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Diffusion Slip Velocity: Theory and Experiment

H. Lang

Max-Planck-Institut für Strömungsforschung, Göttingen, Germany

and S. K. Loyalka

Nuclear Engineering Department, University of Missouri, Columbia, Missouri

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A theoretical and experimental study of the phenomenon of diffusion slip in a binary gas mixture is presented. To provide some physical insight, a very general variational expression given earlier by Loyalka is rederived via the use of a method developed recently. The case of Maxwellian diffuse specular reflection is considered in some detail and the inadequacies of previous theoretical results based on the early arguments of Maxwell, kinetic models and simple intermolecular force laws are discussed. Although in general, the variational results (or the equivalent results given here) together with the assumptions of Lennard Jones potential and diffusive reflection give a satisfactory agreement with the available experimental data, it is found that for isobaric (isotopic) mixtures, in the choice of the intermolecular and gas-surface interaction parameters special care should be taken in that the results are quite sensitive to small variations in the values of these parameters.

I. Introduction

Since the classical work of Maxwell[1] it is known that velocity or temperature gradients near walls lead to the familiar surface effects of viscous and temperature slip in the range of sufficiently low pressures. These phenomena have been studied quite well both experimentally and theoretically. In the flow of gas mixtures, diffusive slip occurs due to the concentration gradient tangential to the wall. In contrast to the phenomena mentioned earlier, little was known about this almost unstudied effect. The diffusive slip was first discussed by Kramers and Kistemaker[2]. These authors obtained an expression for the diffusive slip by using Maxwell's momentum balance at the wall and established the existence of diffusive slip by measuring the pressure difference that results in a closed system. Since that time, this effect has been studied, both experimentally and theoretically[3–14] by several authors. The earlier theoretical treatments, however, included only the effects of the masses and the accommodation coefficients.

A theoretical relation for the diffusion slip coefficient σ_{12} including the effects of intermolecular

Reprint requests to Dr. H. Lang, Max-Planck-Institut für Strömungsforschung, D-3400 *Göttingen*, Böttingerstraße 6/8.

forces was given first by BROCK[5] (using an improved ansatz for the Chapman-Enskog approximation far from the wall) and by ZHDANOV[6] (using Grad's thirteen moment equations for gas mixtures). Since both authors apply, in principle, only Maxwell's momentum balance, an essential improvement on the formula given by Kramers and Kistemaker was not obtained (this point will be discussed in detail later). All this work (up to 1969) has been summarized in a very interesting article by MASON and MARRARO[3], who also discuss the dusty gas approach.

The limitations and very approximate reasonings involved in the work of Brock and Zhdanov were realized, more recently, by some authors. Thus LANG[7] obtained an expression for the diffusion slip by solving a modelled linearized Boltzmann equation (for a gas-mixture) via the use of half-range moment methods. The same model was used almost simultaneous by SHENDALMAN[9] who employed a variational approach. Although both these results provide considerable insight into the phenomenon and, in general, give fairly good agreement with the experiment results, there are several situations in which important deviations from experimental results are noted. Essentially, the kinetic models considered by these authors had not included the detailed effects of intermolecular forces in a fully satisfactory way. It became clear that the solution should be based on the solution of the appropriate linearized Boltzmann equation itself.

BRETON[10,11] took a useful step in this direction by attempting a half-range moment solution of the Boltzmann equation for a binary gas-mixture. Although Breton was thus able to improve the previous results, his work again suffered from some major handicaps. First, he was able to obtain explicit results only for the rigid spheres, a rather unsatisfactory situation as the slip phenomena of this type can be expected to be sensitive to the type of the intermolecular force law. Next, the half-range moment method leads to some very cumbersome algebra and computations and still there is no simple way to assess the accuracy of these results.

Most recently LOYALKA[12] considered this problem by applying a variational technique to the linearized Boltzmann equation for a multicomponent gas mixture and boundary conditions of a very general type. This result is certainly the most satisfactory derived till to-date as it is applicable to any intermolecular force law and any type of gas-surface interaction. Also the expression possesses the virtues of remarkable simplicity and accuracy. Although the accuracy of this expression was verified by comparing these results with some exact results (in some limiting cases), detailed numerical results based on this expression have not been reported so far.

Thus it seemed to us that it would be of some interest to report a detailed study of the theoretical and experimental work on the diffusion slip problem. It may also be noted that very recently Loyalka has also proposed a modification of Maxwell's method for the calculation of slip quantities[13]. We would also like to illustrate the application of this approach to the present problem as it shows quite clearly the limitations of the results obtained by Kramers-Kistemaker, Brock, Zhdanov, etc.

In our discussions of the experimental papers we shall focus our attention especially upon investigations of the influence of collision cross section on the diffusive slip. SCHMITT and WALDMANN[1] studied the movement of silicon droplets suspended in a non-uniform, but isothermal, gas mixture due to existing concentration gradients. They conclude that the aerosol particle velocity in a binary gas mixture, v_{d}, in which the two gases are diffusing into each other is

$$v_{\mathrm{d}} = -\,\sigma_{12} D_{12}\,(\mathrm{d}x_1/\mathrm{d}z) \tag{1}$$

where σ_{12} represents the diffusion slip factor[4] (see Section II), D_{12} the binary diffusion coefficient, and x_i the mole fraction. The gaseous average molecular velocity is taken to be zero.

Substituting the elementary expression given be KRAMERS and KISTEMAKER[2] into Eq. (1) leads to

$$v_{\mathrm{d}} = -\,\frac{m_1^{1/2} - m_2^{1/2}}{x_1 m_1^{1/2} + x_2 m_2^{1/2}}\, D_{12}\, \frac{\mathrm{d}x_1}{\mathrm{d}z}\,. \tag{2}$$

This means that the particle moves in the direction of the diffusive flux of the heavier gas molecules. These authors found the opposite behaviour for the gas pair N_2/C_2H_6. A large diffusiophoretic velocity of large droplets was especially noticeable in isobaric mixtures such as N_2/C_2H_4 and CO_2/C_3H_8. By fitting their experimental data, Schmitt and Waldmann proposed an empirical expression for the diffusion slip factor

$$\sigma_{12} = 0.95\,\frac{m_1 - m_2}{m_1 + m_2} - 1.05\,\frac{d_1 - d_2}{d_1 + d_2} \tag{3}$$

where d_1 and d_2 are the molecular diameters of the components due to the corresponding Lennard-

Jones (6—12) potentials[15]. According to the relation (3) a sign reversal of σ_{12} for Ar/CO_2 is obtained. Therefore, these authors also investigated the pressure difference which arises for the gas pair Ar/CO_2 for counterdiffusion through a capillary in a closed system[4] and found their experimental values in good agreement with the empirical relation (3). Similarly, by using the diffusion pressure effect[16], in our laboratory, we found a sign reversal for the gas pairs Ar/CO_2 and C_2H_4/Ne in the counter-diffusion through capillaries and through glas frits[8]. Furthermore, the isobaric mixture N_2/C_2H_4 was investigated by Breton[10] using a steady-state flow method (Wicke-Kallenbach-type) and porous membranes of fritted metal and, again, his results are consistent with Eq. (3). Breton also derived an approximate formula which is nearly consistent with Eq. (3) for small differences in masses and collision cross sections of the components and for $x_1 = x_2 = 1/2$.

It is the object of this article to give a critical survey of the theoretical and experimental results and present a comparison between them. In the next section, to clarify the difference between the elementary result using Maxwell's argumentation and the general relation for the diffusion slip coefficient, a modification of Maxwell's original consideration is used. This later result is in precise agreement with the variational results reported earlier and also sheds some light on inadequacies of the results based on Maxwell's argumentation. Further, we give a fairly extensive evaluation of the numerical results obtained by the use of all the various theoretical expressions obtained till to-date and we compare these results with the experimental data obtained by various investigators.

II. Theoretical Results for the Diffusion Slip Factor

For a detailed discussion of the theoretical results we find it convenient to discuss first some useful definitions and relations. Thus, for the pure diffusion transport (no pressure gradient) of a binary mixture in the continuum (hydro-dynamic) regions in a capillary, we have the diffusion equations:

$$\begin{aligned} J_{1d} &= -D_{12}(dn_1/dz) + x_1 J_d\,, \\ J_{2d} &= -D_{12}(dn_2/dz) + x_2 J_d\,, \\ J_d &= J_{1d} + J_{2d} \end{aligned} \tag{4}$$

where J_{id} represents the particle flux density of species i, n_i the particle density, and $x_i = n_i/n$ the mole fraction. Since the pressure is uniform, the mean velocities u_i of the components are nearly constant over the cross-section of the capillary. Thus, the equations may be written in one dimension. Near the walls, however, a small Knudsen layer of thickness of the order of a mean free path of the components is present, but this can be neglected in Eq. (4).

Obviously, the total flux density J_d cannot be calculated from Eq. (4) without a knowledge of the flux ratio $-J_{2d}/J_{1d} = m^*$. Graham (1833) found experimentally that the flux ration m^* is given by

$$m^* = -(J_{2d}/J_{1d}) = (m_1/m_2)^{1/2} \tag{5}$$

where m_i are the molecular weights.

(Note that this Graham's law of diffusion is not identical with Graham's law of effusion in the Knudsen region[3].)

When Eq. (5) is substituted into (4), the total particle flux density J_d is given by

$$J_d = \frac{m_1^{1/2} - m_2^{1/2}}{x_1 m_1^{1/2} + x_2 m_2^{1/2}} D_{12} \frac{dn_1}{dz}\,. \tag{6}$$

The total mass flux density M_d is then

$$M_d = m_1 J_{1d} + m_2 J_{2d} = \frac{m_2 m_1^{1/2} - m_1 m_2^{1/2}}{x_1 m_1^{1/2} + x_2 m_2^{1/2}} D_{12} \frac{dn_1}{dz}\,. \tag{7}$$

The diffusion slip factors σ_{ij}, $\sigma_{ij}^{(v)}$ are defined as[4]

$$\begin{aligned} J_d &= \sigma_{12} D_{12}(dn_1/dz) = \sigma_{21} D_{12}(dn_2/dz) \quad (8) \\ M_d &= m\sigma_{12}^{(v)} D_{12}(dn_1/dz) = m\,\sigma_{21}^{(v)} D_{12}(dn_2/dz) \end{aligned}$$

where

$$m = x_1 m_1 + x_2 m_2\,.$$

From the definitions (7) and Fick's law it follows immediately[4] that

$$\sigma_{12} = \sigma_{12}^{(v)} + (m_1 - m_2)/m\,. \tag{9}$$

When Eqs. (6) and (7) are compared with the definitions (8), we get

$$\sigma_{12} = -\sigma_{21} = \frac{m_1^{1/2} - m_2^{1/2}}{x_1 m_1^{1/2} + x_2 m_2^{1/2}}\,, \tag{10a}$$

$$\sigma_{12}^{(v)} = -\sigma_{21}^{(v)} = \frac{1}{m}\,\frac{m_2 m_1^{1/2} - m_1 m_2^{1/2}}{x_1 m_1^{1/2} + x_2 m_2^{1/2}}\,. \tag{10b}$$

The relations (10) correspond to the diffusion slip formulas suggested by KRAMERS and KISTEMAKER[2], who used a momentum balance consideration. Thus, it follows from the statement that the total momentum flux to the wall must be zero (no pressure gradient)[3] that

$$\tfrac{1}{4} n_1 \bar{v}_1 m_1 u_1 \alpha_1 + \tfrac{1}{4} n_2 \bar{v}_2 m_2 u_2 \alpha_2 = 0 \qquad (11)$$

where, $u_i = J_{i\mathrm{d}}/n_i$ also, α_i are the momentum accommodation coefficients for Maxwellian boundary conditions and $\bar{v}_i$ the mean thermal velocities of the components. It follows from Eq. (11)

$$m^* = -(m_1/m_2)^{1/2}\,\alpha_1/\alpha_2 \,. \qquad (12)$$

Thus Graham's law of diffusion is obtained ($\alpha_1 = \alpha_2 = 1$). Although the flux ratio (11) is accurate in the limit of large Knudsen numbers (as long as the mean free paths of the components are much larger than the diameter and smaller than the length of the capillary), this must not generally be expected in the continuum limit. There, gas collisions are predominate and a more general form of Graham's law of diffusion should be assumed

$$m^* = -(m_1/m_2)^{1/2}\,\theta_1/\theta_2 \qquad (13)$$

where the parameters θ_i are complicated functions of intermolecular forces, masses, accommodation coefficients, and concentrations of the species.

The momentum transfer balance, corresponding to Eq. (13) is written as

$$\tfrac{1}{4} n_1 \bar{v}_1 u_1 \theta_1 + \tfrac{1}{4} n_2 \bar{v}_2 u_2 \theta_2 = 0 \,. \qquad (14)$$

The diffusion slip factors σ_{12}, $\sigma_{12}^{(\mathrm{v})}$ can be obtained from (14) as

$$\sigma_{12} = \frac{m_1^{1/2}\theta_1 - m_2^{1/2}\theta_2}{x_1 m_1^{1/2}\theta_1 + x_2 m_2^{1/2}\theta_2}\,, \qquad (15\mathrm{a})$$

$$\sigma_{12}^{(\mathrm{v})} = \frac{1}{m}\,\frac{m_2 m_1^{1/2}\theta_1 - m_1 m_2^{1/2}\theta_2}{x_1 m_1^{1/2}\theta_1 + x_2 m_2^{1/2}\theta_2}\,. \qquad (15\mathrm{b})$$

If we start from the elementary momentum balance Eq. (11) we obtain the relations (15a, 15b) with $\theta_1 = \alpha_1$ and $\theta_2 = \alpha_2$. This special case will be designated by $\sigma_{12,\mathrm{KK}}'$, $\sigma_{12}^{(\mathrm{v})}{}_{,\mathrm{KK}}$ (the index K.K. indicates Kramers-Kistemaker-value).

Although the final results given here were previously obtained[12], we now present a derivation of the diffusion slip factor using a modification of Maxwell's method[13]. This is done in a simple manner and leads to a better understanding of the way in which intermolecular forces enter into the diffusive slip.

We consider a semi-infinite expanse of a gas mixture bounded by a flat plate located at $x = 0$ and lying in the z direction. The gas is at a constant total pressure and temperature. The flow in the z direction is caused by the presence of partial concentration gradients,

$$k_i = \frac{1}{n_i}\,\frac{\partial n_i}{\partial z} \qquad (16)$$

tangential to the wall. The mass velocity far from the wall is independent of the x coordinate and equal to its extrapolation to the wall, the diffusion slip velocity q_{asy}. From the definitions Eqs. (8) we obtain

$$q_{\mathrm{asy}} = (M_{\mathrm{d}}/\varrho) = \sigma_{12}^{(\mathrm{v})} D_{12}\,(\mathrm{d}x_1/\mathrm{d}z)\,. \qquad (17)$$

The average speeds are much smaller than the thermal speed and the partial concentration gradients are assumed to be small and thus, the linearized form of the Boltzmann equations can be considered

$$c_x\,(\partial \boldsymbol{\Phi}(x, \boldsymbol{c})/\partial_x) = \mathbf{L}\boldsymbol{\Phi}(x, \boldsymbol{c}) - \boldsymbol{k}\,c_z \qquad (18)$$

where $\mathbf{L}$ is the linearized Boltzmann collision operator for the gas mixture, $\boldsymbol{\Phi}(x, \boldsymbol{c})$ is a measure of the perturbation in the distribution function $\boldsymbol{f}(x, \boldsymbol{c})$ from the local Maxwellian $\mathbf{f}^{(\mathrm{M})}(x, \boldsymbol{c})$, i.e.

$$\begin{aligned} \boldsymbol{f} &= \mathbf{f}^{(\mathrm{M})}(\boldsymbol{1} + \boldsymbol{\Phi}(x, \boldsymbol{c})) \\ &= \mathbf{f}^{(0)}(\boldsymbol{1} + \boldsymbol{k}\,z + \boldsymbol{\Phi}(x, \boldsymbol{c})) \end{aligned} \qquad (19)$$

and $\boldsymbol{f}(x, \boldsymbol{c})$ and $\boldsymbol{\Phi}(x, \boldsymbol{c})$ are vector functions with components $f_i(x, \boldsymbol{c})$ and $\Phi_i(x, \boldsymbol{c})$, respectively.

$\mathbf{f}^{(0)}$ is a diagonal matrix such that

$$f_{ij}^{(0)} = n_{i,0}\,(m_i/2\,n\,k\,T)^{3/2} \exp\{-\,m_i\,c^2/2\,k\,T\}\,\delta_{ij} \qquad (20)$$

where δ_{ij} is the Kronecker delta and $\boldsymbol{c} = (c_x, c_y, c_z)$ is the molecular velocity.

For $x \to \infty$, the function $\boldsymbol{\Phi}(x, \boldsymbol{c})$ has the form

$$\lim_{x\to\infty} \boldsymbol{\Phi}(x, \boldsymbol{c}) = \frac{1}{k\,T}\,\boldsymbol{m}\,c_z\,q_{\mathrm{asy}} + c_z\,\boldsymbol{\Phi}_{\mathrm{d}}(c) \qquad (21)$$

where $\boldsymbol{m}$ is a vector with components m_i, q_{asy}, at present an unknown constant, is the asymptotic mass velocity of the mixture and $c_z\,\boldsymbol{\Phi}_{\mathrm{d}}(c)$ is the solution of the Chapman Enskog diffusion equation

$$\boldsymbol{k}\,c_z = \mathbf{L}(c_z\,\boldsymbol{\Phi}_{\mathrm{d}}(c))\,. \qquad (22)$$

Further, $c_x c_z \boldsymbol{\Phi}_p(c)$ is the solution of the Chapman-Enskog viscosity equation

$$\frac{1}{k\,T}\,\boldsymbol{m}\,c_x\,c_z = \mathbf{L}(c_x\,c_z\,\boldsymbol{\Phi}_p(c))\,. \qquad (23)$$

It is useful to consider a Hilbert space in which the scaler product is determined by

$$(\varrho_1(x,\boldsymbol{c}),\, \varrho_2(x,\boldsymbol{c})) = \int \mathrm{d}\boldsymbol{c}\, \varrho_1(x,\boldsymbol{c})\, \mathrm{f}^0\, \varrho_2(x,\boldsymbol{c})\,. \tag{24}$$

Thus, the Chapman Enskog diffusion term $c_z \boldsymbol{\Phi}_\mathrm{d}(c)$ satisfies

$$(\boldsymbol{m}\, c_z,\, c_z \boldsymbol{\Phi}_\mathrm{d}(c)) = 0 \tag{25}$$

also, we have

$$(\boldsymbol{m}\, c_z,\, \boldsymbol{k}\, c_z) = 0$$

and

$$(c_x c_z \boldsymbol{\Phi}_p(c),\, \boldsymbol{k}\, c_z) = 0\,. \tag{26}$$

Let us consider the scalar product (24) of Eq. (18), respectively on $\boldsymbol{m} c_z$ and $c_x c_z \boldsymbol{\Phi}_p(c)$. Using Eqs. (22), (25), (26) and the asymptotic relation for $\boldsymbol{\Phi}$ from Eq. (21) it follows[12] that

$$(\boldsymbol{m}\, c_x c_z,\, \boldsymbol{\Phi}) = 0 \tag{27}$$

and

$$(c_x c_z \boldsymbol{\Phi}_p(c),\, c_x \boldsymbol{\Phi}) = \frac{q_\mathrm{asy}}{k\,T}\,(c_x^2 c_z \boldsymbol{\Phi}_p(c),\, \boldsymbol{m}\, c_z) + (c_x^2 c_z \boldsymbol{\Phi}_p(c),\, c_z \boldsymbol{\Phi}_\mathrm{d}(c))\,. \tag{28}$$

The derivation of the diffusion slip formula given by Kramers and Kistemaker is based only on relation (27) (cp. Eq. (11)] of the vanishing of total momentum flux at the wall. In addition to Eq. (27), the Eq. (28) is another condition that the perturbation $\boldsymbol{\Phi}$ must satisfy.

To determine the unknown q_asy we make an assumption about $\boldsymbol{\Phi}$ at the wall. Let us write $\boldsymbol{\Phi}$ at the wall in the form

$$\boldsymbol{\Phi}(0,\boldsymbol{c}) = \eta(-c_x)\,\boldsymbol{\Phi}(0,\boldsymbol{c}) + \eta(c_x)\,\boldsymbol{\Phi}(0,\boldsymbol{c})$$

with

$$\eta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0\,. \end{cases} \tag{29}$$

For the perturbation of the molecules impinging on the wall we make the ansatz

$$\eta(-c_x)\,\boldsymbol{\Phi}(0,\boldsymbol{c}) = \left(\boldsymbol{\Phi}_\mathrm{asy}\,(0,\boldsymbol{c}) + \frac{\boldsymbol{m}}{k\,T}\,c_z\, a\right)\eta(-c_x)\,. \tag{30}$$

The first term on the right side corresponds to Maxwell's assumption that the extrapolation of the distribution function far from the wall to the wall can be used as an approximation for the distribution function of the arriving molecules. The second term on the right side is an added term to correct Maxwell's assumption.

To complete our ansatz for $\boldsymbol{\Phi}(0,\boldsymbol{c})$, a knowledge of the distribution function of the molecules leaving the wall is necessary.

The linearized boundary conditions may be written formally as

$$\boldsymbol{\Phi}(0,\boldsymbol{c}) = \mathbf{A}\,\boldsymbol{\Phi}(0,\boldsymbol{c}),\ c_x > 0 \tag{31}$$

where $\mathbf{A}$ is the matrix operator of the gas-wall interaction. For Maxwellian boundary conditions (specular and diffuse reflection), the wall collision operator has the form (we are retaining only that part which contributes to the final results),

$$\mathbf{A} = (\mathbf{1} - \boldsymbol{\alpha})\, R\, \eta(-c_x) \tag{32}$$

where $\mathbf{1}$ is the unit matrix and $\boldsymbol{\alpha}$ is a diagonal matrix with the elements $\alpha_i \delta_{ij}$. R is the reflection operator, and has the property

$$R\, f(x,\boldsymbol{c}) = f(x,\, -\boldsymbol{c})\,. \tag{33}$$

Substituting Eqs. (30), (31) into Eq. (29) leads to

$$\boldsymbol{\Phi}(0,\boldsymbol{c}) = [\eta(-c_x) + \eta(c_x)\,\mathbf{A}] \left(\boldsymbol{\Phi}_\mathrm{asy}(0,\boldsymbol{c}) + \frac{\boldsymbol{m}}{k\,T}\,c_z\, a\right) \tag{34}$$

where $\boldsymbol{\Phi}_\mathrm{asy}(0,\boldsymbol{c})$ is given by Eq. (21).

As compared with Eq. (21), there are two unknown quantities, q_asy and a, and to fix these constants the two equations (27) and (28) are used. Equation (27) combined with the simplified Maxwellian ansatz (30) where $a = 0$ leads, in principle, to the elementary formulas, it has for q_asy and $\sigma_{12}^{(\mathrm{v})}$, designated respectively by $q_{\mathrm{asy,\,el}}$ and $\sigma_{12,\,\mathrm{el}}^{(\mathrm{v})}$. The quantity a dimension of velocity together with the second equation (28), corrects the elementary results of Maxwell. Substituting Eq. (34) into the two relations (27) and (28), at $x = 0$, gives us (after a simple algebraic manipulation):

$$q_\mathrm{asy} = \sigma_{12}^{(\mathrm{v})} D_{12}\,\frac{\mathrm{d}x_1}{\mathrm{d}z}$$

where

$$\sigma_{12}^{(\mathrm{v})} = \frac{k\,T}{\eta}\left\{(c_\mathrm{x}^2 c_z \boldsymbol{\Phi}_p(c),\, \eta(c_x)\,(\mathbf{1} - \mathbf{A}]\, c_z \boldsymbol{\Phi}_p(c)) + \frac{(\boldsymbol{m}\, c_x c_z,\, \eta(c_x)\,[\mathbf{1} - \mathbf{A}]\, c_x c_z \boldsymbol{\Phi}_p(c))\,(\boldsymbol{m}\, c_x c_z,\, \eta(c_x)\,[\mathbf{1} - \mathbf{A}]\, c_x \boldsymbol{\Phi}_p(c))}{(\boldsymbol{m}\, c_x c_z,\, \eta(c_x)[\mathbf{1} - \mathbf{A}]\, \boldsymbol{m}\, c_z)}\right\}. \tag{35}$$

Here, we have used (where η is the viscosity of the gas mixture)

$$(\boldsymbol{m}\, c_x c_z, c_x c_z \boldsymbol{\Phi}_p(c)) = -\eta\,.$$

The diffusion slip formula (35) is identical with the variational result presented earlier[12]. We shall consider, now, some simple cases of this very general expression.

The first order expansions for the Chapman-Enskog solutions for a monoatomic binary gas mixture are

$$\begin{aligned}
&\Phi_{p,1}(c) = -2\beta_1 b_1\,, \quad \Phi_{p,2}(c) = -2\beta_2 b_{-1}\,,\\
&\Phi_{d,1}(c) = -\left[d_0\, m_1^{1/2}\frac{\varrho_2}{\varrho} + \left(\frac{5}{2} - \beta_1 c^2\right) d_1\right]\beta_1^{1/2}\frac{\mathrm{d}x_1}{\mathrm{d}z},\\
&\Phi_{d,2}(0) = -\left[-d_0\, m_2^{1/2}\frac{\varrho_1}{\varrho}\right.\\
&\qquad\qquad \left. + \left(\frac{5}{2} - \beta_2 c^2\right) d_{-1}\right]\beta_2^{1/2}\frac{\mathrm{d}x_1}{\mathrm{d}z}
\end{aligned}\tag{36}$$

with $\beta_i = (m_i/2\,k\,T)$, $\boldsymbol{m}_i = m_i/m_0$, $m_0 = m_1 + m_2$

where the coefficients $b_1, b_{-1}, d_0, d_1, d_{-1}$ are defined in the work of CHAPMAN and COWLING[12, 17]. These coefficients are connected with the dynamical viscosity of the mixture η, the binary diffusion coefficient D_{12} and the thermal diffusion ratio k_{T}. Note that:

$$\begin{aligned}
&\eta = p_1 b_1 + p_2 b_{-1}\,, \quad p_i = m_i\, k\, T\,,\\
&D_{12} = \frac{1}{2}\, x_1 x_2 d_0 \left(\frac{2\,k\,T}{m_0}\right)^{1/2},\\
&k_{\mathrm{T}} = -\frac{5}{2}\left[x_1\left(\frac{m_0}{m_1}\right)^{1/2}\frac{d_1}{d_0} + x_2\left(\frac{m_0}{m_1}\right)^{1/2}\frac{d_{-1}}{d_0}\right].
\end{aligned}\tag{37}$$

Using the first order approximations (36) and Maxwellian boundary conditions as given by Eq. (32) we can write the diffusion slip factor $\sigma_{12}^{(\mathrm{v})}$, σ_{12} in the form:

$$\begin{aligned}
\sigma_{12}^{(\mathrm{v})} &= \sigma_{12,\mathrm{mod}}^{(\mathrm{v})} + \sigma_{12,\mathrm{el}}^{(\mathrm{v})}\,,\\
\sigma_{12} &= \sigma_{12,\mathrm{mod}}^{(\mathrm{v})} + \sigma_{12,\,\mathrm{el}}
\end{aligned}$$

where the subscript el stands for the results that are derived by using the elementary arguments of Maxwell, and the subscript mod indicates the extra terms that appear when the modified approach is considered. Explicitly, we have:

$$\begin{aligned}
\sigma_{12,\mathrm{el}}^{(\mathrm{v})} &= \frac{1}{m}\,\frac{\alpha_1 m_1^{1/2} m_2 - \alpha_2 m_2^{1/2} m_1}{x_1 m_1^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_2}\\
&\quad - \left(\frac{k\,T}{8}\right)^{1/2}\frac{\alpha_1 x_1 (d_1/D_{12}) + \alpha_2 x_2 (d_{-1}/D_{12})}{x_1 m_1^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_2}\,,\\
\sigma_{12,\,\mathrm{el}} &= \frac{\alpha_1 m_1^{1/2} - \alpha_2 m_2^{1/2}}{x_1 m_1^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_2}\\
&\quad - \left(\frac{k\,T}{8}\right)^{1/2}\frac{\alpha_1 x_1 (d_1/D_{12}) + \alpha_2 x_2 (d_{-1}/D_{12})}{x_1 m_1^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_2}\,,
\end{aligned}\tag{38}$$

and

$$\begin{aligned}
\sigma_{12,\mathrm{mod}}^{(\mathrm{v})} &= \frac{\alpha_1\alpha_2}{2}\,\frac{\varepsilon\, m_2^{1/2} - m_1^{1/2}}{(x_1\varepsilon + x_2)(x_1 m_1^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_2)}\\
&\quad - \left(\frac{k\,T}{8}\right)^{1/2}\frac{1}{x_1\varepsilon + x_2}\left(\alpha_1\, x_1\frac{d_1}{D_{12}}\,\omega_1 + \alpha_2 x_2\frac{d_{-1}}{D_{12}}\,\omega_2\right)
\end{aligned}\tag{39}$$

where,

$$\begin{aligned}
\omega_1 &= \frac{\varepsilon}{m_1^{1/2}} - \frac{1}{2}\,\frac{\alpha_1 x_1\varepsilon + \alpha_2 x_2}{x_1 m_1^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_2}\,,\\
\omega_2 &= \frac{1}{m_2^{1/2}} - \frac{1}{2}\,\frac{\alpha_1 x_1\varepsilon + \alpha_2 x_2}{x_1 m_1^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_2}\,,\\
\varepsilon &= b_1/b_{-1}\,.
\end{aligned}$$

The formulas (38) are identical with the result given by BROCK[5] as a consequence of the same elementary derivation. The only difference between the Kramers-Kistemaker relations given by Eqs. (12a), (12b) and Eqs. (38) is the small contribution by the thermal diffusion terms. As a consequence of Eq. (28), $\sigma_{12,\mathrm{mod}}^{(\mathrm{v})}$, given by Eq. (39) is a new contribution to $\sigma_{12}^{(\mathrm{v})}$ and σ_{12}. This contribution is responsible for the influences of intermolecular forces, as we can show in the following.

For the special cases $x_1 = x_2 = 1/2$, an isobaric mixture ($m_1 = m_2$) and $\alpha_1 = \alpha_2$, from Eq. (38) we get,

$$\sigma_{12}^{(\mathrm{v})} = \sigma_{12,\,\mathrm{el}} = (1 - \alpha_2/\alpha_1) + \alpha_{12}/5 \tag{40}$$

where the relation (37) for the thermal diffusion ratio has been used. α_{12} is the thermal diffusion factor given by

$$\alpha_{12} = (k_{\mathrm{T}}/x_1 x_2)\,. \tag{41}$$

Further, for an equimolar mixture, it is of considerable interest to obtain an expression for σ_{12} that would display explicitly the role of the small differences between masses m_i, the accommodation coefficients α_i and the intermolecular potential parameters. We have derived such a result by using appropriate limiting situations in the Eqs. (38), (39), and after a fairly long and tedious calculation (the details of this calculation would not be given here) we find,

$$\sigma_{12,\,\mathrm{el}} = \frac{\Delta m}{2m}\left[1 + D^* \frac{2A^* + 15}{2A^*}\right] + \frac{\Delta s}{2s}[4D^*] + \frac{\Delta\alpha}{2\alpha}[2 - 4D^*] \qquad (42\mathrm{a})$$

and

$$\sigma^{(\mathrm{v})}_{12,\mathrm{mod}} = \frac{\Delta m}{2m}\left\{\alpha \frac{6A^* - 5}{6A^* + 10} + \alpha D^* \frac{-42A^{*2} + 95A^* + 75}{12A^{*2} + 20A^*}\right\} - \frac{\Delta s}{2s}\left\{\alpha \frac{6A^*}{3A^* + 5} - 10\alpha D^* \frac{3A^* + 1}{3A^* + 5}\right\} - \frac{\Delta\alpha}{2\alpha} 2\alpha D^* \qquad (42\mathrm{b})$$

where the quantities s_i are effective collision diameters defined by the viscosity[18],

$$s_1^2 = d_1^2 \Omega_{11}^{(2,2)*}, \quad s_2^2 = d_2^2 \Omega_{22}^{(2,2)*},$$

$$s_{12}^2 = d_{12}^2 \Omega_{12}^{(2,2)*}, \quad d_{12} = \frac{d_1 + d_2}{2}, \quad s_{12} = s.$$

The quantities $\Omega^{(i,j)*}$ are the reduced Omega integrals, conveniently divided by their corresponding rigid-sphere values. Furthermore, we have [15, 18]

$$A^* = \frac{\Omega_{12}^{(2,2)*}}{\Omega_{12}^{(1,1)*}}, \quad B^* = \frac{5\,\Omega_{12}^{(1,2)*} - 4\,\Omega_{12}^{(1,3)*}}{\Omega_{12}^{(1,1)*}},$$

$$C^* = \frac{\Omega_{12}^{(1,2)*}}{\Omega_{12}^{(1,1)*}}$$

which for rigid elastic spherical molecules become

$$A^* = B^* = C^* = 1.$$

Generally, A^*, B^*, and C^* are nearly unity.

For D^*, arising in the thermal diffusion terms, we have,

$$D^* = \frac{6C^* - 5}{55 - 12B^* + 16A^*}.$$

The quantities $\Delta m/m$, $\Delta s/s$ and $\Delta\alpha/\alpha$ are relative differences of the masses m_i, effective collision cross sections s_i and accommodation coefficients α_i and are given by (Recall that we are considering here the case of an equimolar mixture),

$$\Delta m = m_1 - m_2, \; \Delta s = s_1 - s_2, \; \Delta\alpha = \alpha_1 - \alpha_2,$$

$$m = \frac{m_1 + m_2}{2}, \quad s = \frac{s_1 + s_2}{2}, \quad \alpha = \frac{\alpha_1 + \alpha_2}{2}.$$

For an equimolar, isobaric mixture we obtain from Eq. (42a)

$$\sigma_{12,\,\mathrm{el}} = \frac{\Delta s}{2s} 4D^* + \frac{\Delta\alpha}{2\alpha}\{2 - 4D^*\}. \qquad (43)$$

For this case the thermal diffusion factor α_{12} can be written as[18]

$$\alpha_{12} = 10\,D^* (\Delta s/s). \qquad (44)$$

Inserting Eq. (44) into Eq. (43) and neglecting the small thermal diffusion term in the contribution of the accommodation coefficients to $\sigma_{12,\,\mathrm{el}}$ leads to Brock's result given by Eq. (40). **Brock**[5] has compared Eq. (40) with the experimental data of Schmitt and Waldmann for aerosols in diffusion fields and found that the influence of the collision cross section in his formula is too small. He interpreted the discrepancy as an effect of the difference between the accommodation coefficients. Although that is an important point, the principal reason for the discrepancy lies elsewhere. This will be evident from the discussion that follows.

For an equimolar, isobaric mixture it follows from Eq. (42b) that

$$\sigma^{(\mathrm{v})}_{12,\mathrm{mod}} = -\frac{\Delta s}{2s}\left\{\alpha \frac{6A^*}{3A^* + 5} - 10\alpha D^* \times \frac{3A^* + 1}{3A^* + 5}\right\} - \frac{\Delta\alpha}{2\alpha} 2\alpha D^*. \qquad (45)$$

The term $\sigma^{(\mathrm{v})}_{12,\mathrm{mod}}$ includes the contributions of the second moment equation (28) to the diffusion slip factor σ_{12} and contains the main effect of the collision cross sections in the first term within the brackets. This term is much larger than the influence of the collision cross section introduced by the contribution of $\sigma_{12,\,\mathrm{el}}$. For a hard sphere intermolecular force law we obtain

$$\sigma_{12} = \frac{\Delta m}{2m}(1{,}1574 + \alpha \cdot 0{,}1303) - \frac{\Delta d}{2d}(\alpha \cdot 0{,}6652 - 0{,}0678) + \frac{\Delta\alpha}{2\alpha}(1{,}9322 - \alpha \cdot 0{,}0338). \qquad (46)$$

But, using Eq. (46) and assuming $\alpha_1 = \alpha_2 = 1$ leads to an incorrect sign for some gas pairs with nearly the same masses. Thus using Eq. (42), realistic potentials should be taken.

Maxwell's elementary momentum consideration represented by Eq. (27) supplies the main contribution to the influence of the masses and the coefficients and the second moment equation (28) modifies Maxwell's result to include the influence of the intermolecular potentials between the molecules.

After this detailed presentation of the modified Maxwellian method, it is useful to summarize results obtained earlier by other authors who used various approximate theories, kinetic models, etc.

From Eqs. (15) we obtain

$$\sigma_{12,\mathrm{K\cdot K}} = \frac{m_1^{1/2}\alpha_1 - m_2^{1/2}\alpha_2}{x_1 m^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_2}, \tag{47a}$$

$$\sigma^{(\mathrm{v})}_{12,\mathrm{K.K}} = \frac{1}{m}\,\frac{m_2 m_1^{1/2}\alpha_1 - m_1 m_2^{1/2}\alpha_2}{x_1 m_1^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_2}. \tag{47b}$$

It can be easily seen that the Eqs. (47) satisfy the relation (9)

$$\sigma_{12} = \sigma^{(\mathrm{v})}_{12} + (m_1 - m_2)/m\,.$$

Thus, using Eqs. (9), (38) and (39) the modified Maxwellian method leads to

$$\sigma_{12} = \sigma_{12,\mathrm{K\cdot K}} - \left(\frac{k\,T}{8}\right)^{1/2} \times \frac{\alpha_1 x_1 (d_1/D_{12}) + \alpha_2 x_2 (d_{-1}/D_{12})}{x_1 m_1^{1/2}\alpha_1 + x_2 m_2^{1/2}\alpha_1} + \sigma^{(\mathrm{v})}_{12,\mathrm{mod}} \tag{48}$$

where $\sigma^{(\mathrm{v})}_{12,\mathrm{mod}}$ is given by Eq. (38).

Zhdanov[6] suggested a complete expression for the slip velocity of a binary mixture of monoatomic gases due to gradients of velocity, temperature, composition and pressure. His results give:

$$\sigma_{12} = \sigma_{12,\mathrm{K\cdot K}} + \delta_{12}\,,$$

$$\delta_{12} = \frac{x_1 m_1^{3/2} + x_2 m_2^{3/2}}{(x_1 m_1 + x_2 m_2)(x_1 m_1^{1/2} + x_2 m_2^{1/2})}\,\frac{\alpha_{12}}{5} - \frac{(m_1 + m_2)(m_1^{1/2} - m_2^{1/2})}{(x_1 m_1 + x_2 m_2)(x_1 m_1^{1/2} + x_2 m_2^{1/2})}\,\frac{\Delta_{12}}{(6\,C^* - 5)} \tag{49}$$

where α_{12} is the thermal diffusion factor and Δ_{12} the correction term[15,17] to the first Chapman-Enskog approximation for the diffusion coefficient $[D_{12}]_1$. The second approximation can be written as $[D_{12}]_2 = [D_{12}]_1/(1 - \Delta_{12})$.

In Zhdanov's formula the accommodation coefficients are assumed to be unity.

For the BGK-model equations for gas mixtures, Lang[7, 16] used the half-range method and he found

$$\sigma_{12} = \frac{m_1^{1/2}\theta_1 - m_2^{1/2}\theta_2}{x_1 m_1^{1/2}\theta_1 + x_2 m_2^{1/2}\theta_2}\,,$$

$$\theta_i = \left\{\frac{m_i}{m^*} \times \frac{\nu_{ii} + \nu_{ij}}{[(\nu_{ii} + \nu_{ij})\,\nu_{ij} + (\nu_{jj} + \nu_{ji})\,\nu_{ji}]^{1/2}} + \frac{2 - \alpha_i}{\alpha_i}\right\}^{-1} \tag{50}$$

where ν_{ii}, ν_{ij} are the collision frequencies and m^* is the reduced mass. The collison frequencies are connected with experimental values of the viscosities of the single components η_i and the binary diffusion coefficient D_{12} by the relations

$$\eta_i = \frac{n_i}{\nu_{ii}\,k\,T}\,, \qquad D_{12} = \frac{n_2}{n}\,\frac{1}{\nu_{12}}\,\frac{k\,T}{m^*}\,. \tag{51}$$

A balance of the total collision frequency leads to

$$n_1 \nu_{12} = n_2 \nu_{21}\,. \tag{52}$$

Shendalman[9] used the same model equations and a variational procedure and arrived at the following formula

$$\sigma_{12} = \frac{\beta'_1}{1 - \beta'_1 x_1}\left\{1 - \frac{x_2 - x_1(1 - \beta'_1)\,\nu'}{\beta'_1(x_1 + x_2\,\nu')}\right\},$$

$$\nu' = \frac{\nu_{11} + \nu_{12}}{\nu_{22} + \nu_{21}}\,, \quad \beta'_1 = 1 - \left(\frac{m_1}{m_2}\right)^{1/2}. \tag{53}$$

In order to fix the collision frequences ν_{ij} the relations (51), (52) can be used.

Breton[10,11] applied the half range method to the linearized Boltzmann equations for the hard sphere potential model and for σ_{12} he gave the expression,

$$\sigma_{12} = \frac{\alpha_1 (m_1 d_2)^{1/2} - \alpha_2 (m_2 d_1)^{1/2}}{x_1 \alpha_1 (m_1 d_2)^{1/2} + x_2 \alpha_2 (m_2 d_1)^{1/2}} \tag{54}$$

where d_i are the hard sphere diameters. In order to compare this formula with experimental results, he suggests that the diameter d_i occurring here be replaced by the corresponding Lennard-Jones potential parameters σ_i. (No doubt, this is a somewhat questionable procedure.)

III. Comparison between Experimental and Theoretical Results and Discussion

a) *Diffusiophoresis*

WALDMANN and SCHMITT investigated the diffusiophoretic velocity of oil droplets in mixtures of different gases. The experimental apparatus was described in papers[14, 19]. Their experimental results are compared with theoretical relations for σ_{12} in Table 1 ($\alpha_1 = 1, \alpha_2 = 1$). The collision cross sections used were taken from the book of Hirschfelder, CURTISS and BIRD[15], Table 1-A. To relate the force constants between unlike molecules to those between like molecules the convenient combining laws,

$$d_{12} = \frac{(d_1 + d_2)}{2}, \quad \varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{1/2}$$

are used.

From Table 1 it can be seen that the elementary values $\sigma_{12,\mathrm{K.K}}$ given by Eq. (10a) fails in these cases, where the masses are nearly the same. When the heavier mass has the smaller collision cross section, then the collision cross section effect has the same sign as the mass effect, as can be seen from the empirical relation (3) or Eq. (42). Thus, the elementary value $\sigma_{12,\mathrm{K.K}}$ for the gas pairs N_2/C_2H_2 and N_2/O_2 has the true sign, though the quantitative agreement is poor. Furthermore, neither Zhdanov's theoretical result nor Brock's formula lead to an essential improvement of the elementary formula. All these formulas are derived using Maxwell's momentum balance, which does not correctly account for the influence of the collision cross section. In the rows (7) and (8) we present the theoretical results found by the modified Maxwellian method, Eqs. (38), (39) and Eq. (42). We can see that these theoretical results are in a very good agreement with the measured values. Only for the gas pair N_2/C_3H_8 is the quantitative agreement not as good.

In Table 2 we show the influence of the accommodation coefficients on the diffusion slip using the

Table 1. Comparison of theoretical and experimental diffusive slip factors σ_{12}. (Experimentally determined by diffusiophorese.)

Gas 1					N_2				CO_2
Gas 2	H_2	C_2H_2	C_2H_4	C_2H_6	O_2	A	CO_2	C_3H_8	C_3H_8
Experimental values	0.9	0.13	0.073	0.085	− 0.10	− 0.22	− 0.20	− 0.13	0.11
Theoretical values									
Eq. (10a)	1.15	0.037	− 0.0007	− 0.035	− 0.067	− 0.18	− 0.22	− 0.23	− 0.0010
Eq. (49)	1.18	0.035	− 0.0038	− 0.040	− 0.070	− 0.19	− 0.24	− 0.24	− 0.0015
Eq. (3)	0.65	0.11	0.073	0.062	− 0.10	− 0.21	− 0.17	− 0.05	0.12
Eq. (54)	1.08	0.11	0.07	0.06	− 0.10	− 0.22	− 0.18	− 0.07	0.12
Eqs. (38), (39)	1.21	0.13	0.102	0.088	− 0.093	− 0.22	− 0.19	− 0.07	0.11
Eq. (42)	0.95	0.13	0.100	0.086	− 0.094	− 0.22	− 0.19	− 0.07	0.11
Eq. (50)	0.61	0.14	0.12	0.13	− 0.062	− 0.13	− 0.06	+ 0.08	0.13
Eq. (53)	0.69	0.13	0.11	0.11	− 0.063	− 0.14	− 0.08	+ 0.04	0.12

In evaluating the theoretical formulas, $\alpha_1 = \alpha_2 = 1$ and $x_1 = x_2 = 1/2$ were used (temperature = 20°C).

Table 2. Influence of the accommodation coefficients on the diffusion slip factor σ_{12}. σ_{12} is calculated from Eqs. (38), (39); $\Delta\alpha/\alpha$ is estimated from Eq. (55).

Gas 1					N_2				CO_2
Gas 2	H_2	C_2H_2	C_2H_4	C_2H_6	O_2	A	CO_2	C_3H_8	C_3H_8
σ_{12} with $\alpha_1 = 0.95$ $\alpha_2 = 1.00$	1.18	0.082	0.15	0.13	− 0.043	− 0.17	− 0.14	− 0.02	0.16
σ_{12} with $\alpha_1 = 1.00$ $\alpha_2 = 0.95$	1.25	0.18	0.049	0.035	− 0.14	− 0.27	− 0.24	− 0.12	0.061
$\Delta\alpha/\alpha$	− 0.3	0	− 0.03	0	0	0	− 0.01	0.06	0

result of the modified Maxwellian method Eqs. (38), (39). It can be seen that σ_{12} for the gas pair N_2/C_3H_8 is very sensitive to a small variation of the accommodation coefficients. The influence of differences between the accommodation coefficients is the crucial point and was not given sufficient attention by other authors. If the mass difference is large, the accommodation effects are not so important. It seems reasonable to assume that $\alpha = (\alpha_1 + \alpha_2)/2 \approx 1$. In this way, using Eq. (42) the relative difference between the accommodation coefficients can be estimated as

$$\frac{\Delta\alpha}{\alpha} \cong \sigma_{12,\mathrm{exptl.}} - \sigma_{12}(\alpha_1 = \alpha_2 = 1)\,. \tag{55}$$

This relation is evaluated in the fifth row of Table 2. Only for the gas pairs N_2/H_2 and N_2/C_3H_8 do we find a notable difference between the accommodation coefficients.

Furthermore, Breton's simple formula Eq. (54) is generally in a good agreement with the experimental results. The relations based on a relaxation model for the Boltzmann equation, Eqs. (50) and (53), give qualitatively a correct picture of the slip behavior, but quantitatively the agreement is not always adequate. Only for the gas pair N_2/C_3H_8 the sign is not correct. This discrepancy is due to the approximate nature of the model used.

b) *Diffusion bridge (Wicke-Kallenbach experiment)*[3]

As shown in Fig. 1, two gases flow across opposite ends of a capillary tube or opposite faces of a porous medium, and the emerging streams are analyzed. The flow rates can be controlled and adjusted in such a way that the pressure difference across the capillary or porous medium is negligable. The flux ratio $1/m^* = -J_{1\mathrm{d}}/J_{2\mathrm{d}}$ is compared with experimental values in Table 3. (The experimental values are taken from Table 2 in Reference[10]). Unfortunately, only measurements of counter-diffusion through porous media have been reported.

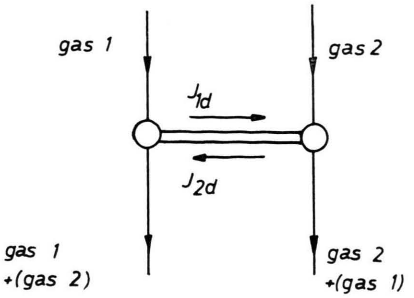

Fig. 1. Diffusion bridge (Wicke-Kallenbach experiment).

Table 3. Comparison of theoretical and experimental flux ratios. (Determined by Wicke-Kallenbach type experiments the values are taken from Table 2, Reference[10].)

a	He-O_2		2.74	2.83	2.45	2.77
	N_2-O_2		1.08	1.07	1.11	1.10
	CO_2-O_2		0.85	0.87	0.92	0.91
b	He-Ar		3.18	3.16	2.74	3.11
c	He-N_2	I	2.27	2.65	2.22	2.54
		II	2.33			
		III	2.25			
d	He-N_2	A	2.52	2.65	2.22	2.54
		B	2.58			
		C	2.59			
e	He-N_2		2.86	2.65	2.22	2.54
	He-Ar		3.75	3.16	2.75	3.11
	He-i-C_4H_{10}		3.08	3.81	2.65	2.73
	He-C_5H_{12}		3.11	4.24	2.84	2.89

[a] Reference[20], [b] Reference[21], [c] Reference[22], [d] Reference[23], [e] Reference[24].

For $1/m^*$ Breton suggested the following relation[11]

$$\frac{1}{m^*} = -\frac{J_{1\mathrm{d}}}{J_{2\mathrm{d}}} = \frac{\alpha_2}{\alpha_1}\left(\frac{m_2}{m_1}\right)^{1/2}\left(\frac{d_1}{d_2}\right)^{1/2}. \tag{56}$$

From Eqs. (10) and (12) it follows generally that

$$\frac{1}{m^*} = \left(\frac{m_2}{m_1}\right)^{1/2}\frac{\theta_1}{\theta_2} = \frac{1 - \sigma_{12}x_1}{1 + \sigma_{12}x_2}\,. \tag{57}$$

Equation (57) using the result for σ_{12} from Eqs. (38), (39) is compared in Table 3 with experiments, too. Since the flux ration $1/m^*$ has a concentration dependence, we used an "averaged" value for the flux ratio by inserting $x_1 = x_2 = 1/2$ into Eq. (57). In the experiments, the fluxes and therefore, the flux ratio must be a constant across the capillary or porous medium even for large concentration differences between their end. Obviously, the linearized one-dimensional theory is only approximately valid. From Table 3 it can be seen that the flux ratio derived by the modified Maxwellian method gives generally better results than Eq. (56).

Here, the elementary value from Eq. (5) approaches the experimental result for most cases better than the other theoretical results. This can be interpreted easily as follows: Almost porous media are working in the transition region between the diffusion slip regime and the Knudsen regime at mean Knudsen numbers Kn ($1/10 < \mathrm{Kn} < 10$).

Therefore, the measurements show a shift from m_{D}^* given for the diffusion slip regime, to m_{Kn}^*, given for the Knudsen regime at large Knudsen numbers. As mentioned in connection with Eq. (5), the elementary value for m_{D}^*, given by Fig. 5 or more general by Eq. (12) is identiced with m_{Kn}^*. Thus, from the above it is clear that an approach to the "elementary value" is observed. For instance, the values of $1/m^*$ for the gas pair He-N_2 reported by Wakao and Smith (row d) move from 2.52 to 2.59 with decrease of the mean pure radius (or increase of mean Knudsen number) and an appearent approaching to the elementary diffusion slip value is seen. Furthermore, the effect at the accommodation was left open. In addition, in some cases surface diffusion in micropores can exist.

It should be mentioned that the flux ratio is not as sensitive to a small variation of the parameters as the diffusive slip coefficient. Generally, the collision cross sections have the same order of magnitude and the accommodation coefficients are nearly unity. Thus it can be seen from Eq. (56) that

$$(1/m^*) \simeq (m_2/m_1)^{1/2}\,.$$

From Eq. (57) we obtain

$$\sigma_{12} = (m^* - 1)/(x_1 m^* + x_2)\,. \tag{58}$$

It is evident that a small deviation of m^* from one is important.

c) *Diffusion Pressure Effect*

The experimental apparatus and techniques have been described previously[3,4,16]. The experiment is illustrated on Figure 2. At the beginning the two volumes V', V'' are filled to the same pressure $p(0)$ with different gas. The capillary C (radius R, length l) connecting the two volumes is opened and the different diffusion velocities give rise to a pressure difference between the two volumes, which cause a compensating hydrodynamic flow. The pressure difference increases to a maximum $\Delta p_{\max}$, the total particle flow vanishes and thus, the pure diffusion flow given by Eq. (5) is compensated by a hydrodynamic Poiseuille flow and we have,

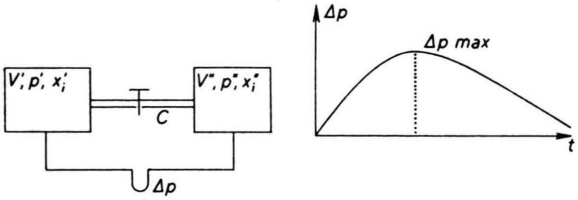

Fig. 2. Two bulb apparatus (Diffusion pressure effect) $\Delta p = p'' - p'$; $\Delta x_i = x_i'' - x_i'$.

$$\sigma_{12} D_{12} \frac{\mathrm{d}n_1}{\mathrm{d}z} = \frac{R^2 p}{8 \eta k T} \frac{\mathrm{d}p}{\mathrm{d}z}$$

or

$$\mathrm{d}p = (8\eta/R^2)\, \sigma_{12} D_{12} (\mathrm{d}n_1/n)\,. \tag{59}$$

Taking into account that $\mathrm{d}p \ll p(0)$ and $\mathrm{d}n_i \ll n_i(0)$ respectively, we can write

$$\mathrm{d}p = (8\eta/R^2)\, \sigma_{12} D_{12}\, \mathrm{d}x_1(0)$$

or by integrating along the capillary

$$\Delta p_{\max} = (8\,\overline{D_{12}}/R^2) \int_{x_1'(0)}^{x_1''(0)} \sigma_{12}\, \eta\, \mathrm{d}x_1(0) \tag{60}$$

where the small concentration dependence of the binary diffusion coefficient has been neglected. Usually, in evaluating the measurements an effective diffusive slip coefficient $(\sigma_{12})_{\mathrm{eff}}$ is determined by

$$\Delta p_{\max} = (8\,\overline{D_{12}}/R^2)\, (\sigma_{12})_{\mathrm{eff}}\, \bar{\eta} \cdot \Delta x_1(0) \tag{61}$$

where the binary diffusion coefficient $\overline{D_{12}}$ and the dynamical viscosity of the mixture $\bar{\eta}$ are due to the concentrations $x_1 = x_2 = 1/2$.

From Eqs. (60), (61) we obtain the theoretical value for the effective slip coefficient which can be compared with the experimental one as

$$(\sigma_{12})_{\mathrm{eff}} = \frac{\int_{x_1'(0)}^{x_1''(0)} \sigma_{12}\, \eta\, \mathrm{d}x_1(0)}{\bar{\eta} \cdot \Delta x_1(0)}\,. \tag{62}$$

In the Tables 4 and 5 experimental results of the effective diffusive slip coefficient $(\sigma_{12})_{\mathrm{eff}}$ reported in the papers of WALDMANN and SCHMITT[4] and paper[16], respectively, are compared with theoretical values calculated from Eq. (62) by a numerical integration. The value for σ_{12} was taken from Eq. (38) with $\alpha_1 = \alpha_2 = 1$. It can be seen from both tables that the agreement between the calculated and the measured values of $(\sigma_{12})_{\mathrm{eff}}$ is very good. Generally, it seems reasonable to assume that $\alpha_1 = \alpha_2 = 1$. For the isobaric gas pair N_2/C_2H_4 a larger difference between theory and experiment exists, as can be seen from Table 4. But, this difference can be easily explained by the high sensitivity of the diffusive slip factor σ_{12} to a small variation of the accommodation coefficients as compared with Table 2. The same situation may appear for the gas pair C_2H_4/N_e. Here, we obtain $\sigma_{12} = 0.084$

Table 4. Diffusive Slip Factors from the Diffusion Pressure Effect (Reference [4]).

Gaspair	N_2-H_2			A-N_2			CO_2-N_2		O_2-N_2		N_2-C_2H_4	A-CO_2
p Mean pressure Torr	10.8	19	68	7.0	10.6	24	10.6	24	10.6	24	10.6	10.6
$(\sigma_{12})_{\text{exptl.}}$	0.9	1.10	1.68	0.13	0.16	0.21	0.14	0.18	0.056	0.082	0.04	0.026
$(\sigma_{12})_{\text{eff}}$	1.23			0.21			0.18		0.091		0.10	0.030
$\sigma_{12}(x_i = 1/2)$ Eqs. (38), (39)	1.21			0.22			0.19		0.094		0.10	0.031
$\sigma_{12}(x_i = 1/2)$ Eq. (3)	0.71			0.21			0.17		0.10		0.073	0.036

Temperature 20 °C; Capillary radius $0.98 \cdot 10^{-2}$ cm, Capillarylength 4.8 cm.

Table 5. Diffusive Slip Factors from the Diffusion Pressure Effect (Reference [16]).

Gaspair	N_2-H_2					A-N_2					Ne-C_2H_4		
Mean pressure	20.2	51.0	104.0	198.0	482.0	21.0	33.5	50.0	83.0	181.0	18.0	22.5	34.5
$(\sigma_{12})_{\text{exptl.}}$	0.84	1.03	1.08	1.12	1.14	0.18	0.17	0.21	0.21	0.25	0.033	0.033	0.031
$(\sigma_{12})_{\text{eff}}$			1.23					0.21				0.031	
$\sigma_{12}(x_i = 1/2)$ Eq. (38), (39)			1.21					0.22				0.040	
$(\sigma_{12})(x_i = 1/2)$ Eq. (3)			0.71					0.21				0.061	

Temperature 25 °Q; Capillary radius $0.03{,}10^{-2}$ cm Capillary length 5 cm.

($\alpha_1 = 0.095$, $\alpha_2 = 1$) and $\sigma_{12} = 0.016$ ($\alpha_1 = 1$, $\alpha_2 = 0.95$). From Tables 4 and 5 the pressure dependence of $(\sigma_{12})_{\text{exptl.}}$ is seen (see Appendix A). Diffusive slip factors have been calculated for the temperatures 20 °C and 25 °C and for complete accomodation ($\alpha_1 = \alpha_2 = 1$). However, the differences obtained were in every case negligable.

In our work[16] we have also investigated the gas pair A/CO_2. We found the sign reversal in agreement with the paper[4], but the measured values of σ_{12} were higher. The differences may be explained by differences between the accommodation coefficient. Possibly other effects such as adsorption of CO_2 influence the measurement and the discrepancy is under investigation.

We conclude that in order to compare theory with experiment, especially for isobaric mixtures, an independent measurement of the partial accommodation coefficient is needed.

IV. Conclusions

The use of relaxation model equations[7,9] to replace the complicated collision terms of the Boltzmann equations leads to a qualitative description of the diffusive slip factor even for isobaric mxitures, but the quantitative agreement is not always good. The application of these model equations can be useful for a practical treatment of the diffusion over the whole transition region between small and large Knudsen numbers. The application of the half range method to the linearized Boltzmann equations for hard spheres leads to an interesting simple formula for the diffusive slip factor[10,11], Eq. (54), generally in good agreement with experiment. For nearly isobaric mixtures, there exists a strong need for a diffusive slip formula which allows a general force law between the molecules and any kind of boundary interaction. This need is fulfilled in a precise and simple way by the variational results[12] and the equivalent modified Maxwellian method[13] (equivalent for a simple ansatz) only. Results obtained by these methods were always found[13] in a very good agreement with exact results (whenever they are available) and the comparison with experiments raises the confidence in these methods. However, further experimental results are needed and, especially, measurements of the partial accommodation coefficients of the components should be made.

Appendix A

It can be easily shown[7] that the increase of σ_{12} with larger capillary diameter and/or higher pressure is consistent with the statement of some authors[25, 26] that the flux ratio m^* approaches the following limit:

$$m^* = -J_{2\mathrm{d}}/J_{1\mathrm{d}} \to -m_1/m_2 . \qquad (\mathrm{A.1})$$

Thus $$M_\mathrm{d} = m_1 J_{1\mathrm{d}} + m_2 J_{2\mathrm{d}} \to 0$$

and furthermore from Eq. (5) $\sigma_{12}^{(\mathrm{v})} \to 0$.

Comparing with Eq. (6) we find in this limit

$$\sigma_{12} \to (m_1 - m_2)/m = \sigma_{12}^{(0)} . \qquad (\mathrm{A.2})$$

From Eq. (42a) we should obtain approximately

$$\sigma_{12} \to \tfrac{1}{2}(m_1 - m_2)/m . \qquad (\mathrm{A.3})$$

(Small contributions of the collision cross sections and accommodation coefficients can be neglected for the corresponding gas pairs.)

From Eq. (A.2) we obtain the following Table

Gaspair	N_2—H_2	A—N_2	CO_2-N_2	O_2-N_2	C_2H_4-Ne
$\sigma_{12}^{(0)}$	1.73	0.36	0.445	0.133	0

Thus, $\sigma_{12}^{(0)}$ can explain the pressure dependence of σ_{12} in the Tables 4 and 5. But, the transition from Eq. (42a) to Eq. (A.2) has not been sufficiently explained to date.

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