03080	6.28213	11.26657	19.15420	30.62958	49.29003	77.10798	129.76167
1.50	0.7857	2.17413	4.38854	7.61352	12.37489	18.83764	28.47653	41.49753	64.07642
1.75	0.6068	1.67673	3.28697	5.58409	8.82081	13.03356	18.96257	26.51244	38.72684
2.0	0.4868	1.31687	2.58136	4.32312	6.69729	9.70462	13.76776	18.75540	26.38593
2.5	0.3388	0.90538	1.74713	2.87350	4.34342	6.14638	8.45703	11.18268	15.02094
3.0	0.2531	0.67103	1.28240	2.08627	3.10745	4.33752	5.86431	7.63022	9.98015
4.0	0.1608	0.42242	0.79816	1.28250	1.87901	2.58373	3.42763	4.38600	5.57704
5.0	0.1135	0.29671	0.55707	0.88907	1.29102	1.76101	2.31315	2.93477	3.67862
10.0	0.0391	0.10120	0.18773	0.29594	0.42301	0.56881	0.73452	0.91818	1.12434

METHOD OF CALCULATION

The upper limit in the integral of eq. (16) is a function of A and can be calculated for a fixed value of A (which corresponds to an 'effective' relative orientation of the interacting dipoles) from the equation $\phi(y') = 0$. The values of y' for the different values of A are given in Table I. Recently Barua *et al*, (1965) have evaluated the integral by putting an average value of y within the bracket of eq. (15) so that for $A = 0$ each term in eq. (14) is equal to the corresponding term in the expression for the Lennard-Jones (12 : 6) potential (Stogryn and Hirschfelder 1959). With this approximation they obtained :

$$[\bar{y}_n^2 - \bar{y}_n^6]^{n+3/2} = \frac{4^n \cdot n! (2n+2)! (2n+3)! (2n+1)!}{(4n+5)! (n+1)!} \quad \dots (17)$$

As a further approximation, they had taken the upper limit of the integral as unity so that the eq. (16) reduces to

$$\int_{d^*}^{\infty} r^{*2} (-\phi^*/T^*)^{n+3/2} dr^* = \int_1^{\infty} r^{*2} (-\phi^*/T^*)^{n+3/2} \cdot dr^* \\ = \frac{2}{3} \left[\frac{4(A + \bar{y}_n^2 - \bar{y}_n^6)}{T} \right]^{n+3/2} \cdot \frac{1}{2n+1} \quad \dots (18)$$

As the main purpose of Barua *et al* (1965) was to obtain the percentage of dimers for polar gases needed for the study of pressure dependence of transport properties, they were justified in making these approximations in order to simplify the calculations. However, as the main contribution to the total second virial coefficient $B(T)$, $B_v(T)$ must be evaluated precisely.

The summation in eq. (16) converges very rapidly for higher reduced temperatures and lower values of A . Otherwise, the convergence is slow and a large number of terms are needed in the series to obtain an accuracy of five significant figures. The integral of each term in the series of eq. (16) was divided into three equal intervals and for each interval a nine-point Gaussian integration was done. $B_v^*(T^*)$ has been calculated for T^* , ranging from 0.4 to 10 and for the values of A from 0 to 1.6 and are given in Table 2. We estimate the accuracy to be generally of the order of 0.01% and this is indicated by the good agreement with the results obtained by Stogryn and Hirschfelder (1959) for the Lennard-Jones (12:6) model (i.e. for $A = 0$).

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