JULY 15, 1940 PHYSICAL REVIEW VOLUME 58

On the Theory of the Thermal Diffusion Coefficient for Isotopes

R. CLARK JONES
Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

(Received May 4, 1940)

Enskog's general theory of thermal diffusion holds for a gas of spherically symmetrical molecules which is sufficiently dilute that collisions of more than two molecules at a time are of negligible importance. The first approximation to the thermal diffusion constant of a mixture of two isotopes is derived from this theory. The result is presented in terms of suitably defined cross-section integrals, in which the intermolecular forces are not yet specialized. This general formula for the thermal diffusion constant α is then worked out explicitly for several well-known molecular models: the elastic sphere model, the inverse power model, the Sutherland model, and the Lennard-Jones model. The various limitations on the accuracy of the theory are discussed, and the theoretical results are compared with the very few experimental data which are as yet available. The comparison indicates that the customary molecular models of kinetic theory are hardly adequate to give a satisfactory account of thermal diffusion. These models are relatively satisfactory for the elementary free-path phenomena to which they are usually applied, but they are not sufficiently precise to meet the more exacting test of thermal diffusion. The best check between theory and experiment is obtained for neon with the Sutherland model. The use of this model, however, places the entire burden of accounting for the observed decrease of α with temperature on the attractive part of the intermolecular forces, whereas in view of the smallness of this attractive force as determined by other methods, it can hardly be doubted that the decrease is actually due to the increased "softness" of the repulsive force at low temperatures.

THE importance of the phenomenon of thermal diffusion has recently been enhanced by the striking success of its use in separating isotopes.[1, 2] With this success has come the need for a more complete knowledge of the value of the thermal diffusion coefficient for a mixture of isotopes. The theoretical value of this coefficient for two simple molecular models has already been stated,[3, 4] but the relation of these results to the general theory of thermal diffusion has not been given. It is the purpose of this paper to indicate the general expression for the coefficient of thermal diffusion in the case of isotopes, and to derive from this general expression the results which have previously been stated without proof. We shall also derive the theoretical value of the coefficient for certain other molecular models, and compare these theoretical results with the small amount of experimental data which is available.

NOTATION AND DEFINITIONS

The phenomenon of thermal diffusion consists in the fact that a temperature gradient in a mixture of two gases gives rise to a gradient of the relative concentration of the two constituents. We shall discuss here only the case of a mixture of two isotopes of the same gas. Let c_1 be fractional *particle* density of the lighter molecules, and c_2 the corresponding quantity for the heavier molecules. The concentrations c_1 and c_2 are thus also the fractional partial pressures of the two species. We clearly have

$$c_1+c_2=1. \tag{1}$$

Let $\mathbf{v}_1$ be the *convection* velocity of the lighter molecules, and $\mathbf{v}_2$ the convection velocity of the heavier molecules. The convection velocity of the gas as a whole is given by

$$\mathbf{v}=c_1\mathbf{v}_1+c_2\mathbf{v}_2. \tag{2}$$

The coefficient of ordinary diffusion, D_{12}, and the coefficient of thermal diffusion, D_T, are then defined as the quantities which appear in the equation of diffusion

$$\begin{aligned} c_1(\mathbf{v}_1-\mathbf{v}) &= c_1c_2(\mathbf{v}_1-\mathbf{v}_2) \\ &= -D_{12}\ \mathrm{grad}\ c_1+D_T\ \mathrm{grad}\ \log T. \end{aligned} \tag{3}$$

Unlike the coefficient of ordinary diffusion, the

---

[1] K. Clusius and G. Dickel, Zeits. f. physik. Chemie **44**, 397 (1939).

[2] R. Clark Jones and W. H. Furry, Rev. Mod. Phys., to be published.

[3] W. H. Furry, R. Clark Jones, and L. Onsager, Phys. Rev. **55**, 1083 (1939).

[4] R. Clark Jones and W. H. Furry, Phys. Rev. **57**, 547L (1940).

coefficient of thermal diffusion is proportional to the product c_1c_2. We are therefore led to introduce another quantity, the thermal diffusion constant α, which is related to D_T by

$$\alpha = D_T/(D_{12}c_1c_2). \tag{4}$$

In the remainder of this paper we shall refer to α rather than D_T.

Qualitative Remarks

To a far greater extent than is the case with the three ordinary gas coefficients, the value of the thermal diffusion constant is sensitive to the molecular model. The free-path arguments of elementary kinetic theory are quite inadequate to give either its existence or its sign. Chapman[5] has dwelt at some length on the difficulties which beset any attempt to explain the effect upon elementary grounds. Recently, however, Frankel[6] has shown that it is possible to derive by means of a dimensional argument all of the essential features of the coefficient for the important special case of the inverse power model. This will be discussed in more detail later on when we examine this model.

The history of the theoretical development of thermal diffusion is rather interesting, but it will not be discussed here because it is presented elsewhere—briefly in reference 2, and more completely in reference 9.

The theory of thermal diffusion appears as a by-product of any sufficiently complete and rigorous kinetic theory of the phenomena of thermal conductivity, viscosity, and diffusion in gases. Two correct presentations of such a theory are now available. The first was given by Enskog[7] in his doctoral dissertation, as supplemented by an article[8] which appeared later. The second is in the recent book by Chapman and Cowling.[9] The former is more abstract and rather difficult to read. The latter has the disadvantage that its notation differs from that used by Enskog and most other recent writers on this subject. Chiefly because it is more concise, the notation of Enskog will be used in this article. The relation of the notation used by Chapman and Cowling to that used here, will, however, be indicated.

The theory of Enskog holds for a gas of spherically symmetrical molecules which is sufficiently dilute that triple collisions are of negligible importance in comparison with collisions of two molecules. The general expression obtained for α is the ratio of an infinite determinant to one of its minors; the elements of the determinants are integrals over the velocity spaces of the two molecules. The result which we shall present in this paper is the first approximation to the exact result.

The case of isotopes represents a simplification in the value of α as compared with the case of dissimilar molecules which is analogous to the simplicity of the coefficient of self-diffusion as compared with the coefficient of diffusion for two dissimilar gases. This simplification occurs because in the case of a gas consisting of a mixture of isotopes, we may suppose that the force fields of all the molecules are identical, since the field of force is determined only by the electronic configuration, and not by the mass of the nucleus.

Detailed Theory

The exact result is expressible in terms of integrals over the orbit of a molecule of species 1 as it moves in the field of a molecule of species 2. If the force fields of the molecules fall off with distance with sufficient rapidity for the gas to have an equation of state which is independent of the shape of its container, it is always possible to define an impact parameter and a relative velocity at infinity for a collision between two molecules. Let the impact parameter be indicated by b, and the relative velocity at infinity by g. Enskog then changes the scale of b and g according to the transformation:

$$g = (2kT/m)^{\frac{1}{2}}\gamma, \tag{5}$$

$$b = s\sigma(\gamma)\beta, \tag{6}$$

where $m = m_1m_2/(m_1+m_2)$ is the reduced mass, s is an arbitrary constant length, and $\sigma(\gamma)$ is an arbitrary function of γ and therefore of g. This method of factorization of the impact

---

[5] S. Chapman, Phil. Mag. **7**, 1 (1929).

[6] S. P. Frankel, Phys. Rev. **57**, 661L (1940).

[7] D. Enskog, Doctoral Dissertation, Upsala, 1917.

[8] D. Enskog, Arkiv f. Mat., Astron., och Fysik **16**, No. 16 (1922).

[9] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases* (Cambridge, 1939).

parameter, b, leads in practice to a considerable simplification of the formulae, provided that s and $\sigma(\gamma)$ are suitably chosen.

Let $\theta(\beta, \gamma)$ be the angle of deflection suffered by either molecule when it is deflected by the field of force of another, as measured in the center of gravity coordinate system. We may now define the quantities

$$\Theta^{(l)}(\gamma)=\int_0^\infty \{1-P_l(\cos\theta)\}\beta d\beta \tag{7}$$

and in turn the quantities

$$\Omega^{(l,k)}=\int_0^\infty e^{-\gamma^2}\sigma^2(\gamma)\gamma^k\Theta^{(l)}(\gamma)d\gamma. \tag{8}$$

The Ω's are dimensionless collision cross sections suitably averaged over β and γ. Enskog would write s, σ, $\Theta^{(l)}$, and $\Omega^{(l,k)}$ with the subscript 12. Since we shall have little occasion to refer to these quantities except when they refer to a collision between a molecule of species 1 and a molecule of species 2, we shall continue to omit the subscript. Note that it is not $\Omega^{(l,k)}$, but rather $s^2\Omega^{(l,k)}$ which is independent of the choice of s and σ. The expression (12) for α is independent of s, but this is not true of the expressions for the coefficients of viscosity and diffusion.

The procedure of Chapman and Cowling[9] is similar. They define the quantities

$$\phi^{(l)}=\int_0^\infty \{1-\cos^l\theta\}gbdb \tag{9}$$

and

$$\Omega^{(l)}(r)=\pi^{\frac{1}{2}}\int_0^\infty e^{-\gamma^2}\gamma^{2r+2}\phi^{(l)}d\gamma. \tag{10}$$

The relation between the two sets of quantities is thus

$$\begin{aligned}\phi^{(1)}&=s^2\sigma^2g\Theta^{(1)};\quad \phi^{(2)}=\tfrac{2}{3}s^2\sigma^2g\Theta^{(2)},\\ \Omega^{(1)}(r)&=s^2(2\pi kT/m)^{\frac{1}{2}}\Omega^{(1,2r+3)}\\ \Omega^{(2)}(r)&=\tfrac{2}{3}s^2(2\pi kT/m)^{\frac{1}{2}}\Omega^{(2,2r+3)}.\end{aligned} \tag{11}$$

There are no one-to-one relations of the type (11) for values of l greater than two.

We have already stated that the exact expression for α which is valid for a mixture of any two gases whose molecules are spherically symmetrical comes out of the theory as the ratio of two infinite determinants. In the case of isotopes, we may consider that the force fields of all the molecules are identical, since the force fields are determined entirely by the electronic configuration of the atoms or molecules. The first approximation to the exact expression, which is given by Enskog[*] and Chapman and Cowling,[†] may then be developed in a series of ascending powers of $(m_2-m_1)/(m_2+m_1)$. Only the first term of this series is important for most pairs of isotopes.

In the notation of Enskog, the first term of this series expansion is

$$\alpha=\frac{45}{2}\,\frac{m_2-m_1}{m_2+m_1}\,\frac{(2\Omega^{(1,7)}-5\Omega^{(1,5)})(15\Omega^{(1,5)}+2\Omega^{(2,7)})}{\Omega^{(2,7)}(165\Omega^{(1,5)}-60\Omega^{(1,7)}+12\Omega^{(1,9)}+16\Omega^{(2,7)})}. \tag{12}$$

Since this expression is homogeneous and of order zero in the $\Omega^{(l,k)}$'s, the expression for α in terms of the $\Omega^{(l)}(r)$'s used by Chapman and Cowling will differ only in the substitution of $(3/2)\Omega^{(2)}(2)$ for $\Omega^{(2,7)}$, and of $\Omega^{(1)}(r)$ for $\Omega^{(1,2r+3)}$.

We now proceed to the evaluation of this expression for certain simple molecular models, namely: elastic spheres, the inverse power model, the Sutherland model, and the Lennard-Jones model. The values of $\Theta^{(l)}$ which we shall use are sprinkled through the literature in a variety of notations. In the case of the elastic sphere and inverse power models, the derivations of the quantities $\Theta^{(l)}$ will be presented, not because the derivations are elsewhere unavailable, but because they may be given so simply and briefly that it seems worth while to give them as illustrations of the concrete meaning of the formulae.

THE ELASTIC SPHERE MODEL

We shall suppose each molecule to behave as a smooth, rigid, elastic sphere of diameter s. The molecules of species 1 have the mass m_1, and the molecules of species 2 have the mass m_2, where $m_1<m_2$.

Let us observe the collision between one molecule of species 1 and another of species 2.

---

[*] Reference 8, p. 51.

[†] Reference 9, p. 253.

We shall imagine ourselves at rest in the center of gravity system at a point removed a short distance from the place where the collision is about to occur. The spheres will enter our field of view moving in opposite directions along straight lines which are necessarily parallel. The perpendicular distance between the two lines is the impact parameter b. If b is greater than s, no collision will occur, and the angle of deflection θ is zero. For the case in which b is less than s, let us indicate the angle between the line of centers at the moment of impact and the previous direction of motion by χ. We clearly have

$$\sin\chi = b/s = \beta, \tag{13}$$

if we identify the diameter s with the s which appears in (6), and set $\sigma(\gamma)=1$. Since we are in the center of gravity coordinate system, the conservation of energy and momentum now requires that the spheres bounce off in a direction such that the angle between the new and old directions of motion is 2χ. This is perhaps most easily seen by noting that the components of velocity parallel to the line of centers at impact must be reversed in the collision, whereas the perpendicular components are unaltered. The angle of deflection is thus

$$\begin{aligned} \theta &= \pi - 2\chi, & \beta &\leqslant 1 \\ &= 0, & \beta &\geqslant 1. \end{aligned} \tag{14}$$

The integral in (7) is most easily evaluated by changing the variable of integration from β to $x=\cos\theta$. From (13) and (14) we have $dx=\frac{1}{4}\beta d\beta$, so that in this case the expression (7) for $\Theta^{(l)}$ becomes

$$\Theta^{(l)} = \tfrac{1}{4}\int_{-1}^{+1}\{1-P_l(x)\}dx = \tfrac{1}{2}, \quad l>0. \tag{15}$$

The integral of the latter term in the curly bracket vanishes for l greater than zero, since for this range of integration, the Legendre polynomials are orthogonal to $P_0(x)=1$.

The expression (8) for $\Omega^{(l,k)}$ with $\sigma=1$, $\Theta^{(l)}=\frac{1}{2}$, becomes simply

$$\Omega^{(l,k)} = \tfrac{1}{4}[\tfrac{1}{2}(k-1)]! \tag{16}$$

The expression corresponding to (16) in the notation of Chapman and Cowling† is

$$\Omega^{(l)}(r) = \frac{s^2}{8}\left[2-\frac{1+(-1)^l}{l+1}\right]\left(\frac{2\pi kT}{m}\right)^{\frac{1}{2}}(r+1)! \tag{17}$$

The substitution of (16) in (12) then yields for the elastic sphere model

$$\alpha = \frac{105}{118}\,\frac{m_2-m_1}{m_2+m_1}. \tag{I}$$

This result was first given by Furry, Jones and Onsager.[3]

THE INVERSE POWER MODEL

In this model the molecules are considered to be centers of a repulsive force which falls off as the inverse νth power of the distance of separation; the repulsive force is given by

$$F = \kappa/r^{\nu}, \tag{18}$$

where κ is a constant which determines the strength of the repulsion at a given distance.

In order to discuss the details of a collision between two such molecules, let us use a polar coordinate system r, ϕ, with its plane in the plane of motion of the molecules, and with its origin at one of the two molecules. In terms of the reciprocal radius $u=1/r$, the equation of motion is then[9a]

$$\left(\frac{du}{d\phi}\right)^2 = \frac{1}{b^2} - u^2 - \frac{2}{mg^2b^2}\int_r^{\infty} F dr, \tag{19}$$

where, as in (5), m is the reduced mass. We now subject g and b to the transformations (5) and (6), with

$$s = (\kappa/2kT)^{1/(\nu-1)}, \quad \sigma(\gamma) = \gamma^{-2/(\nu-1)}. \tag{20}$$

These transformations, along with the substitution $x=bu$ and the relation (18), reduce (19) to the form

$$\left(\frac{dx}{d\phi}\right)^2 = 1 - x^2 - \frac{2}{\nu-1}\left(\frac{x}{\beta}\right)^{\nu-1}. \tag{21}$$

The value of x which corresponds to the value of r at the distance of closest approach is the smallest positive root of

$$1 - x^2 - (2/(\nu-1))(x/\beta)^{\nu-1} = 0. \tag{22}$$

---

† Reference 9, p. 168.

[9a] W. F. Osgood, *Mechanics* (Macmillan, 1937), p. 109.

Let this root be indicated by $x_0(\beta)$. Then the angle which is swept out by the molecule as it moves from infinity to the point of closest approach is, according to (21),

$$\chi=\int_0^{x_0}\{1-x^2-(2/(\nu-1))(x/\beta)^{\nu-1}\}^{-\frac{1}{2}}dx. \tag{23}$$

This angle will be the same when measured in the center of gravity system. The angle of deflection θ is now, as in the case of elastic spheres, the quantity $\pi-2\chi$. By (23), the angle θ depends only on ν and β, and therefore $\Theta^{(l)}$ is a number which depends only on ν and l. Following Enskog,[8] we set

$$\Theta^{(l)}=A_l^{(\nu)}. \tag{24}$$

The numbers $A_l^{(\nu)}$ have been evaluated by Chapman[10] for $l=1$ and 2, and $\nu=3$, 5, 7, 9, 11 and 15, by means of numerical integration. The values obtained by Chapman are tabulated in Table I, except that the values for $\nu=9$ are those obtained by Hassé and Cook.[11]

There is a variety of notations for the quantities which we have indicated by $A_l^{(\nu)}$:

Enskog[8]		Chapman and Cowling[9]		Jeans,[12] Chapman[10]
$A_1^{(\nu)}$	$=$	$A_1(\nu)$	$=$	$I_1(\nu)/2\pi$
$A_2^{(\nu)}$	$=$	$3A_2(\nu)/2$	$=$	$3I_2(\nu)/2\pi.$

The quantities A_1 and A_2 which were used by Maxwell are the same as $I_1(5)$ and $I_2(5)$.

TABLE I. *Quantities for the inverse power model.*

ν	$A_1^{(\nu)}$	$A_2^{(\nu)}$	$f(\nu)$	$6f(\nu)/5$	$C(\nu)$
3	0.8115	1.825	1.500	1.800	0.714
4.5				1.58	0.80
5	0.4220	0.6541	1.2918	1.5501	0.8156
6				1.512	0.831
7	0.3855	0.5349	1.2335	1.4802	0.8431
8				1.454	0.854
9	0.3808	0.4956	1.1930	1.4316	0.8648
10				1.412	0.874
11	0.3835	0.4778	1.1631	1.3957	0.8823
12				1.382	0.890
13				1.370	0.896
14				1.359	0.901
15	0.3931	0.4642	1.1248	1.3498	0.9064
∞	0.5000	0.5000	1.0000	1.2000	1.0000

By virtue of (20) and (24), we now have

$$\Omega^{(l,\,k)}=\tfrac{1}{2}A_l^{(\nu)}\Gamma\left(\frac{k+1}{2}-\frac{2}{\nu-1}\right). \tag{25}$$

As we have noted before, the expression (12) for α is homogeneous and of order zero in the Ω's. This means that we may multiply $\Omega^{(l,\,k)}$ as given by (25) by any quantity whatever which does not depend on the indices l and k. One of the simple choices for such a multiplying factor is $(\Omega^{(1,5)})^{-1}$, which leads to

$$\begin{aligned}&\Omega^{(1,\,5)}\rightarrow 1;\\&\Omega^{(1,\,7)}\rightarrow 3-2/(\nu-1);\\&\Omega^{(1,\,9)}\rightarrow\{4-2/(\nu-1)\}\{3-2/(\nu-1)\};\\&\Omega^{(2,\,7)}\rightarrow 3f(\nu),\end{aligned} \tag{26}$$

where

$$f(\nu)=\{1-2/(3(\nu-1))\}A_2^{(\nu)}/A_1^{(\nu)}. \tag{27}$$

Substitution of (26) in (12) now yields for the inverse power law

$$\alpha=\frac{105}{118}\,\frac{m_2-m_1}{m_2+m_1}\,\frac{\nu-5}{\nu-1}C(\nu), \tag{II}$$

where

$$C(\nu)=\frac{59}{21}\,\frac{(15/f)+6}{43+16\{f-1/(\nu-1)+1/(\nu-1)^2\}} \tag{28}$$

is a function of ν whose value lies between 0.8 and 0.9 for values of ν between 5 and 15. The behavior of most gases corresponds to a value of ν within this range. The functions $f(\nu)$ and $C(\nu)$ are tabulated in Table I, as is also the function $(6/5)f(\nu)$ because of its importance in the determination of the coefficient of self-diffusion D, which is also important in the theory of separating isotopes by thermal diffusion. The inverse power model predicts

$$D=(6/5)f(\nu)\eta/\rho, \tag{29}$$

where η and ρ are the coefficient of viscosity and the density, respectively.

The result (II) was first obtained by Jones and Furry.[4]

Probably the most interesting aspect of (II) is the vanishing of α for $\nu=5$, that is, for Maxwellian molecules. For values of ν greater than

---

[10] S. Chapman, Memoirs and Proc. of the Manchester Lit. and Phil. Soc. **66**, No. 1 (1922).

[11] H. R. Hassé and W. R. Cook, Proc. Roy. Soc. **125**, 196 (1929).

[12] J. H. Jeans, *Dynamical Theory of Gases* (Cambridge, fourth edition, 1925).

TABLE II. *Values for various gases of n, of R_T according to the inverse power model, and of the Sutherland constant C.*

GAS	REFERENCE	T°K	n	$R_T(n)$	C
A	*a*	221	0.89	0.18	138
		333	0.80	0.34	147
		423	0.76	0.41	142
		498	0.71	0.51	150
		979	0.62	0.70	140
He	*a*	48	0.644	0.64	6
		123	0.646	0.64	21
		210	0.652	0.63	37
		333	0.669	0.59	66
		423	0.667	0.59	83
		1022	0.645	0.64	173
Ne	*a*	244	0.668	0.59	34
		333	0.657	0.62	61
		423	0.644	0.64	70
		498	0.644	0.64	82
		1030	0.623	0.69	128
Xe	*b*	347	0.92	0.13	250
		425	0.91	0.15	303
		525	0.83	0.29	254
Br_2	*c*	330	0.833	0.28	162
		475	0.985	0.02	496
Cl_2	*c*	293–523	$\sim$1.0	$\sim$0	$\sim$400
I_2	*c*	420	0.92	0.13	301
		482	1.04	−0.06	590
HCl	*a*	293–523	$\sim$1.0	$\sim$0	$\sim$350
HI	*c*	294–524	$\sim$1.0	$\sim$0	$\sim$400
O_2	*d*	333	0.775	0.38	126
		398	0.735	0.46	122
		448	0.731	0.47	132
		498	0.655	0.62	91
H_2	*d*	333	0.666	0.60	66
		398	0.694	0.54	96
		448	0.667	0.60	90
		498	0.679	0.57	108
N_2	*d*	333	0.737	0.46	102
		398	0.713	0.50	107
		448	0.687	0.55	103
		498	0.645	0.64	85
NH_3	*d*	291–573	$\sim$1.0	$\sim$0	$\sim$550
NO	*g*	308	0.79	0.36	128
		498	0.64	0.66	121
N_2O	*f*	325	0.97	0.05	277
		349–551	$\sim$0.87	$\sim$0.22	$\sim$255
CH_4	*e*	308	0.860	0.23	174
		348	0.825	0.30	168
		398	0.795	0.35	166
		448	0.769	0.40	165
		498	0.728	0.48	146
C_2H_6	*e*	308	0.958	0.07	260
		498	0.801	0.34	213
C_3H_8	*e*	308	0.965	0.06	267
		498	0.830	0.29	244
CO_2	*f*	325	0.92	0.13	240
		525	0.85	0.25	281
CO	*h*	347	0.72	0.49	96
		450	0.69	0.55	103
		525	0.63	0.68	98
SO_2	*i*	287–472	$\sim$1	$\sim$0	$\sim$425

[a] M. Trautz and H. Binkele, Ann. d. Physik **5**, 561 (1930).
[b] M. Trautz and R. Heberling, Ann. d. Physik **20**, 118 (1934).
[c] M. Trautz and H. Winterkorn, Ann. d. Physik **10**, 511 (1931).
[d] M. Trautz and R. Heberling, Ann. d. Physik **10**, 155 (1931).
[e] M. Trautz and K. Sorg, Ann. d. Physik **10**, 81 (1931).
[f] M. Trautz and F. Kurtz, Ann. d. Physik **9**, 981 (1931).
[g] M. Trautz and E. Gabriel, Ann. d. Physik **11**, 606 (1931).
[h] M. Trautz and A. Melster, Ann. d. Physik **7**, 409 (1930).
[i] M. Trautz and W. Weizel, Ann. d. Physik **78**, 305 (1925).
Note: Further data for high temperatures may be found in Tables 17 to 30 of M. Trautz and K. Sorg, Ann. d. Physik **7**, 427 (1930).

5, α is positive, whereas for values of ν less than 5, α is negative. It is very pleasing that this rather mysterious behavior may be explained by the elementary dimensional argument which is advanced by Frankel;[6] his argument shows that α is zero for Maxwellian molecules, and that the coefficient changes sign at $\nu=5$, being positive for ν greater than 5. Frankel's argument is no small achievement, since an elementary argument to show the existence and sign of the effect has long been desired.

The inverse power model, which is quite successful in explaining the temperature dependence of the elementary coefficients for most gases, is less successful in the case of thermal diffusion because the latter phenomenon is so much more sensitive to the molecular model; the value and sign of the thermal diffusion coefficient depend essentially on the nature of the intermolecular forces, and approximations which are adequate for the treatment of free-path phenomena do not suffice for thermal diffusion. Equation (II) indicates that α should be independent of the temperature; this is not confirmed, even approximately, by experiment.

Because no other model has the simplicity of this one, however, we shall probably continue to use it for some time to obtain an estimate of the value of α. In comparing the results of various molecular models, it is convenient to consider the ratio of the experimental or predicted value of α to that predicted by (I) for hard spheres. This ratio will be denoted by R_T. In the case of the inverse power model, we have

$$R_T = \frac{\nu-5}{\nu-1} C(\nu). \tag{30}$$

An estimate of an appropriate value of ν for a given gas may be obtained from its second virial coefficient, or more conveniently from the temperature variation of the viscosity. If the viscosity varies as T^n, a dimensional argument suffices to show that n and ν are related by

$$\nu = (2n+3)/(2n-1). \tag{31}$$

In terms of n, (30) becomes

$$\begin{aligned} R_T &= 2(1-n)C((2n+3)/(2n-1)) \\ &\cong 1.7(1-n). \end{aligned} \tag{32}$$

Using the relation (32), Brown[13] has in this manner given an estimate of the value of R_T for a number of gases. Brown's table, with rather extensive changes and additions, is given as Table II. The more precise of the relations (32) is tabulated in Table III.

The predictions of Table II should not be taken too seriously, particularly in those cases where very small values of R_T are predicted; in such cases the inverse power model is completely inadequate.

TABLE III. *R_T as a function of n according to the inverse power model.*

n	$\nu = \frac{2n+3}{2n-1}$	$R_T = 2(1-n)C(\nu)$	n	$\nu = \frac{2n+3}{2n-1}$	$R_T = 2(1-n)C(\nu)$
1.1	4.33	−0.159	0.85	6.71	0.252
1.075	4.48	−0.120	0.8	7.67	0.340
1.05	4.65	−0.081	0.75	9	0.432
1.025	4.81	−0.040	0.7	11	0.529
1.0	5	zero	0.675	12.42	0.580
0.975	5.21	0.041	0.65	14.32	0.632
0.950	5.44	0.082	0.6	21	0.74
0.925	5.71	0.124	0.55	41	0.86
0.9	6	0.166	0.5	∞	1.000

INTERMOLECULAR FORCES

It is now thought that the best simple approximation to the forces exerted between molecules of the noble gases can be expressed as the sum of an inverse seventh power attraction and an exponential repulsion.[14] For the range of radii which are concerned in molecular collisions at ordinary temperatures, a force of this kind can be approximated quite well by an equation of the form

$$F = \kappa/r^{\nu} - \kappa'/r^{\nu'}. \tag{33}$$

An equation of this form has been used by Lennard-Jones[15] in the theoretical interpretation of the equation of state observed for various gases. The implication in kinetic theory of such a law of force has never been completely worked out, however, because of the enormous mathematical complexity to which it leads. The special cases of $\nu = \infty$ and $\nu' = 3$ have been worked out as far as terms of the first order in the attractive force. These cases are, respectively, the Sutherland and the Lennard-Jones model.

THE SUTHERLAND MODEL

The molecules are considered to be smooth elastic spheres of diameter s, surrounded by an attractive field of force which decreases as the inverse νth power of the distance. The attractive force between two molecules is taken to be

$$F = -\kappa/r^{\nu}. \tag{34}$$

It follows from the work of James[16] that for this case

$$\Theta^{(1)} = \tfrac{1}{2}\{1 + 2i_1(\nu)\epsilon/(kT\gamma^2)\} \tag{35}$$

and

$$\Theta^{(2)} = \tfrac{1}{2}\{1 + 3i_2(\nu)\epsilon/(kT\gamma^2)\}, \tag{36}$$

---

[13] Harrison Brown, Phys. Rev. **57**, 242L (1940).

[14] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge, 1939).

[15] J. E. Lennard-Jones, Proc. Roy. Soc. **106**, 463 (1924).

[16] C. G. F. James, Proc. Camb. Phil. Soc. **20**, 447 (1921).

where $i_1(\nu)$ and $i_2(\nu)$ are functions of ν defined by

$$
\begin{aligned}
i_1(\nu) &= 2\int_0^1 y^{3-\nu}(1-y^2)^{\frac{1}{2}}\int_0^y x^{\nu-1}(1-x^2)^{-\frac{3}{2}}dxdy \\
&= \tfrac{1}{2}-4(\nu-1)\textstyle\sum_r \dfrac{r+1}{(2r+\nu)(2r+1)(2r+3)(2r+5)} \qquad r=0,\ 1,\ 2,\ \cdots
\end{aligned}
\tag{37}
$$

and

$$
\begin{aligned}
i_2(\nu) &= 4\int_0^1 y^{3-\nu}(2y^2-1)(1-y)^{\frac{1}{2}}\int_0^y x^{\nu-1}(1-x^2)^{-\frac{3}{2}}dxdy \\
&= \tfrac{1}{3}-8(\nu-1)\textstyle\sum_r \dfrac{r+1}{(2r+\nu)(2r+3)(2r+5)(2r+7)} \qquad r=0,\ 1,\ 2,\ \cdots
\end{aligned}
\tag{38}
$$

and where

$$\epsilon=\kappa/\{(\nu-1)s^{\nu-1}\} \tag{39}$$

is the negative potential energy of two molecules at the moment of contact. The s and σ of (6) have the same values as in the case of simple elastic spheres.

The insertion of (35) and (36) in (8) then yields

$$\Omega^{(1,k)}=\frac{1}{4}\left\{\left(\frac{k-1}{2}\right)!+2i_1(\nu)(\epsilon/kT)\left(\frac{k-3}{2}\right)!\right\} \tag{40}$$

and

$$\Omega^{(2,k)}=\frac{1}{4}\left\{\left(\frac{k-1}{2}\right)!+3i_2(\nu)(\epsilon/kT)\left(\frac{k-3}{2}\right)!\right\}. \tag{41}$$

The last two expressions, as well as (35) and (36), are valid only to terms in the first order of ϵ/kT. Our results will therefore be correct only when ϵ/kT is small compared with unity.

The relation obtained by substituting (40) and (41) in (12) is, for the Sutherland model

$$\alpha=\frac{105}{118}\frac{m_2-m_1}{m_2+m_1}\frac{(1-i_1(\nu)\epsilon/kT)(1+\{(5i_1(\nu)+2i_2(\nu))/7\}\epsilon/kT)}{(1+i_2(\nu)\epsilon/kT)(1+\{(39i_1(\nu)+16i_2(\nu))/59\}\epsilon/kT)}. \tag{III}$$

To terms of the first order in ϵ/kT, Eq. (III) is equivalent to

$$\alpha=\frac{105}{118}\frac{m_2-m_1}{m_2+m_1}(1-F(\nu)\epsilon/kT), \tag{III$'$}$$

where

$$F(\nu)=\{391i_1(\nu)+407i_2(\nu)\}/413, \tag{42}$$

whence

$$R_T=1-F(\nu)\epsilon/kT. \tag{43}$$

The error involved in ignoring higher powers of ϵ/kT is probably less in (III) than in (III′).

The quantities $i_1(\nu)$ and $i_2(\nu)$ have been evaluated by Enskog[7] and James,[16] and are tabulated along with $F(\nu)$ in Table IV. The notation used here is that of Chapman and Cowling, which is related to that of Enskog according to

$$\alpha(\nu)=i_1/i_2,\quad \delta(\nu)=3i_2/2. \tag{44}$$

The table of $i_1(\nu)$ and $i_2(\nu)$ given by Chapman and Cowling contains errors which are here corrected.

THE LENNARD-JONES MODEL

In this model the molecules interact according to a force law of the form (33), with $\nu'=3$. This choice of ν' is made not because of its physical appropriateness ($\nu'=7$ would be a better choice),

TABLE IV. *Quantities for the Sutherland model.*

ν	$i_1(\nu)$	$i_2(\nu)$	$F(\nu)$
2	$1/3=0.3333$	$4/15=0.2667$	0.5784
3	$(12-\pi^2)/8=0.2663$	$(\pi^2-8)/8=0.2337$	0.4824
4	$3-4\log 2=0.2274$	$8(3\log 2-2)/3=0.2118$	0.4240
5	$(3\pi^2-28)/8=0.2011$	$3(10-\pi^2)/2=0.1956$	0.3831
6	0.182	0.183	0.353
7	$1/6=0.1667$	$5(9\pi^2-88)/24=0.1722$	0.3275
9	$13/90=0.1444$	$7/45=0.1556$	0.2900

TABLE V. *Quantities for the Lennard-Jones model.*

ν	$B_1^{(\nu)}$	$B_2^{(\nu)}$	$g(\nu)$	$D(\nu)$
3	−0.812	−1.825	1.000	1.000
5	(−0.331)	−0.7244	0.589	0.653
7	−0.173	−0.4137	0.299	0.376
9	−0.077	−0.2474	0.126	0.218
11	−0.016	−0.1430	0.025	0.125
15	+0.0564	−0.0266	−0.081	0.088
∞	+0.2662	+0.3506	−0.266	−0.216

but because of its mathematical convenience. It follows from the work of Lennard-Jones,[17] and Chapman and Cowling, that

$$\Theta^{(l)}=A_l^{(\nu)}+B_l^{(\nu)}\kappa'/\{\kappa^{2/(\nu-1)}(2kT\gamma^2)^{(\nu-3)/(\nu-1)}\}, \tag{45}$$

where the A's are the quantities already introduced in (24), and the B's are quantities which must be determined by numerical quadrature. The $B_1^{(\nu)}$ and $B_2^{(\nu)}$ used here are related to the quantities used by Chapman and Cowling according to

$$B_1^{(\nu)}=\mathcal{B}_1(\nu),\quad B_2^{(\nu)}=3\mathcal{B}_2(\nu)/2. \tag{46}$$

The values of $B_1^{(\nu)}$ tabulated in Table V were determined by Chapman and Cowling, and the values of $B_2^{(\nu)}$ by Lennard-Jones.[17] The values of $B_1^{(5)}$, $B_1^{(3)}$, and $B_2^{(3)}$ are not given by the writers mentioned, but the latter two must clearly be the negatives of $A_1^{(3)}$ and $A_2^{(3)}$. The value of $B_1^{(5)}$ was then determined by interpolation in the expression $B_2/(B_1-0.05)$, which is nearly constant for $\nu=3$, 7, 9, and 11. It is assumed in stating (45) that s and σ have the same values as for the inverse power model.

From (8) and (45) we now have

$$\Omega^{(l,k)}=\tfrac{1}{2}A_l^{(\nu)}\Gamma\left(\frac{k+1}{2}-\frac{2}{\nu-1}\right)+\tfrac{1}{2}B_l^{(\nu)}\frac{\kappa'}{\kappa^{2/(\nu-1}2kT^{(\nu-3)/(\nu-1)}}\left(\frac{k-3}{2}\right)! \tag{47}$$

and substitution of this expression in (12) gives for the Lennard-Jones model

$$\alpha=\frac{105}{118}\frac{m_2-m_1}{m_2+m_1}C(\nu)\left(\frac{\nu-5}{\nu-1}+\frac{\kappa' g(\nu)}{\kappa^{2/(\nu-1)}(2kT)^{(\nu-3)/(\nu-1)}}\right)\left(1+\frac{\kappa D(\nu)}{\kappa^{2/(\nu-1)}(2kT)^{(\nu-3)/(\nu-1)}}\right), \tag{IV}$$

where

$$g(\nu)=-B_1/\{A_1\Gamma(3-2/(\nu-1))\} \tag{48}$$

and

$$D(\nu)=g(\nu)\left\{\frac{10B_2/(B_1f)-15}{15+6f}+\frac{117+32B_2/B_1}{177+48\{f-1/(\nu-1)+1/(\nu-1)^2\}}\right\} \tag{49}$$

and $f(\nu)$ is the same function that arose in the case of the inverse power model. The functions $g(\nu)$ and $D(\nu)$ are also tabulated in Table V. Equations (45), (47) and (IV) are correct only to the first order in $\kappa'/\{\kappa^{2/(\nu-1)}(2kT)^{(\nu-3)/(\nu-1)}\}$.

Equation (IV) has the property that it predicts α to be independent of temperature for a value of ν slightly less than 15; for smaller values of ν, it indicates that α will *increase* as the temperature decreases.

THE LIMITATIONS INVOLVED IN EQUATION (12)

It has already been stated that (12) is the first approximation to the exact result as given by the ratio of two infinite determinants. We may obtain a rough estimate of the error involved in the first approximation by the following considerations.

---

[17] J. E. Lennard-Jones, Proc. Roy. Soc. **106**, 441 (1924).

It was shown by Enskog[18] in 1912 that for the case in which both the mass and the concentration of the lighter molecules are negligible in comparison with the corresponding quantities for the heavier particles, the *exact* value of α for the inverse power model is

$$\alpha=\frac{1}{2}\,\frac{\nu-5}{\nu-1}. \tag{50}$$

On the other hand, it is shown by Chapman and Cowling that the value of α given by the first approximation is in this case

$$\alpha=\frac{\nu-5}{\nu-1}\bigg/\left\{5-\frac{4}{5}\,\frac{(3\nu-5)(\nu+1)}{(\nu-1)^2}\right\}. \tag{51}$$

Comparison of (50) and (51) indicates that the first approximation gives 10/13 of the exact result for elastic spheres, 8/9 of the exact value for $\nu=9$, and a vanishing error as ν approaches 5.

This limiting case, the Lorentzian case, is a particularly bad case for all of the coefficients which refer to a mixture of two gases, however. The first approximation gives a result which for elastic spheres is about 98 percent of the exact result for the coefficients of conductivity, viscosity, and self-diffusion of a simple gas, whereas in the Lorentzian case, the first approximation is in error by 8, 12, and 15 percent, respectively. If, then, one wishes to draw an analogy between the coefficient of self-diffusion and the thermal diffusion coefficient of isotopes, one might make the slightly enlightened guess that the expression (12) is about 5 percent low for elastic spheres, with a smaller error for smaller values of ν. This is at best only a guess.

The theory of Enskog which we have been using is, of course, a purely classical theory. The introduction of quantum mechanics changes the statistics obeyed by the molecules, and requires that the general theory of Enskog be redone from the beginning. This has been done by Hellund and Uehling.[19] The difference between classical and quantum statistics is, however, of negligible importance for gases at ordinary temperatures and pressures. The chief change brought about by quantum mechanics lies in the calculation of the collision cross sections, and this change is easily made within the framework of Enskog's theory; the quantities $\Theta^{(l)}$ and $\Omega^{(l,k)}$ which are to be inserted in (12) should be computed quantum-mechanically. Even here the difference between the classical and quantum cross sections is small, except possibly for hydrogen and helium. The most important quantum-mechanical effect is the fact that the wave functions for a collision between identical and nonidentical particles must have different symmetries, with the result that the cross sections for a collision between identical and between nonidentical particles are not equal. This effect was pointed out by Hellund and Uehling.[19]

Professor Mott-Smith (University of Illinois) has worked out the details of this symmetry effect for elastic spheres (private communication), and the writer hopes that he will soon publish his interesting considerations.

Comparison with Experiment

Direct experimental determinations of the thermal diffusion coefficient of isotopes are very few in number. Nier[20, 21] has measured the value of α over two temperature ranges for methane, and over three temperature intervals for neon. His results are shown in Table VI. The quantity R_T is the ratio of the observed value of α to that predicted by (I).

Hassé and Cook[11] give viscosity data for neon at nine temperatures in the range 91.66°–717.6°K. The values of n obtained from these data for the temperature ranges 91.66°–194.7°, 91.66°–288.1°, and 288.1°–575.1°, are, respec-

Table VI. *Values of α determined experimentally by Nier.*

Species 1	Species 2	Temp. Range	α	R_T
$C^{12}H_4$	$C^{13}H_4$	296°–728°	$0.0080\pm\sim5\%$	0.30
		296°–573°	$0.0074\pm\sim5\%$	0.27
Ne^{20}	Ne^{22}	283°–617°K	$0.0302\pm\ 2\%$	0.71
		90°–294°K	$0.0188\pm\ 2\%$	0.44
		90°–195°K	$0.0165\pm\ 8\%$	0.39

---

[18] D. Enskog, Ann. d. Physik **38**, 731 (1912).

[19] E. J. Hellund and E. A. Uehling, Phys. Rev. **56**, 818 (1939).

[20] A. O. Nier, Phys. Rev. **56**, 1009 (1939).

[21] A. O. Nier, Phys. Rev. **57**, 338 (1940).

tively, 0.745, 0.716, and 0.676. According to the inverse power model the values of R_T which correspond to these values of n, are by Table III, 0.44, 0.50, and 0.58. These values are to be compared with the experimental values of R_T for roughly the same temperature ranges: 0.39, 0.44, and 0.71. Of course, the fact that n varies with temperature at all indicates that the inverse power model is lacking.

The value of R_T as predicted by viscosity data may also be obtained from the Sutherland model. According to the work of James,[16] the constant C which appears in the Sutherland equation for the viscosity is given by

$$C=i_2(\nu)\epsilon/k. \tag{52}$$

If we assume $\nu=7$, the value predicted by the quantum theory of van der Waals forces, we find from (III) and (52) that

$$R_T=\frac{(1-0.9679\ C/T)(1+0.9771\ C/T)}{(1+C/T)(1+0.9110\ C/T)}, \tag{53}$$

$$\cong\frac{1-0.98\ C/T.}{1+0.92\ C/T}. \tag{54}$$

The experimental data of Hassé and Cook for neon may be fitted rather well over the entire range of temperature by the Sutherland relation with $C=60°$. With this value of C, the values of R_T predicted by (54) for the temperatures 142°, 192°, and 450°, are, respectively, 0.42, 0.54, and 0.77. These values agree with experiment somewhat better than in the case of the inverse power model. The same difficulty faces us here, however, that has led to the rejection of the Sutherland model as being more than a convenient interpolation formula; namely, the fact that the value of $\epsilon/k=350°$, which by (52) corresponds to $C=60°$, is much larger than the value which is indicated by other and more reliable measurements of this quantity, such as the latent heat of vaporization of the crystalline solid, and measurements of the second virial coefficient. According to Buckingham,[22] such considerations point quite definitely to a value of ϵ/k of about 30° or 40°.

Buckingham has been able to fit the experimental measurements of the second virial coefficient of neon by a formula of the Lennard-Jones type (33) with $\nu'=7$, and with a value of ν which may vary in the range 9 to 15. For all of these values of ν, however, the Lennard-Jones model (with $\nu'=3$) predicts that α will fall or at least not rise as the temperature increases. Since this behavior is not at all in agreement with experiment, we must conclude that the Lennard-Jones model is not useful in connection with thermal diffusion in the case of neon. Whether this failure is due to the choice of $\nu'=3$, or whether the difficulty is more deeply seated, the writer is unable to say or guess.

The methane molecule does not possess a spherically symmetrical field of force, and we should therefore not expect that the theory of Enskog, which holds only for spherically symmetrical molecules, would give results in close agreement with experiment. The inverse power model is particularly inappropriate in application to methane, inasmuch as the value of n varies between 1.028 and 0.728 in the temperature range 91.5°–522.8°K. From Table II, we find that for the temperatures 448° and 498°, the values of n are 0.77 and 0.73; we then find from Table III that the corresponding values of R_T are 0.40 and 0.49. These values may be compared with the experimental results 0.27 and 0.30. The Sutherland equation fits the viscosity data much better, with C equal to about 160°. With this value of C, the values of R_T predicted by (54) for the temperatures 430° and 512° are 0.48 and 0.54, which are in very poor agreement with experiment.

The comparison of theory with experiment is sufficiently good in the case of neon to encourage us that we are on the right track, but on the other hand is sufficiently poor to indicate that much remains to be done. In particular, we are faced with the task of working out the predictions of more complicated molecular models than those which have been considered up to the present time. The models discussed in the present paper have proved quite satisfactory for the treatment of free-path phenomena, but they are not sufficiently precise to meet the test of thermal diffusion.

---

[22] R. A. Buckingham, Proc. Roy. Soc. **168**, 264 (1938).

ACKNOWLEDGMENT

On the same day that the manuscript of the present paper was handed to the secretary for retyping, Professor W. H. Furry of this department received a letter from Professor H. M. Mott-Smith (University of Illinois) which contained much of the material in this paper. In subsequent correspondence it was suggested by Professor Mott-Smith that the writer proceed with publication.

The writer would like to thank Professor W. H. Furry for helpful comments on the manuscript.

JULY 15, 1940 PHYSICAL REVIEW VOLUME 58

On Directional Correlation of Successive Quanta

DONALD R. HAMILTON*
Harvard University, Cambridge, Massachusetts

(Received May 6, 1940)

A theoretical investigation shows that there should be a correlation between the directions of propagation of the quanta emitted in two successive transitions of a single radiating system. This correlation is described by a function $W(\theta)$ which gives the relative probability that the second quantum will be emitted at an angle θ with the first; W is determined by the angular momenta of the three levels involved in the two transitions and by the multipole order of the radiation emitted in these transitions. The explicit forms of W for all angular momenta and for dipole and quadrupole radiation are given; experimental determination of W in any given case should limit these factors to a small number of possibilities. This has particular interest as a means of investigating the nuclear energy levels involved in γ-radiation; here W should be observable by measuring the variation with θ of gamma-gamma coincidence counting rates.

INTRODUCTION

It has been suggested by Dunworth[1] that there might be some correlation between the directions of emission of two successive gamma-quanta emitted by a nucleus when this nucleus passes from an excited level A to the ground level C, by way of a definite intermediate level B. This suggestion was pointed out to the author by Dr. I. A. Getting in connection with the latter's search for such a correlation by means of gamma-gamma coincidence experiments. The present paper is a theoretical discussion of the question.

The problem of resonance radiation[2] is basically similar to the present one, since both are concerned with the radiation from an excited level in which a system finds itself as the result of an anisotropic process. This process is, in the first case, an absorption from a unidirectional (and usually polarized) beam of light; in the second, an emission of a quantum in one particular direction.

An explicit formulation involves the transitions between the $(2J+1)$ m-states of each level. ($\mathbf{J}$ is total angular momentum of a level, the m are the eigenvalues of J_z.) We designate the states of the nucleus as A_l, B_n, C_p; subscripts are values of m. For a given multipole order of the transition AB (or BC), the angular distribution of quanta emitted in a transition A_lB_n (or B_nC_p) depends only on $|\Delta m|$, where $\Delta m \equiv (p-n)$ or $(n-l)$; hence we write these distributions as $\varphi_{|n-l|}(\theta)$ and $f_{|p-n|}(\theta)$. The relative probabilities of the various transitions A_lB_n and B_nC_p are denoted by g_{ln} and G_{np}, respectively. Now suppose that the nuclei are initially oriented at random—i.e., all states A_l equally populated for any arbitrary axis of quantization. In the transition AB, the sum of the probabilities of all components A_lB_n with a given Δm is independent of Δm; hence the probability that a quantum emitted at an angle θ_1 with the axis has been emitted in a transition with given Δm is proportional to $\varphi_{|\Delta m|}(\theta_1)$. The relative populations of the B_n are then $\sum_l g_{ln}\varphi_{|n-l|}(\theta_1)$ and the angular distribution of radiation from the decay of state B_n alone is $\sum_p G_{np}f_{|p-n|}(\theta_2)$.

---

* Society of Fellows.

[1] J. V. Dunworth, Rev. Sci. Inst. **11**, 167 (1940).

[2] V. F. Weisskopf, Ann. d. Physik **9**, 27 (1931).