

# Geometry of Three Convex Bodies Applicable to Three-Molecule Clusters in Polyatomic Gases

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An expression for the configuration integral for three overlapping convex bodies, which is a generalization of Hadwiger–Ishihara's formula for two convex bodies, has been found. As an application of this expression, two- and three-molecule cluster integrals (or second and third virial coefficients) for polyatomic molecules in gases are discussed on the basis of a square-well potential with convex cores.

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**KEY WORDS:** Statistical thermodynamics of gases; intermolecular forces; nonspherical molecules.

## 1. INTRODUCTION

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

$$P/kT = n + B(T)n^2 + C(T)n^3 + \dots \quad (1)$$

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, ..., virial coefficients.

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

$$P/kT = \sum_{l=1}^{\infty} b_l(T)z^l, \quad n = \sum_{l=1}^{\infty} lb_l(T)z^l \quad (2)$$

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. The following relationships hold between the virial coefficients and the cluster integrals:

$$b_2 = -B, \quad b_3 = 2B^2 - \frac{1}{2}C, \dots \quad (3)$$

The  $l$ -molecule cluster integral  $b_l(T)$  has  $l - 1$  zeros ( $l = 2, 3, \dots$ ), 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.<sup>(1)</sup> For this reason we use  $b_3(T)$ , instead of  $C(T)$ , for comparison of theory with experiment.

The second virial coefficient is positive for  $T > T_B$  and negative for  $T < T_B$ ,  $T_B$  being the so-called Boyle temperature. It is convenient to define the volume  $b$  by

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

and consider the dimensionless quantities  $b_l/b^{l-1}$  as functions of  $T/T_B$ .

Figure 1 shows typical examples of the two- and three-molecule cluster integrals, which are obtained by the use of observed virial coefficients<sup>(2)</sup>

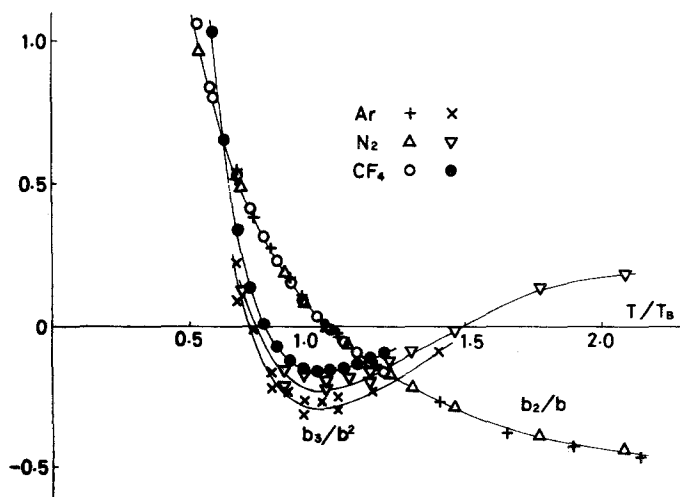


Fig. 1. Experimental values of  $b_2/b$  and  $b_3/b^2$  as functions of  $T/T_B$ .  $T_B = 408$  K,  $b = 67.5 \text{ \AA}^3$  for argon;  $T_B = 323$  K,  $b = 52.1 \text{ \AA}^3$  for nitrogen;  $T_B = 517$  K,  $b = 174 \text{ \AA}^3$  for carbon tetrafluoride.

and the relations (3). 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<sub>2</sub>, and CF<sub>4</sub> are not similar, and that the three-molecule cluster integral is sensitive to the characteristics of the intermolecular forces.

The second virial coefficient  $B(T)$  is given by

$$2B(T) = \left\langle \int [1 - \exp(-U_{12}/kT)] d\tau_2 \right\rangle \quad (5)$$

Here  $U_{12}$  is the intermolecular potential for the pair (1, 2);  $d\tau_2$  is the volume element occupied by the arbitrarily chosen "center" of the molecule 2, and  $\langle \rangle$  indicates the average with respect to the orientation of molecule 2, molecule 1 being kept fixed.

The third virial coefficient  $C(T)$  is given, under the assumption of potential additivity, by the expression

$$3C(T) = \left\langle \iint (1 - \exp \frac{-U_{12}}{kT}) \left( 1 - \exp \frac{-U_{13}}{kT} \right) \times \left( 1 - \exp \frac{-U_{23}}{kT} \right) d\tau_2 d\tau_3 \right\rangle \quad (6)$$

with the same notation.

The purpose of the present paper is to perform the integration for  $C(T)$  analytically on the basis of a particular model of the nonspherical intermolecular potential.

## 2. MOLECULES WITH CONVEX CORES

For nonpolar polyatomic molecules, Kihara<sup>(3)</sup> proposed an intermolecular potential function

$$U(\rho) = U_0[(\rho_0/\rho)^{12} - 2(\rho_0/\rho)^6] \quad (7)$$

which is similar to that of Lennard-Jones but with the variable  $\rho$  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, the sizes and shapes of the molecules can be taken into account in a realistic way.

A merit of the core potential (7) is that the second virial coefficient  $B(T)$  can be integrated analytically.

For the purpose of discussing both  $B(T)$  and  $C(T)$ , it is appropriate to use a simpler model of the intermolecular potential: We assume, instead of (7), the square-well potential function

$$U(\rho) = \begin{cases} \infty & \text{for } \rho < \sigma \\ -\epsilon < 0 & \text{for } \sigma < \rho < 2\sigma \\ 0 & \text{for } 2\sigma < \rho \end{cases} \quad (8)$$

Here  $\rho$  is the distance between the convex cores;  $\epsilon$  and  $\sigma$  are potential parameters. A parallel body of the core with thickness  $\sigma/2$ , which will be denoted by core +  $\sigma/2$  in the following, represents the impenetrable part of a molecule. (A body formed by all points whose distances from the surface of a convex body  $A$  are smaller than or equal to  $\rho$  is called "the parallel body of  $A$  with thickness  $\rho$ " and is denoted by  $A + \rho$ .)

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  $L$ ). For any convex body, the inequality  $S \leq M^2/4\pi$  holds.

The fundamental measures of the parallel body core +  $\rho$  are given by Steiner's formulas:

$$\begin{aligned} M_{\text{core} + \rho} &= M + 4\pi\rho \\ S_{\text{core} + \rho} &= S + 2M\rho + 4\pi\rho^2 \\ V_{\text{core} + \rho} &= V + S\rho + M\rho^2 + (4\pi/3)\rho^3 \end{aligned}$$

in which, and throughout the present paper,  $M$ ,  $S$ , and  $V$  indicate the fundamental measures of the core.

The second virial coefficient  $B(T)$  for the potential (8) is a linear function of

$$x \equiv e^{\epsilon/kT} - 1 \quad (9)$$

which can be expressed in the form

$$2B(T) = J^{(0)} - xJ^{(1)} \quad (10)$$

Here  $J^{(0)}$  and  $J^{(1)}$  indicate  $\langle \int d\tau_2 \rangle$  in (5) integrated over the regions  $\rho_{12} < \sigma$  and  $\sigma < \rho_{12} < 2\sigma$ , respectively,  $\rho_{12}$  being the intercore distance.

The integrals  $J^{(i)}$  can be evaluated on the basis of the Hadwiger–Isihara formula<sup>(3)</sup> for systems of two convex bodies  $A$  and  $B$ . Keeping the body  $A$  fixed, and keeping the orientation of the body  $B$  also fixed, let us move  $B$  around  $A$ , keeping contact on the surface of  $A$ . Then, the locus of the "center" of  $B$  forms the surface of another convex body, named  $A + B$ . Its volume  $V_{A+B}$  averaged over the orientation of  $B$  is given by

$$\langle V_{A+B} \rangle = V_A + V_B + (4\pi)^{-1}(S_A M_B + S_B M_A) \quad (11)$$

where  $V_A$ ,  $S_A$ , and  $M_A$  denote the fundamental measures of the body  $A$ . By virtue of this formula,  $J^{(0)}$  and  $J^{(1)}$  are given by

$$J^{(0)} = \langle V_{\text{core} + \sigma + \text{core}} \rangle, \quad J^{(1)} = \langle V_{\text{core} + 2\sigma + \text{core}} \rangle - J^{(0)}$$

in which

$$\begin{aligned} \langle V_{\text{core} + \sigma + \text{core}} \rangle &= (4\pi/3)\sigma^3 + 2M\sigma^2 + 2[S + (4\pi)^{-1}M^2]\sigma \\ &\quad + 2[V + (4\pi)^{-1}MS] \end{aligned}$$

Here Steiner's formulas have been used. Finally,

$$\begin{aligned}
 B(T) &= (2\pi/3)\sigma^3(1 - 7x) + M\sigma^2(1 - 3x) \\
 &+ [S + (4\pi)^{-1}M^2]\sigma(1 - x) + V + (4\pi)^{-1}MS \quad (12)
 \end{aligned}$$

The third virial coefficient  $C(T)$  for our present model is a cubic function of  $x$ ,

$$3C(T) = I^{(0)} - 3xI^{(1)} + 3x^2I^{(2)} - x^3I^{(3)} \quad (13)$$

Here  $I^{(i)}$  indicate  $\langle \iint d\tau_2 d\tau_3 \rangle$  in (6) integrated over the following regions:

$$\begin{aligned}
 I^{(0)}: & \quad \rho_{12} < \sigma, & \quad \rho_{13} < \sigma, & \quad \rho_{23} < \sigma \\
 I^{(1)}: & \quad \sigma < \rho_{12} < 2\sigma, & \quad \rho_{13} < \sigma, & \quad \rho_{23} < \sigma \\
 I^{(2)}: & \quad \sigma < \rho_{12} < 2\sigma, & \quad \sigma < \rho_{13} < 2\sigma, & \quad \rho_{23} < \sigma \\
 I^{(3)}: & \quad \sigma < \rho_{12} < 2\sigma, & \quad \sigma < \rho_{13} < 2\sigma, & \quad \sigma < \rho_{23} < 2\sigma
 \end{aligned}$$

$\rho_{ik}$  being the intercore distance for the pair  $(i, k)$ .

In order to evaluate the integrals  $I^{(i)}$ , we define a function  $F(A, B, C)$  of three convex bodies  $A, B$ , and  $C$ . Keeping the body  $A$  fixed, and keeping the orientations of the bodies  $B$  and  $C$  also fixed, we let  $B$  and  $C$  move around over the configurations in which all the pairs  $AB, AC$ , and  $BC$  overlap. Then the arbitrarily chosen "center" of  $B$  and the center of  $C$  generate together a six-dimensional domain. The six-dimensional volume of this domain averaged over the orientations of  $B$  and  $C$  is denoted by  $F(A, B, C)$ . In terms of this function, the  $I^{(i)}$  are given by

$$\begin{aligned}
 I^{(0)} &= F(\text{core} + \sigma/2, \text{core} + \sigma/2, \text{core} + \sigma/2) \\
 I^{(1)} &= F(\text{core} + \sigma, \text{core} + \sigma, \text{core}) - I^{(0)} \\
 I^{(2)} &= F(\text{core} + 3\sigma/2, \text{core} + \sigma/2, \text{core} + \sigma/2) - I^{(0)} - 2I^{(1)} \\
 I^{(3)} &= F(\text{core} + \sigma, \text{core} + \sigma, \text{core} + \sigma) - I^{(0)} - 3I^{(1)} - 3I^{(2)}
 \end{aligned}$$

### 3. THE CONFIGURATION INTEGRAL FOR THREE OVERLAPPING CONVEX BODIES

The function  $F(A, B, C)$  is a generalization of  $\langle V_{A+B} \rangle$  to a system of three convex bodies.

In a particular case where one of the convex bodies, say  $A$ , is much larger than the other two,  $F(A, B, C)$  should reduce to  $V_A \langle V_{B+C} \rangle$  or, by making use of (11),

$$V_A[V_B + V_C + (4\pi)^{-1}(S_B M_C + S_C M_B)]$$

Taking this asymptotic form into account, we let

$$\begin{aligned} F(A, B, C) = & V_A V_B + V_A V_C + V_B V_C \\ & + (4\pi)^{-1}[V_A(S_B M_C + S_C M_B) + V_B(S_A M_C + S_C M_A) \\ & + V_C(S_A M_B + S_B M_A) + G(A, B, C)] \end{aligned} \quad (14)$$

In another particular case where the three convex bodies are spheres of radii  $a$ ,  $b$ , and  $c$ ,  $F(A, B, C)$  is calculated to be

$$\begin{aligned} F(A, B, C) = & (4\pi)^2[3^{-2}(a^3 b^3 + a^3 c^3 + b^3 c^3) \\ & + 3^{-1}abc(a^2 b + ab^2 + a^2 c + ac^2 + b^2 c + bc^2) + a^2 b^2 c^2] \end{aligned}$$

or

$$G(A, B, C) = (4\pi)^3 a^2 b^2 c^2$$

Among monomials of the fundamental measures which become  $(4\pi)^3 a^2 b^2 c^2$  for spheres, the smallest is  $S_A S_B S_C$  and the largest is  $(4\pi)^{-3} M_A^2 M_B^2 M_C^2$ . Hence it is expected that

$$S_A S_B S_C \leq G(A, B, C) \leq (4\pi)^{-3} M_A^2 M_B^2 M_C^2 \quad (15)$$

Expression (14) with (15) is a generalization of the Hadwiger–Isihara formula. Although we are not able to give a mathematical proof of relation (15), we have ascertained that it is correct. Some examples follow.

In case the body  $C$  is much smaller than  $A$  and  $B$ , which means  $S_C \ll \min(S_A, S_B)$  and  $M_C \ll \min(M_A, M_B)$ ,  $F(A, B, C)$  is equal to  $\langle V_{A+B} \rangle \langle V_{B+C} \rangle$  up to the terms in

$$\begin{aligned} & V_A V_B + (4\pi)^{-1}(V_A S_B + V_B S_A) M_C \\ & + (4\pi)^{-1}[(V_A M_B + V_B M_A) S_C + (4\pi)^{-1} S_A S_B M_C^2] \end{aligned}$$

Namely,  $G(A, B, C) = (4\pi)^{-1} S_A S_B M_C^2$  satisfies the inequality (15).

Figure 2 shows the result of a computer calculation by the Monte Carlo method for a system of three identical “spherocylinders,” which are parallel bodies of a rod or a disk type.

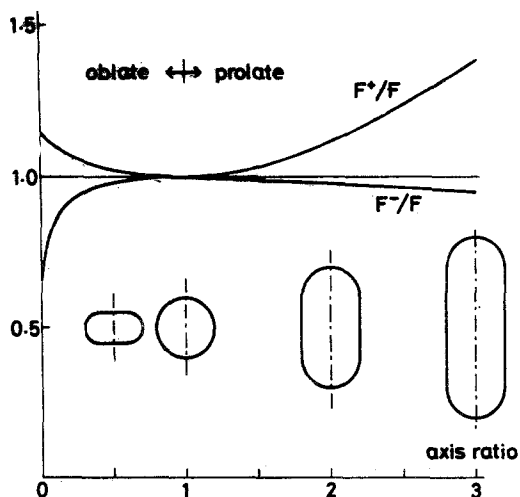


Fig. 2. The ratios  $F^+/F$  and  $F^-/F$  for three identical spherocylinders. Here  $F^+$  indicates the upper bound of  $F$  in which  $G(A, B, C)$  is replaced by  $(4\pi)^{-3}M_A^2M_B^2M_C^2$ ;  $F^-$  represents the lower bound in which  $G(A, B, C)$  is replaced by  $S_A S_B S_C$ .

In application to molecules, the arithmetic mean of the upper and lower bounds can be used as an approximation to  $G(A, B, C)$ .

#### 4. COMPARISON OF THEORY WITH EXPERIMENT

As an example we consider  $\text{CF}_4$  molecule, choosing a regular tetrahedron defined by the four fluorine atoms as its core. For a regular tetrahedron inscribed in a unit sphere, the three fundamental measures are

$$V = 8\sqrt{3}/27 = 0.51320, \quad S = 8\sqrt{3}/3 = 4.61880$$

$$M = 2\sqrt{6} \cos^{-1}(-1/3) = 9.36015$$

By making use of  $1.36 \text{ \AA}$  for the  $\text{CF}$  bond length, we have  $V = 1.29 \text{ \AA}^3$ ,  $S = 8.54 \text{ \AA}^2$ , and  $M = 12.73 \text{ \AA}$  for the core of carbon tetrafluoride. From experimental results for the second virial coefficient and expression (12) we obtain

$$\sigma = 2.28 \text{ \AA} \quad \text{and} \quad \epsilon/k = 157 \text{ K}$$

In Fig. 3, the calculated two- and three-molecule cluster integrals are

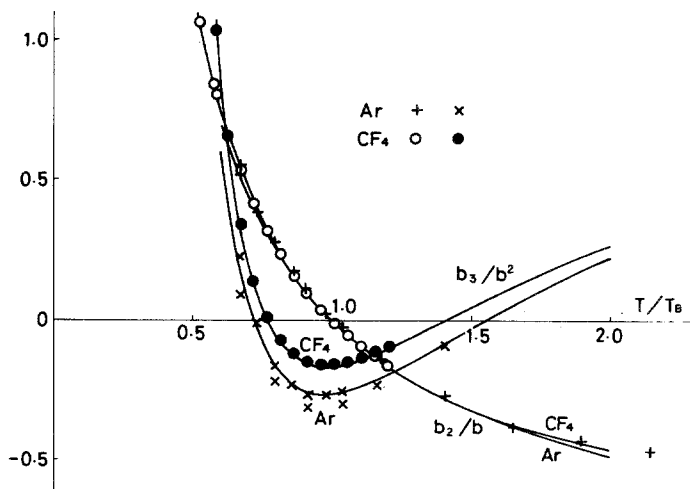


Fig. 3. Calculated cluster integrals for the square-well potential with convex molecular cores. The core is a regular tetrahedron for  $\text{CF}_4$  and a point for Ar.

compared with experimental values. For comparison, corresponding curves in the case of a point core are included.

Figure 3 also shows that the least zero of  $b_3(T)$  divided by  $T_B$  increases as the relative size of the core increases. Since the critical temperature  $T_c$  is the limit of such least zeros of  $b_l(T)$  for  $l \rightarrow \infty$ , the ratio  $T_c/T_B$  is expected to increase as the relative size of the core increases. This is in accord with experimental results, which are shown in Fig. 4.

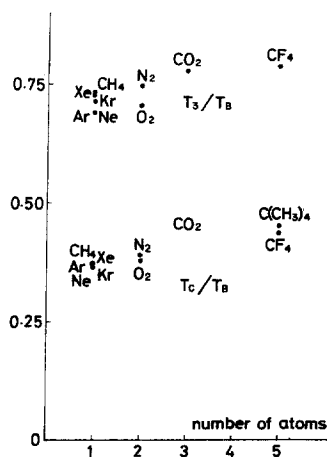


Fig. 4. The ratio  $T_c/T_B$  of the critical to the Boyle temperatures, and the ratio  $T_3/T_B$  of the least zero of  $b_3(T)$  to the Boyle temperature. Here "number of atoms" indicates the number of atoms, excluding hydrogens, in a molecule.



## 5. CONCLUDING REMARKS

For any convex-core potential of the form (8), there exists a spherical-core potential

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

which gives the same second virial coefficient as  $B(T)$  given by (12). Here  $\rho$  is the distance between the new spherical cores,  $\sigma'$  is a new parameter, and  $\epsilon$  is the same as before.

The third virial coefficient calculated for this spherical-core potential is expected, and in fact confirmed, to be a good approximation to  $C(T)$  given by (13). (For a very small core, or  $M^2/4\pi\sigma^2 \ll 1$ , this approximation is exact; in this case, the radius of the new spherical core is  $M/4\pi$ , and  $\sigma' = \sigma$ .)

Discussions about two- and three-molecule cluster integrals on the basis of a more realistic intermolecular potential (7) become possible by virtue of this kind of approximation. Details will be given elsewhere.

## REFERENCES

1. T. Kihara and J. Okutani, *Chem. Phys. Lett.* **8**:63 (1971).
2. J. D. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon Press, Oxford (1969).
3. T. Kihara, *Rev. Mod. Phys.* **25**:831 (1953); *Advan. Chem. Phys.* **5**:147 (1963).