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The Chapman–Enskog and Kihara Approximations for Isotopic Thermal Diffusion in Gases

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Kihara's first approximation for isotopic thermal diffusion in gases, which is a simplification of the Chapman–Enskog approximation, is derived in a simple and intuitive manner; the derivation elucidates the physical meaning of the approximation. The second approximation in this scheme is also given; it indicates the high accuracy of the first approximation.

KEY WORDS: Isotopic thermal diffusion; kinetic theory of gases; Chapman–Enskog and Kihara approximations.

1. INTRODUCTION

In 1949 the present author(1) suggested a simplification of the well-known expressions for the transport coefficients of gases due to Chapman and Enskog. This scheme is called the Kihara approximation, in contrast with the original Chapman–Enskog approximation; expressions obtained by this scheme are widely used in the literature.(2–10)

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In either of these approximations, the transport coefficients are given in terms of the effective cross sections $\Omega^{(l)}(r)$ defined by

$$\Omega^{(l)}(r) = \left(\frac{kT}{2\pi m^*}\right)^{1/2} \int_0^\infty \exp(-g^{*2})\, g^{*2r+3} \int (1 - \cos^l \theta)\, d\sigma\, dg^* \tag{1}$$

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

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; m^* is the reduced mass; T is the absolute temperature; and k is the Boltzmann constant. The purpose of the Kihara simplification was to obtain expressions which contain only $\Omega^{(l)}(r)$ with smaller l and r while nevertheless attaining sufficient accuracy.

From (1) we find the identity

$$\frac{d \ln \Omega^{(l)}(r)}{d \ln T} = \frac{\Omega^{(l)}(r+1)}{\Omega^{(l)}(r)} - \left(r + \frac{3}{2}\right) \tag{2}$$

Both sides vanish identically for the Maxwellian molecular model and take on small magnitudes in general. By virtue of this characteristic, the coefficient of viscosity η of a pure gas and the coefficient of thermal conductivity κ of a pure monatonic gas are obtained(1) in the forms

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

$$\kappa = \frac{3k}{2}\,\frac{25kT}{16m\Omega^{(2)}(2)} \left[1 + \frac{2}{21}\left(\frac{\Omega^{(2)}(3)}{\Omega^{(2)}(2)} - \frac{7}{2}\right)^2\right] \tag{4}$$

where m is the molecular mass. These expressions are substantially simpler and nevertheless no less accurate(11) than those in the second Chapman–Enskog approximation given in terms of $\Omega^{(2)}(2)$, $\Omega^{(2)}(3)$, and $\Omega^{(2)}(4)$. Similarly, the second approximation to the coefficient of self-diffusion D is of the form

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

n being the number density of the molecules. The Chapman–Enskog approximation corresponding to (5) contains $\Omega^{(1)}(3)$, moreover.

Now let us consider a binary gas mixture in which both the temperature T and the mole fractions $n_A/(n_A + n_B)$ and $n_B/(n_A + n_B)$ are inhomogeneous. Here n_A and n_B denote the number densities of the species A and B, respectively. The flow velocity of the species A relative to that of B is related to the gradient of the mole fraction and the temperature gradient by

$$\mathbf{v}_A - \mathbf{v}_B = -\frac{(n_A + n_B)^2}{n_A n_B}\left[D\,\nabla \frac{n_A}{n_A + n_B} + D_T\,\nabla \ln T\right] \tag{6}$$

Here D is the coefficient of diffusion and D_T is the coefficient of thermal diffusion; the dimensionless quantity

$$k_T \equiv D_T/D \tag{7}$$

is called the thermal diffusion ratio. Theoretical expressions for these transport coefficients contain three kinds of effective cross sections, $\Omega_A^{(l)}(r)$, $\Omega^{(l)}(r)$, and $\Omega_B^{(l)}(r)$, between AA, AB, and BB, respectively.

For isotopic mixtures, the intermolecular force is similar and hence

$$m_{\mathrm{A}}^{1/2}\Omega_{\mathrm{A}}^{(l)}(r) = (2m^*)^{1/2}\Omega^{(l)}(r) = m_{\mathrm{B}}^{1/2}\Omega_{\mathrm{B}}^{(l)}(r) \tag{8}$$

where m_{A} and m_{B} are the molecular masses and $m^* \equiv m_{\mathrm{A}}m_{\mathrm{B}}/(m_{\mathrm{A}} + m_{\mathrm{B}})$. We let $m_{\mathrm{A}} > m_{\mathrm{B}}$.

For heavy isotopes, which we consider throughout, the relative mass difference $(m_{\mathrm{A}} - m_{\mathrm{B}})/(m_{\mathrm{A}} + m_{\mathrm{B}})$ is small, and k_T is proportional to this quantity,

$$k_T \equiv \frac{n_{\mathrm{A}}n_{\mathrm{B}}}{(n_{\mathrm{A}} + n_{\mathrm{B}})^2}\,\frac{m_{\mathrm{A}} - m_{\mathrm{B}}}{m_{\mathrm{A}} + m_{\mathrm{B}}}\,k_T{}^* \tag{9}$$

The quantity $k_T{}^*$ is called "reduced thermal diffusion ratio."

The first approximation in our scheme yields⁽¹⁾

$$k_T{}^* = \frac{15}{8}\,\frac{2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)}{\Omega^{(2)}(2)} \tag{10}$$

This was first derived from the Chapman–Enskog approximation

$$k_T{}^* = \frac{15[2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)][5\Omega^{(1)}(1) + \Omega^{(2)}(2)]}{\Omega^{(2)}(2)[55\Omega^{(1)}(1) - 20\Omega^{(1)}(2) + 4\Omega^{(1)}(3) + 8\Omega^{(2)}(2)]} \tag{11}$$

by disregarding the second and higher powers of the right-hand terms of (2). The difference between (10) and (11) is notable: it amounts to 5% for the rigid sphere model of molecules. After laborious higher order calculations, Mason⁽⁵⁾ found that (10) is definitely more accurate than (11).

A purpose of the present paper is to derive the expression (10) in a simple and intuitive manner, and thereby to elucidate its physical meaning. Another purpose is to give a second approximation to $k_T{}^*$ in the present scheme, which will indicate the high accuracy of the first approximation (10).

We shall obtain an expression for $k_T{}^*$ by considering the case in which the mole fractions in (6) are uniform:

$$\mathbf{v}_{\mathrm{A}} - \mathbf{v}_{\mathrm{B}} = -\frac{m_{\mathrm{A}} - m_{\mathrm{B}}}{m_{\mathrm{A}} + m_{\mathrm{B}}}\,Dk_T{}^*\,\nabla \ln T \tag{12}$$

Here D is the coefficient of self-diffusion.

2. A SIMPLE DERIVATION OF THE FIRST APPROXIMATION

If all the molecules in a gas were of the species A, the velocity distribution $f_A(\mathbf{c}_A)$ would be of the form

$$f_A^{(0)}(\mathbf{c}_A)\left[1 + a_1\left(\frac{5}{2} - \frac{m_A c_A^2}{2kT}\right)\left(\frac{m_A}{2kT}\right)^{1/2}\mathbf{c}_A\cdot\nabla \ln T\right]$$

in which $f_A^{(0)}(\mathbf{c}_A)$ is the Maxwellian distribution. Similarly, if all were B,

$$f_B^{(0)}(\mathbf{c}_B)\left[1 + a_1\left(\frac{5}{2} - \frac{m_B c_B^2}{2kT}\right)\left(\frac{m_B}{2kT}\right)^{1/2}\mathbf{c}_B\cdot\nabla \ln T\right]$$

It is known that, in the first approximation,

$$a_1 = \frac{15}{16n}\left(\frac{kT}{m^*}\right)^{1/2}\frac{1}{\Omega^{(2)}(2)} \tag{13}$$

Here n is the total number density of the molecules, and the relationships (8) have been used.

In a homogeneous mixture of isotopes A and B, the species A flows with a velocity $\mathbf{v}_A$ and the species B with a velocity of $\mathbf{v}_B$. Thus $f_A^{(0)}(\mathbf{c}_A)$ should be replaced by $f_A^{(0)}(\mathbf{c}_A - \mathbf{v}_A)$, i.e., the velocity distribution should be of the form

$$f_A(\mathbf{c}_A) = f_A^{(0)}(\mathbf{c}_A)\left[1 + \frac{m_A}{kT}\mathbf{c}_A\cdot\mathbf{v}_A + a_1\left(\frac{5}{2} - \frac{m_A c_A^2}{2kT}\right)\left(\frac{m_A}{2kT}\right)^{1/2}\mathbf{c}_A\cdot\nabla \ln T\right] \tag{14}$$

This is our first approximation. A similar expression holds for $f_B(\mathbf{c}_B)$.

The relative flow velocity $\mathbf{v}_A - \mathbf{v}_B$ is determined from the condition that the momentum transfer between the two species should vanish on the average:

$$\int\int\int f_A(\mathbf{c}_A) f_B(\mathbf{c}_B)(m_B\mathbf{c}_B - m_B\mathbf{c}_B')|\mathbf{c}_B - \mathbf{c}_A|\, d\sigma\, d\mathbf{c}_A\, d\mathbf{c}_B = 0 \tag{15}$$

Here $\mathbf{c}_A$ and $\mathbf{c}_B$ are the velocities before a collision and $\mathbf{c}_A'$ and $\mathbf{c}_B'$ are those after the collision.

Equation (15) can be transformed into

$$\int\int\int f_A(\mathbf{c}_A) f_B(\mathbf{c}_B)(\mathbf{g} - \mathbf{g}')g\, d\sigma\, dg\, d\mathbf{G} = 0$$

where the center-of-mass velocity $\mathbf{G}$ and the relative velocities $\mathbf{g} \equiv \mathbf{c}_B - \mathbf{c}_A$ and $\mathbf{g}' \equiv \mathbf{c}_B' - \mathbf{c}_A'$ have been introduced. On performing the integration, we obtain

$$\begin{aligned}&8\left(\frac{m^*}{kT}\right)^{1/2}(\mathbf{v}_A - \mathbf{v}_B)\Omega^{(1)}(1)\\ &\quad = -3\frac{m_A - m_B}{m_A + m_B}a_1[2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)]\,\nabla \ln T\end{aligned} \tag{16}$$

From (12), (13), (16), and the first approximation to (5), we finally obtain the expression (10).

3. SECOND APPROXIMATION

The second approximation to the velocity distribution $f_A(\mathbf{c}_A)$ in our present scheme takes the form

$$f_A(\mathbf{c}_A) = f_A^{(0)}(\mathbf{c}_A)\left\{1 + \left[1 + b_1 S^{(1)}\left(\frac{m_A c_A^2}{2kT}\right)\right]\frac{m_A}{kT}\mathbf{c}_A\cdot\mathbf{v}_A + \left[a_1 S^{(1)}\left(\frac{m_A c_A^2}{2kT}\right) + a_2 S^{(2)}\left(\frac{m_A c_A^2}{2kT}\right)\right]\left(\frac{m_A}{2kT}\right)^{1/2}\mathbf{c}_A\cdot\nabla\ln T\right\} \tag{17}$$

in which $S^{(l)}(x)$ denote $S^{(l)}_{3/2}(x)$, the Sonine polynomials of order 3/2:

$$S^{(1)}(x) = \tfrac{5}{2} - x, \qquad S^{(2)}(x) = (35/8) - \tfrac{7}{2}x + \tfrac{1}{2}x^2$$

An expression similar to (17) applies to the function $f_B(\mathbf{c}_B)$ with the same a_1, a_2, and b_1. Our second approximation to a_1 and the first approximation to a_2 are the following:

$$a_1 = [a_1]_1\left[1 + \frac{2}{21}\left(\frac{\Omega^{(2)}(3)}{\Omega^{(2)}(2)} - \frac{7}{2}\right)^2\right] \tag{18}$$

$$a_2 = [a_1]_1\,\frac{4}{21}\left(\frac{\Omega^{(2)}(3)}{\Omega^{(2)}(2)} - \frac{7}{2}\right) \tag{19}$$

where $[a_1]_1$ is the first approximation (13) used in Section 2.

The coefficient b_1 is to be determined on the basis of the Boltzmann equation

$$\mathbf{c}_A\cdot\nabla f_A(\mathbf{c}_A) = (\partial f_A/\partial t)_{\text{coll}}$$

in which the right-hand side indicates the rate of change due to molecular collisions. For $f_A(\mathbf{c}_A)$ on the left, we can substitute the Maxwellian $f_A^{(0)}(\mathbf{c}_A)$, obtaining

$$f_A^{(0)}(\mathbf{c}_A)\left(\frac{m_A c_A^2}{2kT} - \frac{5}{2}\right)\mathbf{c}_A\cdot\nabla\ln T = \left(\frac{\partial f_A}{\partial t}\right)_{\text{coll}} \tag{20}$$

By multiplying $\mathbf{c}_A$ on both sides and integrating with respect to $\mathbf{c}_A$, or by making use of (15) directly, we obtain

$$16\left(\frac{m^*}{kT}\right)^{1/2}(\mathbf{v}_A - \mathbf{v}_B)\{4\Omega^{(1)}(1) - b_1[2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)]\}$$
$$= -\frac{m_A - m_B}{m_A + m_B}\{24a_1[2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)] + 5a_2[-4\Omega^{(1)}(3) + 28\Omega^{(1)}(2) - 35\Omega^{(1)}(1)]\}\,\nabla\ln T$$

By multiplying by $(5/2 - m_A c_A^2/2kT)\mathbf{c}_A$ on both hand sides of (20) and integrating, we have

$$\begin{aligned}2\left(\frac{m^*}{kT}\right)^{1/2}&(\mathbf{v}_A - \mathbf{v}_B)\{4[2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)]\\ &- b_1[4\Omega^{(1)}(3) - 20\Omega^{(1)}(2) + 55\Omega^{(1)}(1) + 8\Omega^{(2)}(2)]\}\\ &= \frac{m_A - m_B}{m_A + m_B}\{3a_1[4\Omega^{(1)}(3) - 20\Omega^{(1)}(2) + 15\Omega^{(1)}(1)]\\ &\quad - 23a_2[2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)]\}\ \nabla \ln T\end{aligned}$$

Here use has been made of integral formulas given in Refs. 9 and 10.

On eliminating b_1 in these two equations and making use of (5), (12), (18), and (19), we finally obtain

$$k_T^* = \frac{15}{8}\frac{2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)}{\Omega^{(2)}(2)}(1 + \delta_0 + \delta_1 + \delta_2 + \delta_3) \tag{21}$$

where

$$\delta_0 = -\frac{4\Omega^{(1)}(3) - 20\Omega^{(1)}(2) + 15\Omega^{(1)}(1)}{4\Omega^{(1)}(3) - 20\Omega^{(1)}(2) + 55\Omega^{(1)}(1) + 8\Omega^{(2)}(2)}$$

$$\delta_1 = \frac{5}{126}\left(\frac{\Omega^{(2)}(3)}{\Omega^{(2)}(2)} - \frac{7}{2}\right)\frac{-4\Omega^{(1)}(3) + 28\Omega^{(1)}(2) - 35\Omega^{(1)}(1)}{2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)}$$

$$\delta_2 = \frac{23}{126}\left(\frac{\Omega^{(2)}(3)}{\Omega^{(2)}(2)} - \frac{7}{2}\right)\frac{2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)}{5\Omega^{(1)}(1) + \Omega^{(2)}(2)}$$

$$\delta_3 = \frac{2}{21}\left(\frac{\Omega^{(2)}(3)}{\Omega^{(2)}(2)} - \frac{7}{2}\right)^2$$

Here terms containing higher powers of temperature derivatives of effective cross sections have been disregarded, e.g., $4\Omega^{(1)}(3) - 20\Omega^{(1)}(2) + 55\Omega^{(1)}(1) + 8\Omega^{(2)}(2)$ has been replaced by $40\Omega^{(1)}(1) + 8\Omega^{(2)}(2)$ in δ_2.

For the rigid sphere model of molecules the correction terms are

$$\delta_0 = -0.051, \qquad \delta_1 = +0.020, \qquad \delta_2 = +0.013, \qquad \delta_3 = +0.024$$

the sum $\delta_0 + \delta_1 + \delta_2 + \delta_3 = 0.006$ almost vanishing. In general, $\delta_0 + \delta_1 + \delta_2 + \delta_3$ is negligible; this fact indicates that our first approximation (10) is sufficiently accurate.

4. CONCLUDING REMARKS

The Chapman–Enskog approximation (11) corresponds to

$$k_T^* = \frac{15}{8}\frac{2\Omega^{(1)}(2) - 5\Omega^{(1)}(1)}{\Omega^{(2)}(2)}(1 + \delta_0)$$

This expression follows from a form of velocity distribution similar to (17) in which the term $a_2S^{(2)}(m_A c_A^2/2kT)$ is omitted. Since this term is as effective as the term $b_1S^{(1)}(m_A c_A^2/2kT)$, and, furthermore, since these two contributions almost cancel each other, the expression (11) is not as accurate as the simple expression (10).

The second approximation (21) is considerably simpler than Mason's⁽⁵⁾ "Kihara-type second approximation," which contains $\Omega^{(3)}(3)$. This approximation was obtained on the basis of a velocity distribution which is similar to (17) but with $1 + b_1S^{(1)} + b_2S^{(2)}$ instead of $1 + b_1S^{(1)}$. Mason's expression is 1.5% larger than (21) in the case of a rigid sphere model of molecules.

REFERENCES

1. T. Kihara, *Imperfect Gases* (Asakura Bookstore, Tokyo, 1949; English translation by U.S. Air Force Office of Research, Wright-Patterson Air Force Base); see also T. Kihara, *Rev. Mod. Phys.* **25**:831 (1953).
2. E. A. Mason, *J. Chem. Phys.* **22**:169 (1954).
3. E. A. Mason and W. E. Rice, *J. Chem. Phys.* **22**:843 (1954).
4. E. A. Mason, *J. Chem. Phys.* **23**:49 (1955).
5. E. A. Mason, *J. Chem. Phys.* **27**:75, 782 (1957).
6. S. C. Saxena and E. A. Mason, *J. Chem. Phys.* **28**:623 (1958); E. A. Mason and S. C. Saxena, *J. Chem. Phys.* **31**:511 (1959).
7. E. A. Mason and F. J. Smith, *J. Chem. Phys.* **44**:3100 (1966).
8. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *The Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
9. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge Univ. Press, 1970).
10. F. H. Ferzigar and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).
11. M. J. Offerhaus, *Physica* **28**:76 (1962).