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Core Potential of Intermolecular Forces Applied to Third Virial Coefficients and Transport Coefficients of Polyatomic Gases

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The three-molecular cluster integrals for oxygen, nitrogen, and carbon tetrafluoride and the coefficients of viscosity and self-diffusion for nitrogen and carbon dioxide are discussed on the basis of the Kihara convex-core potential of intermolecular forces. For the equilibrium property, the relative size of the core is essential; for the transport properties, the nonspherical character of the molecule plays an important role.

KEY WORDS: Statistical thermodynamics and kinetic theory of gases; intermolecular forces; polyatomic molecules.

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1. INTRODUCTION

The equation of state of gases may be expressed in the form

$$P/kT = n + B(T)n^2 + C(T)n^3 + \cdots \tag{1}$$

Here P is the pressure, n is the number density of molecules, k is the Boltzmann constant, and T is the absolute temperature. In this expression $B(T)$, $C(T)$,... are called the second, third,... varial coefficients.

For nonpolar polyatomic molecules, Kihara(1) proposed an intermolecular potential function

$$U(\rho) = U_0[(\rho_0/\rho)^{12} - 2(\rho_0/\rho)^6] \tag{2}$$

which is similar to that of Lennard-Jones but with the variable ρ set equal to the minimum distance between impenetrable molecular cores. The core may take any shape as long as it is a convex body. By properly choosing the cores, we can take into account the sizes and shapes of the molecules in a realistic way.

A convex body is characterized by its three fundamental measures: the volume V, the surface area S, and the measure M, which is the mean curvature integrated over the surface of the convex body (e.g., $M = 4\pi a$ for a sphere of radius a; $M = \pi l$ for a thin rod of length l).

In terms of V, S, and M of the molecular core, the second virial coefficient $B(T)$ of a one-component gas is given in the form

$$B(T) = \int_0^\infty \left[1 - \exp\frac{-U(\rho)}{kT}\right]\left[\left(S + \frac{1}{4\pi}M^2\right) + 2M\rho + 2\pi\rho^2\right] d\rho$$
$$+ V + \frac{1}{4\pi}MS$$

This is calculated to be

$$\begin{aligned} B(T) = {} & (2\pi/3)\rho_0^3 F_3(z) + M\rho_0^2 F_2(z) \\ & + [S + (4\pi)^{-1}M^2]\rho_0 F_1(z) + V + (4\pi)^{-1}MS \end{aligned} \tag{3}$$

where

$$z = U_0/kT$$

$$F_s(z) = -\frac{s}{12}\sum_{t=0}^{\infty}\frac{1}{t!}\Gamma\left(\frac{6t - s}{12}\right)2^t z^{(6t+s)/12}, \qquad s = 1, 2, \text{ and } 3$$

If the core of a molecule is properly chosen, it is possible to determine the parameters U_0 and ρ_0 of the molecule by using the observed values(2) of the second virial coefficient.

The purpose of the present paper is to discuss the third virial coefficient $C(T)$ and also coefficients of viscosity and self-diffusion of polyatomic gases

Table I. Fundamental Measures of the Core and Potential Parameters

	V, Å^3	S, Å^2	M, Å	ρ_0, Å	U_0/k, K
N_2	0	0	2.92	3.60	117
O_2	0	0	3.23	3.20	151
CO_2	0	0	7.23	3.30	316
CF_4 (a)	1.29	8.54	12.73	2.63	352
CF_4 (b)	0.66	5.47	10.18	3.10	297

on the basis of the core potential (2). We treat N_2, O_2, CO_2, and CF_4, for which experimental data are reliable.

Molecular cores are chosen as follows:

N_2: 0.85 × thin rod defined by N atoms.
O_2: 0.85 × thin rod defined by O atoms.
CO_2: Thin rod defined by O atoms.
CF_4: (a) Tetrahedron defined by F atoms, (b) 0.8 × above-mentioned tetrahedron.

Table I gives the fundamental measures of the cores and potential parameters determined from the second virial coefficients.

The case where the convex core is reduced to a spherical core is particularly simple. For this spherical-core potential, tables of functions giving the third virial coefficient have been given by Sherwood and Prausnitz,(3) and the effective cross sections for transport coefficients have been tabulated by Barker *et al.*(4) The problem to be solved in the present paper is how to apply these tables to nonspherical convex-core potentials.

The second virial coefficient is positive for $T < T_B$ and negative for $T < T_B$, where T_B is the so-called Boyle temperature. We define a characteristic volume b by

$$b \equiv \left(T\frac{dB}{dT}\right)_{T=T_B} = \left(\frac{dB}{d\ln T}\right)_{T=T_B} \tag{4}$$

In the present paper (in Figs. 1, 6, and 7), we use the following values:

$T_B = 407$ K, $b = 67.5$ Å^3 for Ar
$T_B = 323$ K, $b = 89.1$ Å^3 for N_2
$T_B = 517$ K, $b = 174$ Å^3 for CF_4
$T_B = 700$ K, $b = 122$ Å^3 for CO_2

2. THREE-MOLECULE CLUSTER INTEGRAL

If the molecular core is sufficiently small, i.e., $M^2/4\pi\rho_0^2 \ll 1$, the expression (3) reduces to

$$B(T) = (2\pi/3)\rho_0^3 F_3(z) + M\rho_0^2 F_2(z)$$

which depends only on M among the three fundamental measures V, S, and M. In other words, the expression for the second virial coefficient remains unaltered when a sphere with the same M is substituted for the molecular core.

The situation is similar for the third virial coefficient $C(T)$: If the core is sufficiently small, it is of the form

$$C(T) = \rho_0^6 \times (\text{function of } z) + M\rho_0^5 \times (\text{function of } z)$$

For molecules with small cores, therefore, $C(T)$ can be evaluated by replacing the core with a sphere of the same M.

The cores of the molecules under consideration are not so small; e.g., $M^2/4\pi\rho_0^2 = 0.38$ for CO_2. The spherical-core approximation is still effective, however, if an appropriate sphere is adopted. We choose the radius, denoted by a, of the sphere in such a way that the second virial coefficient can be reproduced with the same U_0. The results are given in Table II. Note that the radius a is smaller than $M/4\pi$ and the new ρ_0 is larger than the old ρ_0.

In this approximation, we can evaluate $C(T)$ by making use of Sherwood and Prausnitz's table mentioned in Section 1.

The accuracy of this type of approximation has been confirmed by Kihara and Miyoshi(5) on the basis of the square-well potential with convex cores,

$$U(\rho) = \begin{cases} \infty & \text{for } \rho < \sigma \\ -\epsilon < 0 & \text{for } \sigma < \rho < 2\sigma \\ 0 & \text{for } 2\sigma < \rho \end{cases}$$

Table II. Spherical-Core Approximations

	Convex core		Spherical core	
	$M/4\pi$, Å	ρ_0, Å	a, Å	ρ_0, Å
N_2	0.23	3.60	0.20	3.62
O_2	0.26	3.20	0.23	3.22
CO_2	0.58	3.30	0.46	3.40
CF_4 (a)	1.01	2.63	0.90	2.70
CF_4 (b)	0.81	3.10	0.75	3.15

Here ρ is the distance between the molecular cores; ϵ and σ are potential parameters.

The equation of state can also be expressed in the form of power series

$$P/kT = \sum_{l=1}^{\infty} b_l(T)z^l, \qquad n = \sum_{l=1}^{\infty} lb_l(T)z^l \tag{5}$$

in which the fugacity z plays the role of a parameter. Here $b_1 \equiv 1$, and $b_2(T)$, $b_3(T)$,... are called the two-molecule, three-molecule,... cluster integrals. Between the virial coefficients and the cluster integrals, the following relationships hold:

$$b_2 = -B, \qquad b_3 = 2B^2 - \tfrac{1}{2}C,... \tag{6}$$

The l-molecule cluster integral $b_l(T)$ has $l - 1$ zeros ($l = 2, 3,...$), each of which is located between two neighboring zeros of $b_{l+1}(T)$. The least zero of $b_l(T)$ decreases as l increases, and the accumulation point of these least zeros coincides with the critical temperature.(6) For this reason we use $b_3(T)$ instead of $C(T)$ for comparison of theory with experiment.

Figure 1 shows typical examples of the two- and three-molecule cluster integrals, which are obtained by the use of observed virial coefficients(2) and the relation (6). The law of corresponding states does hold well for b_2, but not for b_3. This fact indicates that the intermolecular potential functions for Ar, N_2, and CF_4 are not similar, and that the three-molecule cluster integral is sensitive to the characteristics of the intermolecular forces.

For the three-molecule cluster integrals $b_3(T)$, effects of the nonadditivity of the intermolecular potential cannot entirely be neglected. Figure 2 shows

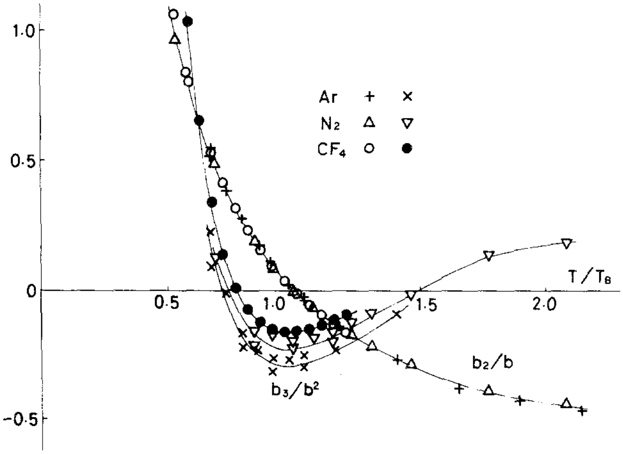

Fig. 1. Experimental values of b_2/b and b_3/b^2 as functions of T/T_B.

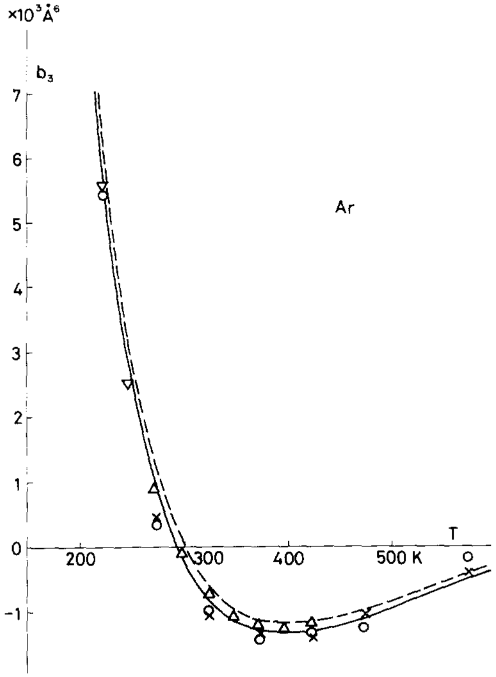

Fig. 2. The three-body cluster integral $b_3(T)$ calculated for argon compared with observed values. The effects of potential nonadditivity are taken into account for the solid line, but not for the broken line.

$b_3(T)$ for argon calculated with and without the assumption of potential additivity. The calculation is based on the Lennard-Jones potential

$$U(r) = U_0[(r_0/r)^{12} - 2(r_0/r)^6] \tag{7}$$

with $r_0 = 3.83$ Å and $U_0/k = 119$ K. It is shown that the potential nonadditivity *slightly* lowers the theoretical curve for $b_3(T)$. We take this fact into consideration for polyatomic molecules.

Curves for $b_3(T)$ calculated in the above-mentioned spherical-core approximation are compared with observed values⁽²⁾ in Figs. 3–5 for O_2, N_2, and CF_4, respectively. The potential additivity is assumed.

The comparison for O_2 is quite satisfactory since the effects of potential nonadditivity will lower slightly the theoretical curve. For N_2, it should be noted that the effects of molecular quadrupole and the effects of potential nonadditivity partly cancel out. (The quadrupole of O_2 is negligible.) Figure 5 shows that the tetrahedron defined by four fluorine atoms is definitely too large as the molecular core of CF_4.

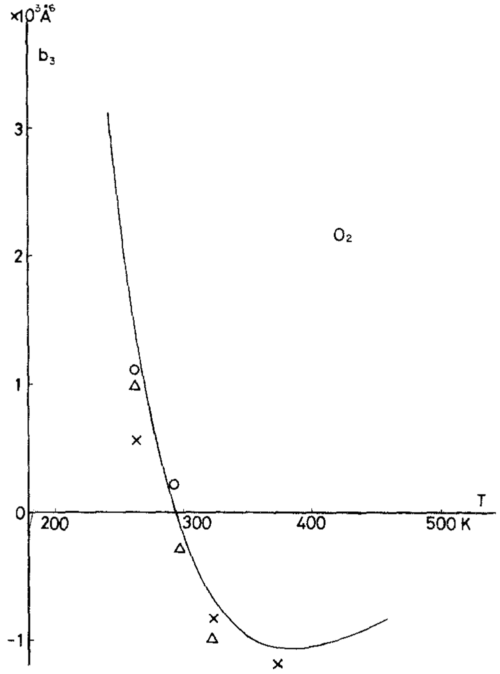

Fig. 3. The cluster integral $b_3(T)$ calculated for oxygen compared with observed values. The effects of nonadditivity of the intermolecular potential are not included, which would lower the theoretical curve.

3. KINETIC PROPERTIES OF GASES

The Chapman–Enskog expressions[(7)] for transport coefficients of gases are given in terms of the effective cross sections $\Omega^{(l,r)}$ defined by

$$\Omega^{(l,r)} = \left(\frac{kT}{2\pi m^*}\right)^{1/2} \int^{\infty} \exp(-g^{*2}) g^{*2r+3} \int (1 - \cos^l \theta)\, d\sigma\, dg^*$$

$$g^* \equiv (m^*/2kT)^{1/2} g; \qquad l = 1, 2; \quad r = l, l + 1, \ldots$$

Here g is the relative velocity, θ is the angle of deflection in the orbit of relative motion, $d\sigma$ is the differential collision cross section, and m^* is the reduced mass. The integrations of $\Omega^{(l,r)}$ have been performed for the Lennard-Jones potential,[(8)] for the spherical-core potential,[(4)] and for several other potentials.

For the convex-core potential (2) between nonspherical but nonpolar molecules, lower and upper bounds of $\Omega^{(l,r)}$ can be evaluated as follows. Here "nonpolar" means also that the center of mass of the molecule is located at the center of geometrical symmetry of the core.

If we calculate an effective cross section by replacing the core with an

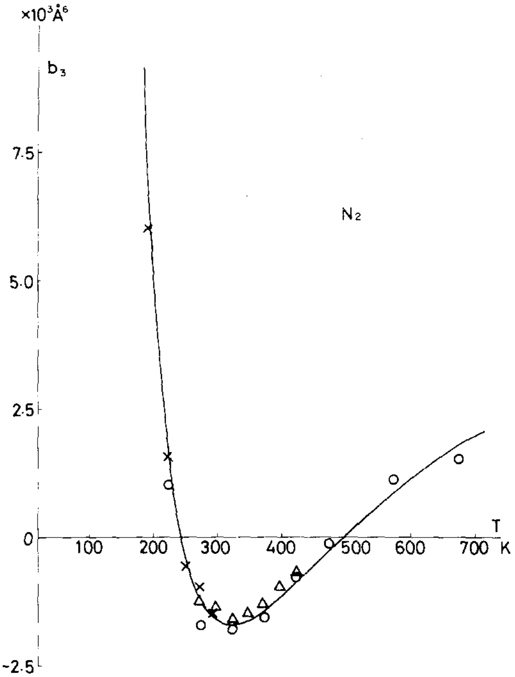

Fig. 4. Similar comparison as in Fig. 3, for nitrogen.

inscribed sphere around the center of mass, leaving U_0 and ρ_0 unaltered, then the result will give a lower bound of the cross section. This replacement corresponds to the assumption that the rotatory motions of the colliding molecules were perfectly free, as if the molecule had no moment of inertia with respect to the center of mass. For a molecule whose core is a thin rod, the inscribed sphere is a point; for such molecules the original potential (2) is reduced to the Lennard-Jones potential (7) with the same U_0 and with r_0 equal to ρ_0.

On the other hand, if we calculate the effective cross section by replacing the convex-core potential with its spherical-core approximation mentioned in Section 2, then the result will give an upper bound. This replacement corresponds to the assumption that the effect of molecular rotation would vanish on the average.

The coefficient of viscosity η of a pure gas and the coefficient of self-diffusion D are given by

$$\eta = \frac{5kT}{8\Omega^{(2,2)}}\left[1 + \frac{3}{49}\left(\frac{\Omega^{(2,3)}}{\Omega^{(2,2)}} - \frac{7}{2}\right)^2\right]$$

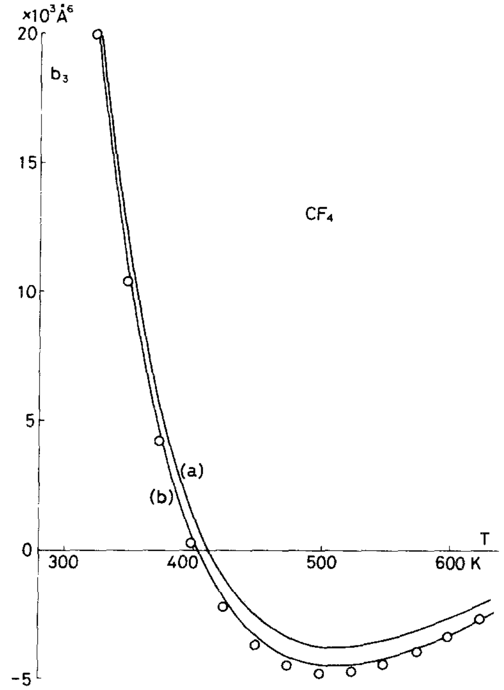

Fig. 5. Similar comparison as in Fig. 3, for carbon tetrafluoride. The core is a tetrahedron defined by F atoms for curve (a) and 0.8 times this tetrahedron for curve (b).

$$D = \frac{3kT}{8nm\Omega^{(1,1)}}\left[1 + \frac{1}{10 + 2\Omega^{(2,2)}/\Omega^{(1,1)}}\left(\frac{\Omega^{(1,2)}}{\Omega^{(1,1)}} - \frac{5}{2}\right)^2\right]$$

where m and n are the molecular mass and the number density of the molecules, respectively. The upper and lower bounds of these coefficients can be obtained by using the lower and upper bounds of the effective cross sections, respectively.

Figures 6 and 7 show η and D for Ar, N_2, and CO_2 in dimensionless forms

$$\eta^* = b^{2/3}(mkT)^{-1/2}\eta, \qquad D^* = b^{2/3}nm^{1/2}(kT)^{-1/2}D$$

as functions of T/T_B. Here T_B is the Boyle temperature and b is the molecular volume defined by (4). The lower-bound curves are almost in common to these molecules. Experimental results for viscosity$^{(9-11)}$ and for self-diffusion$^{(12-14)}$ are in fact between the calculated upper and lower bounds.

It should be noted that the experimental data of η^* for N_2 and CO_2 are closer to the theoretical lower bound, whereas those of D^* lie halfway between the two bounds. This fact can be explained by considering that the

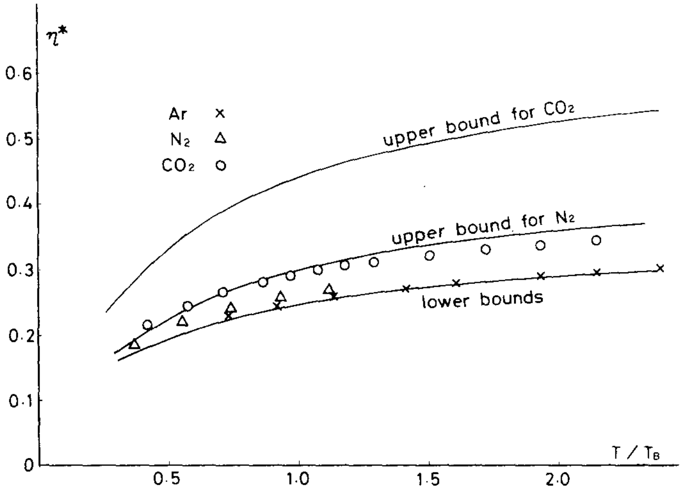

Fig. 6. Viscosity in a dimensionless form of argon, nitrogen, and carbon dioxide.

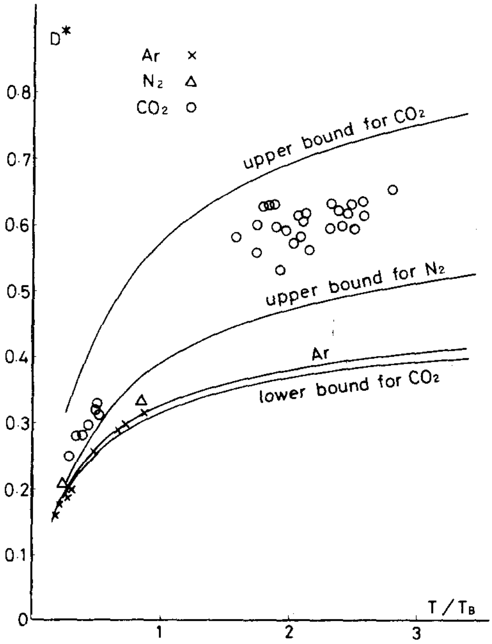

Fig. 7. The coefficient of self-diffusion in a dimensionless form.

replacement of the molecular core by the inscribed sphere is a better approximation for collisions with large angles of deflection, and such collisions are more effective for diffusion than for viscosity.

4. CONCLUSION

For equilibrium properties of gases, the relative size of the molecular core is essential, as shown in Figs. 1 and 5; for transport properties, the nonspherical character of the molecule plays an important role, as elucidated in Figs. 6 and 7.

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