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Hydrodynamic Theory of Multicomponent Diffusion and Thermal Diffusion in Multitemperature Gas Mixtures[1]

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Abstract

A phenomenological theory is developed for multicomponent diffusion, including thermal diffusion, in gas mixtures in which the components may have different temperatures. The theory is based on the hydrodynamic approach of Maxwell and Stefan, as extended and elaborated by Furry [1] and Williams [2]. The present development further extends these earlier treatments to multiple temperatures and multicomponent thermal diffusion. The resulting diffusion fluxes obey generalized Stefan-Maxwell relations which include the effects of ordinary, forced, pressure, and thermal diffusion. When thermal diffusion is neglected, these relations have the same form as the usual single-temperature ones, except that mole fractions are replaced by pressure fractions (i.e., ratios of partial pressures to total pressure). The binary and thermal diffusion coefficients are given in terms of collision integrals. Single-temperature systems and binary systems are treated as special cases of the general theory. A self-consistent effective binary diffusion approximation for multitemperature systems is presented.

1. Introduction and summary

The kinetic theory of gases provides an essentially exact description of multicomponent diffusion in gas mixtures, based on the Chapman-Enskog method for solving the Boltzmann equation [3–5]. This theory is notorious for its extreme complexity; its intricacies are esoteric if not arcane, and it is relatively inaccessible to nonspecialists. The results of the theory, however, are of much wider interest and applicability. It is therefore desirable to develop an elementary approach to multicomponent diffusion which is simpler, easier to work with, and yields essentially correct results with much less effort. One might naively hope that mean free path theories would suffice for this purpose, as they capture the

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essential physics of viscosity and thermal conduction quite nicely. It has long been recognized, however, that such theories do not provide a satisfactory description of diffusion, especially thermal diffusion [1].

Fortunately, there is another approach which is especially well suited to diffusion, namely the hydrodynamical approach of Maxwell and Stefan [4, 6]. This approach has been further extended and elaborated by Furry [1], and Williams [2, 7]. Furry [1], restricted attention to binary mixtures, for which he showed that this approach yields precisely the same binary diffusion coefficients as first-order Chapman-Enskog (FOCE) theory! Moreover, he used the same approach in conjunction with mean-free-path ideas to obtain an approximate expression for the thermal diffusion coefficient in a binary mixture. He did not, however, consider forced and pressure diffusion. Williams [2, 7], extended the hydrodynamic theory to arbitrary multicomponent gases, including the effects of forced and pressure diffusion, but he neglected thermal diffusion. He also used a simplified expression for the collisional rate of momentum exchange between components. The resulting binary diffusion coefficients consequently differ from those of FOCE theory by numerical factors of order unity.

The purpose of the present paper is to further extend the hydrodynamic theory by combining the following ingredients within a single unified framework: (a) accurate expressions for collisional rates of momentum exchange between components, equivalent to those used by Furry, (b) a full multicomponent formulation similar to that of Williams, and (c) a more detailed and complete treatment of thermal diffusion than that given by Furry. We thereby remove the main restrictions and limitations in the treatments of Furry and Williams to obtain a complete description of multicomponent diffusion in arbitrary gas mixtures, including thermal diffusion as well as forced and pressure diffusion.

To obtain still further generality, we allow the individual components in the mixture to have different temperatures. This generalization presents serious complications in the full kinetic theory [5, 8, 9], but is straightforward in the hydrodynamic theory and does not significantly complicate the development. Of course, the resulting multitemperature description is useful only in situations where energy transfer between components is much slower than momentum transfer. This occurs when there are large disparities in particle masses between some or all of the components in the mixture. The classic example is a plasma, where the free electrons are much lighter than the other components. Energy exchange between free electrons and heavy particles is consequently inefficient, so that significant differences between electron and heavy-particle temperatures may persist for relatively long times [8–11]. Similar but less dramatic temperature differences may also occur in mixtures of gases with very different molecular weights (e. g., H_2 and UF_6) if some mechanism exists for preferentially heating or cooling the different components. There may also be situations in which the multitemperature formulation provides a useful description of neutron diffusion.

The development proceeds along the following outline. Momentum equations for the different components of the mixture are presented in Section 2. The momentum exchange terms appearing in these equations are separated into frictional and thermophoretic parts containing appropriate phenomenological coefficients. These equations are then evaluated in the limit of large friction [12], in which they reduce to generalized Stefan-Maxwell relations for the diffusion velocities. The diffusion coefficients in these relations are simply related to the phenomenological coefficients. When thermal diffusion is neglected, the multitemperature Stefan-Maxwell relations have the same form as the usual single-temperature ones, except that mole fractions are replaced by pressure fractions (i.e., ratios of partial pressures to total pressure). In Section 3, elementary kinetic theory arguments based on collision frequencies and the Maxwell-Boltzmann velocity distribution are used to evaluate the phenomenological coefficients. The multitemperature binary and thermal diffusion coefficients are thereby expressed in terms of collision integrals. These integrals turn out to be the same as their counterparts in single-temperature FOCE theory, evaluated at an effective temperature which is a weighted average of the relevant two component temperatures. The thermal diffusion coefficients are susceptible to a simple approximation in which they are very simply related to the binary diffusion coefficients.

The general results are specialized to single-temperature systems in Section 4, and to binary mixtures in Section 5. The former specialization leads to an approximate expression for the conventional thermal diffusion coefficients in a multicomponent system. This expression is the multicomponent generalization of Furry's result for binary mixtures [1], to which it becomes essentially equivalent in that special case. A multitemperature generalization of the self-consistent effective binary diffusion approximation [13], is presented in Section 6.

2. Momentum equations, exchange terms, and the diffusional limit

We consider an arbitrary multicomponent gas mixture in which the different components or species may possess different mean velocities and temperatures. The continuity equation for species i is simply

$$\frac{\partial \varrho_i}{\partial t} + \nabla \cdot (\varrho_i \bar{\boldsymbol{u}}_i) = 0 \tag{1}$$

where ϱ_i and $\bar{\boldsymbol{u}}_i$ are respectively the partial mass density and mean velocity of species i. The momentum equation for species i is

$$\varrho_i \left(\frac{\partial \bar{\boldsymbol{u}}_i}{\partial t} + \bar{\boldsymbol{u}}_i \cdot \nabla \bar{\boldsymbol{u}}_i \right) = -\nabla p_i + \varrho_i \boldsymbol{F}_i + \sum_j \boldsymbol{F}_{ij} \tag{2}$$

where p_i is the partial pressure of species i, $\boldsymbol{F}_i$ is the body force per unit mass acting on species i, $\boldsymbol{F}_{ij} = -\boldsymbol{F}_{ji}$ is the mean force per unit volume of species j on species i, the j summation extends over the N components in the mixture, and viscosity has been neglected. Attention is restricted to ideal gases, for which

$$p_i = \varrho_i R_g T_i / M_i = n_i k_B T_i \,, \tag{3}$$

where T_i, M_i, and n_i are respectively the temperature, molecular weight, and number density of species i, R_g is the universal gas constant, and k_B is Boltzmann's constant. The mass-weighted velocity of the mixture is given by

$$\bar{\boldsymbol{u}} = \frac{1}{\varrho} \sum_i \varrho_i \bar{\boldsymbol{u}}_i \tag{4}$$

where $\varrho = \Sigma_i \varrho_i$ is the total mass density.

We shall presume that $\boldsymbol{F}_{ij}$ is a linear combination of the available vectors pertaining to species i and j, namely $\bar{\boldsymbol{u}}_i$, $\bar{\boldsymbol{u}}_j$, ∇T_i, and ∇T_j. It must also be invariant to Galilean transformations, and it is antisymmetric in (i,j) as already noted. The most general such expression is

$$\boldsymbol{F}_{ij} = \alpha_{ij}(\bar{\boldsymbol{u}}_j - \bar{\boldsymbol{u}}_i) + \beta_{ij} \nabla \ln T_j - \beta_{ji} \nabla \ln T_i \tag{5}$$

where α_{ij} and β_{ij} are phenomenological coefficients characterizing frictional and thermophoretic forces respectively, and $\alpha_{ij} = \alpha_{ji}$. This form will be confirmed by simple kinetic theory considerations in Section 3.

We now consider the limit of large friction, in which we anticipate that diffusional behavior will result [12]. This limit may be formally accomplished by replacing α_{ij} by α_{ij}/ε and taking the limit as $\varepsilon \to 0$. In this limit $\bar{\boldsymbol{u}}_j - \bar{\boldsymbol{u}}_i = O(\varepsilon)$ and $\bar{\boldsymbol{u}}_i = \bar{\boldsymbol{u}} + O(\varepsilon)$ for all i, so that equation (2) reduces to

$$\varrho_i \frac{D\bar{\boldsymbol{u}}}{Dt} = -\nabla p_i + \varrho_i \boldsymbol{F}_i + \sum_j \boldsymbol{F}_{ij} \tag{6}$$

where $D\bar{\boldsymbol{u}}/Dt = \partial \bar{\boldsymbol{u}}/\partial t + \bar{\boldsymbol{u}} \cdot \nabla \bar{\boldsymbol{u}}$. The total momentum equation for the mixture is obtained by summing equation (6) over all species, with the result

$$\varrho \frac{D\bar{\boldsymbol{u}}}{Dt} = -\nabla p + \sum_i \varrho_i \boldsymbol{F}_i \tag{7}$$

where $p = \Sigma_i p_i$ is the total pressure of the mixture. Combining equations (5)–(7) in such a way as to eliminate $D\bar{\boldsymbol{u}}/Dt$, we obtain

$$\begin{aligned} \sum_j \frac{z_i z_j}{D_{ij}} (\bar{\boldsymbol{u}}_j - \bar{\boldsymbol{u}}_i) &= \nabla z_i + (z_i - y_i) \nabla \ln p - \frac{1}{p} \Big(\varrho_i \boldsymbol{F}_i - y_i \sum_j \varrho_j \boldsymbol{F}_j\Big) \\ &\quad - \frac{1}{p} \sum_j (\beta_{ij} \nabla \ln T_j - \beta_{ji} \nabla \ln T_i) \end{aligned} \tag{8}$$

where $y_i = \varrho_i/\varrho$, $z_i = p_i/p$, and the binary diffusion coefficients D_{ij} are given by

$$D_{ij} = \frac{p z_i z_j}{\alpha_{ij}} . \tag{9}$$

For the present we do not define thermal diffusion coefficients analogous to the conventional ones [3], as this would introduce unnecessary algebraic complications. We simply regard and refer to the β_{ij} as thermal diffusion coefficients, albeit unconventional ones.

Equations (8) are generalized Stefan-Maxwell relations for the diffusion velocities. Only $N-1$ of them are linearly independent, as their sum over i yields $0 = 0$. They must therefore be combined with equation (4) to determine a unique solution for the $\bar{\boldsymbol{u}}_i$ in terms of the mass-weighted velocity $\bar{\boldsymbol{u}}$. The diffusional mass fluxes relative to $\bar{\boldsymbol{u}}$ are then given by

$$\mathbf{J}_i = \varrho_i (\bar{\boldsymbol{u}}_i - \bar{\boldsymbol{u}}) \tag{10}$$

in terms of which equation (1) becomes

$$\frac{\partial \varrho_i}{\partial t} + \nabla \cdot (\varrho_i \bar{\boldsymbol{u}}) = - \nabla \cdot \boldsymbol{J}_i . \tag{11}$$

We note that when thermal diffusion is neglected (or $\nabla T_i = 0$ for all i), equations (8) have the same form as the usual single-temperature Stefan-Maxwell relations [3], except that the mole fraction x_i is replaced by the pressure fraction z_i. The latter of course reduces to the former when all the component temperatures are equal.

3. Evaluation of the diffusion coefficients

We now proceed to evaluate the coefficients α_{ij} and β_{ij} using elementary kinetic theory arguments. For this purpose it is convenient to presume that $\bar{\boldsymbol{u}} = 0$, so that the $\bar{\boldsymbol{u}}_i$ may be considered small in an absolute sense. This entails no loss of generality, as it merely implies the use of a reference frame moving with the local mass-averaged velocity of the mixture.

From a microscopic point of view, $\boldsymbol{F}_{ij}$ represents momentum transfer between components due to molecular collisions. It may therefore be written as

$$\boldsymbol{F}_{ij} = \int \delta \boldsymbol{P}_{ij} d\nu_{ij} \tag{12}$$

where $\delta \boldsymbol{P}_{ij}$ is the mean momentum transfer per collision from a molecule of type j with velocity $\boldsymbol{u}_j$ to a molecule of type i with velocity $\boldsymbol{u}_i$, and $d\nu_{ij}$ is the number of collisions per unit volume per unit time between molecules of type i with velocities between $\boldsymbol{u}_i$ and $\boldsymbol{u}_i + d\boldsymbol{u}_i$ and molecules of type j with velocities between $\boldsymbol{u}_j$ and $\boldsymbol{u}_j + d\boldsymbol{u}_j$. The mean momentum transfer per collision is given by

$$\delta \boldsymbol{P}_{ij} = (\mu_{ij}/\sigma_{ij})\, Q_{ij}^{(1)}(|\boldsymbol{u}_j - \boldsymbol{u}_i|)\,(\boldsymbol{u}_j - \boldsymbol{u}_i) \tag{13}$$

where $\mu_{ij} = m_i m_j/(m_i + m_j)$ is the reduced mass, m_k is the mass of a single molecule of type k, σ_{ij} is the total cross-section for ij collisions, and $Q_{ij}^{(1)}(v)$ is the cross-section for relative speed v, which is an integral involving the angle of deflection over all impact parameters [3] and is symmetric in (i,j). The form of $Q_{ij}^{(1)}$ depends on the intermolecular force law. For hard spheres, $Q_{ij}^{(1)}(v) = \sigma_{ij} = \pi(R_i + R_j)^2$, where R_k is the hard sphere radius of a molecule of type k.

The differential collision frequency is given by

$$d\nu_{ij} = \sigma_{ij}|\boldsymbol{u}_j - \boldsymbol{u}_i|\, dn_i dn_j \tag{14}$$

where dn_k is the number density for molecules of type k with velocities between $\boldsymbol{u}_k$ and $\boldsymbol{u}_k + d\boldsymbol{u}_k$. Clearly

$$dn_k = n_k f_k(\boldsymbol{u}_k)\, d\boldsymbol{u}_k \tag{15}$$

where n_k $(= \varrho_k/m_k)$ and $f_k(\boldsymbol{u}_k)$ are respectively the total number density and normalized velocity distribution for molecules of type k. The normalization is such that $\int dn_k = n_k$, so that $\int d\boldsymbol{u}_k f_k(\boldsymbol{u}_k) = 1$. Combining equations (12)–(15), we obtain

$$\boldsymbol{F}_{ij} = n_i n_j \mu_{ij} \int d\boldsymbol{u}\, d\boldsymbol{u}' f_i(\boldsymbol{u}) f_j(\boldsymbol{u}')\, v\, Q_{ij}^{(1)}(v)\, \boldsymbol{v} \tag{16}$$

where $\boldsymbol{u}_i$ and $\boldsymbol{u}_j$ have been replaced by dummy integration variables $\boldsymbol{u}$ and $\boldsymbol{u}'$, $\boldsymbol{v} = \boldsymbol{u}' - \boldsymbol{u}$, and $v = |\boldsymbol{v}|$.

In order to proceed further it is necessary to specify the form of the velocity distributions $f_k(\boldsymbol{s})$, where $\boldsymbol{s}$ is a dummy velocity variable. For this purpose it is convenient to define a standard normalized Maxwellian distribution of the form

$$f_o(s, \gamma) = (\gamma/\pi)^{3/2} \exp(-\gamma s^2) \tag{17}$$

which is normalized so that

$$\int d\boldsymbol{s} f_o(s, \gamma) = 4\pi \int_0^\infty ds\, s^2 f_o(s, \gamma) = 1 \tag{18}$$

where $s = |\boldsymbol{s}|$. We now make the physically reasonable assumption that $f_k(\boldsymbol{s})$ in equation (16) is a normalized Maxwellian with mean velocity $\bar{\boldsymbol{u}}_k$ in which the temperature T_k is evaluated at the point of last collision. As will be seen, the latter condition is needed to obtain nonzero values for the β_{ij} and hence nonzero thermal diffusion. Thus we write

$$f_k(\boldsymbol{s}) = f_o(|\boldsymbol{s} - \boldsymbol{s}_k|, \gamma_k(\boldsymbol{r}_o - \tau_k \boldsymbol{s})) \tag{19}$$

where $\boldsymbol{r}_o$ is the point in space at which $\boldsymbol{F}_{ij}$ is to be evaluated, and τ_k is the mean time between collisions for a molecule of type k, an expression for which is derived in the Appendix. Here

$$\gamma_k(\boldsymbol{r}) = \frac{m_k}{2k_B T_k(\boldsymbol{r})} \tag{20}$$

where $T_k(\boldsymbol{r})$ is the temperature of component k at the point $\boldsymbol{r}$, and $\boldsymbol{s}_k$ is a parameter conjugate to $\bar{\boldsymbol{u}}_k$. One might at first think that $\boldsymbol{s}_k$ should in fact be equal to $\bar{\boldsymbol{u}}_k$, but this is not correct because equation (19) implies that species k has a nonzero drift velocity even when $\boldsymbol{s}_k = 0$. (Indeed, this is the essence of thermal diffusion.) We must therefore regard $\boldsymbol{s}_k$ as being implicitly determined by the condition that the mean velocity computed using $f_k(\boldsymbol{s})$ must be $\bar{\boldsymbol{u}}_k$; i.e.,

$$\int d\boldsymbol{s}\, \boldsymbol{s} f_k(\boldsymbol{s}) = \int d\boldsymbol{s}\, \boldsymbol{s} f_o(|\boldsymbol{s} - \boldsymbol{s}_k|, \gamma_k(\boldsymbol{r}_o - \tau_k \boldsymbol{s})) = \bar{\boldsymbol{u}}_k \,. \tag{21}$$

We note that $\boldsymbol{s}_k \to \bar{\boldsymbol{u}}_k$ as $\tau_k \to 0$, so that $\boldsymbol{s}_k = \bar{\boldsymbol{u}}_k + O(\tau_k)$ for small τ_k.

Now diffusion velocities are much less than typical molecular velocities [1], and distribution functions change only slightly over distances of the order of a mean free path; i.e., of order $\tau_k s$. It follows that $\bar{\boldsymbol{u}}_k$, τ_k and $\boldsymbol{s}_k$ may all be considered small, so that equation (19) may be linearized by expanding to first order in τ_k and $\boldsymbol{s}_k$. This gives

$$f_k(\boldsymbol{s}) = f_o(s, \gamma_k)\,[1 + \Delta_k(\boldsymbol{s})]\,, \tag{22}$$

where

$$\Delta_k(\boldsymbol{s}) = \left[2\gamma_k \boldsymbol{s}_k + \tau_k \left(s^2 - \frac{3}{2\gamma_k}\right) \nabla\gamma_k\right] \cdot \boldsymbol{s}\,. \tag{23}$$

Since we have linearized about the point $\boldsymbol{r}_o$, the quantities γ_k, $\nabla\gamma_k$, T_k, τ_k, $\bar{\boldsymbol{u}}_k$, and quantities derived from them are now all evaluated at $\boldsymbol{r}_o$, and this will henceforth be understood. Combining equations (21)–(23), we obtain

$$\bar{\boldsymbol{u}}_k = \boldsymbol{s}_k + \frac{\tau_k}{2\gamma_k^2} \nabla\gamma_k \tag{24}$$

so that equation (23) may be rewritten as

$$\Delta_k(\boldsymbol{s}) = \left[2\gamma_k \bar{\boldsymbol{u}}_k + \tau_k \left(s^2 - \frac{5}{2\gamma_k}\right) \nabla\gamma_k\right] \cdot \boldsymbol{s}\,. \tag{25}$$

The corresponding linearization of $f_i(\boldsymbol{u}) f_j(\boldsymbol{u}')$ is given by

$$f_i(\boldsymbol{u}) f_j(\boldsymbol{u}') = f_{oi}(\boldsymbol{u}) f_{oj}(\boldsymbol{u}')\,[1 + \Delta_i(\boldsymbol{u}) + \Delta_j(\boldsymbol{u}')] \tag{26}$$

where $f_{ok}(s) = f_o(s, \gamma_k)$, $u = |\boldsymbol{u}|$ and $u' = |\boldsymbol{u}'|$. Combining equations (16) and (26), we obtain

$$\boldsymbol{F}_{ij} = n_i n_j \mu_{ij}(\boldsymbol{H}_{ij} - \boldsymbol{H}_{ji}) \tag{27}$$

where

$$\boldsymbol{H}_{ij} = \int d\boldsymbol{u}\, d\boldsymbol{u}' f_{oi}(u) f_{oj}(u')\, \Delta_i(\boldsymbol{u})\, v Q_{ij}^{(1)}(v)\, \boldsymbol{v}\,. \tag{28}$$

Note that the contribution of the zeroth-order term in equation (26) has vanished by symmetry, corresponding to the fact that there is no net momentum transfer when the diffusion velocities and temperature gradients vanish.

Combining equations (25) and (28), we obtain

$$\boldsymbol{H}_{ij} = \mathbf{A}_{ij} \cdot \bar{\boldsymbol{u}}_i + \boldsymbol{B}_{ij} \cdot \nabla \gamma_i \tag{29}$$

where

$$\mathbf{A}_{ij} = 2\gamma_i \int d\boldsymbol{u}\, d\boldsymbol{u}' f_{oi}(u) f_{oj}(u')\, v Q_{ij}^{(1)}(v)\, \boldsymbol{v}\boldsymbol{u} \tag{30}$$

$$\boldsymbol{B}_{ij} = \tau_i \int d\boldsymbol{u}\, d\boldsymbol{u}' f_{oi}(u) f_{oj}(u')\, v Q_{ij}^{(1)}(v) \left(u^2 - \frac{5}{2\gamma_i}\right) \boldsymbol{v}\boldsymbol{u}\,. \tag{31}$$

These tensor coefficients must be isotropic, since they contain no preferred directions. They may therefore be replaced by equivalent scalars, so that equation (29) becomes.

$$\boldsymbol{H}_{ij} = a_{ij} \bar{\boldsymbol{u}}_i + b_{ij} \nabla \gamma_i \tag{32}$$

where

$$a_{ij} = \frac{2\gamma_i}{3} \int d\boldsymbol{u}\, d\boldsymbol{u}' f_{oi}(u) f_{oj}(u')\, v Q_{ij}^{(1)}(v)\, \boldsymbol{u} \cdot \boldsymbol{v} \tag{33}$$

$$b_{ij} = \frac{\tau_i}{3} \int d\boldsymbol{u}\, d\boldsymbol{u}' f_{oi}(u) f_{oj}(u')\, v Q_{ij}^{(1)}(v) \left(u^2 - \frac{5}{2\gamma_i}\right) \boldsymbol{u} \cdot \boldsymbol{v}\,. \tag{34}$$

We may express b_{ij} in terms of a_{ij} by using the fact that $(\partial/\partial\gamma_i) \exp(-\gamma_i u^2) = -u^2 \exp(-\gamma_i u^2)$. We thereby obtain

$$b_{ij} = \frac{-\tau_i}{2\gamma_i} \frac{\partial a_{ij}}{\partial \gamma_i}\,. \tag{35}$$

The integral in equation (33) may be simplified by transforming to new integration variables $(\boldsymbol{v}, \boldsymbol{w})$, where $\boldsymbol{w} = (\gamma_i \boldsymbol{u} + \gamma_j \boldsymbol{u}')/(\gamma_i + \gamma_j)$. The inverse transformation is given by $\boldsymbol{u} = \boldsymbol{w} - \gamma_{ij} \boldsymbol{v}/\gamma_i$, $\boldsymbol{u}' = \boldsymbol{w} + \gamma_{ij} \boldsymbol{v}/\gamma_j$, where $\gamma_{ij} = \gamma_i \gamma_j/(\gamma_i + \gamma_j)$. It follows that

$$\boldsymbol{u} \cdot \boldsymbol{v} = \boldsymbol{v} \cdot \boldsymbol{w} - (\gamma_{ij}/\gamma_i)\, v^2\,. \tag{36}$$

After a little algebra, one further finds that

$$f_{oi}(u) f_{oj}(u') = f_o(v, \gamma_{ij}) f_o(w, \gamma_i + \gamma_j) \tag{37}$$

where $w = |\boldsymbol{w}|$. Since f_o is normalized, integrating equation (37) over either $(\boldsymbol{u}, \boldsymbol{u}')$ or $(\boldsymbol{v}, \boldsymbol{w})$ gives $1 = 1$. It follows that $d\boldsymbol{u} d\boldsymbol{u}' = d\boldsymbol{v} d\boldsymbol{w}$, so that equations (33), (36), and (37) may be combined to yield

$$a_{ij} = -\frac{8\pi}{3} \gamma_{ij} \int_0^\infty dv f_o(v, \gamma_{ij}) v^5 Q_{ij}^{(1)}(v) \tag{38}$$

where use has been made of equation (18) and the fact that $\int d\boldsymbol{w} f_o(w, \gamma)\, \boldsymbol{w} = 0$.

Notice that a_{ij} is symmetric in (i, j), whereas b_{ij} is not.

The integral in equation (38) can be expressed in terms of a standard first-order collision integral from kinetic theory. The relevant family of integrals is defined by [3]

$$\Omega_{ij}^{(1)}(n, T) = \frac{\pi}{2} \left(\frac{\mu_{ij}}{2k_B T} \right)^n \int_0^\infty dv f_o(v, \mu_{ij}/2k_B T)\, v^{2n+3} Q_{ij}^{(1)}(v) \tag{39}$$

where T is a dummy temperature variable. This reduces to $(n+1)!\,\sigma_{ij}(k_B T/8\pi\mu_{ij})^{1/2}$ for hard spheres [3]. The binary diffusion coefficients in single-temperature FOCE theory are simply related to $\Omega_{ij}^{(1)}(1, T)$. We see from equation (38) that the same integral occurs in the present context with $\mu_{ij}/2k_B T$ replaced by γ_{ij}. This correspondence makes it useful to define an effective temperature T_{ij} for the pair (i, j) at the point $\boldsymbol{r}_o$ by $\mu_{ij}/2k_B T_{ij} = \gamma_{ij}$, which implies that

$$T_{ij} = (m_i T_j + m_j T_i)/(m_i + m_j)\,. \tag{40}$$

When $T_i = T_j = T$, T_{ij} reduces to T and γ_{ij} reduces to $\mu_{ij}/2k_B T$.

Equation (38) now becomes

$$a_{ij} = -\frac{16}{3} \Omega_{ij}^{(1)}(1, T_{ij}) \tag{41}$$

and this combines with equation (35) to yield

$$b_{ij} = \frac{8\tau_i}{3\gamma_i} \frac{\partial \Omega_{ij}^{(1)}(1, T_{ij})}{\partial \gamma_i} = \frac{8\tau_i}{3\gamma_i} \frac{\partial \Omega_{ij}^{(1)}(1, T_{ij})}{\partial T_{ij}} \frac{\partial T_{ij}}{\partial \gamma_{ij}} \frac{\partial \gamma_{ij}}{\partial \gamma_i}\,. \tag{42}$$

We readily find that $\partial\gamma_{ij}/\partial\gamma_i = (\gamma_{ij}/\gamma_i)^2$ and $\partial T_{ij}/\partial\gamma_{ij} = -T_{ij}/\gamma_{ij}$, and it follows from equation (39) that

$$\frac{\partial \Omega_{ij}^{(1)}(1, T)}{\partial T} = \frac{1}{2T} [2\Omega_{ij}^{(1)}(2, T) - 5\Omega_{ij}^{(1)}(1, T)]\,. \tag{43}$$

Equation (42) therefore becomes

$$b_{ij} = \frac{4\tau_i\gamma_{ij}}{3\gamma_i^3}\left[5\Omega_{ij}^{(1)}(1, T_{ij}) - 2\Omega_{ij}^{(1)}(2, T_{ij})\right]. \tag{44}$$

We can now relate the phenomenological coefficients α_{ij} and β_{ij} to a_{ij} and b_{ij}, and thereby to the collision integrals. Combining equations (20), (27), and (32) and comparing the result to equation (5), we obtain

$$\alpha_{ij} = -n_i n_j \mu_{ij} a_{ij} = \frac{16}{3} n_i n_j \mu_{ij} \Omega_{ij}^{(1)}(1, T_{ij}) \tag{45}$$

$$\beta_{ij} = n_i n_j \mu_{ij} \gamma_j b_{ji} = \frac{4\tau_j}{3\gamma_j^2} n_i n_j \mu_{ij} \gamma_{ij}\left[5\Omega_{ij}^{(1)}(1, T_{ij}) - 2\Omega_{ij}^{(1)}(2, T_{ij})\right] \tag{46}$$

where use has been made of equations (41) and (44). Notice that $\beta_{ij} = 0$ if $\tau_j = 0$, which shows that thermal diffusion would indeed vanish if $f_k(s)$ had been evaluated at the point $\boldsymbol{r}_o$ rather than the point of last collision. Combining equations (3), (9), and (45), we obtain

$$D_{ij} = \frac{3k_B^2 T_i T_j}{16p\mu_{ij}\Omega_{ij}^{(1)}(1, T_{ij})}. \tag{47}$$

Note that D_{ij} is independent of composition for given values of T_i, T_j, and p. In the special case of hard spheres, equation (47) reduces to $D_{ij} = (3k_B^2 T_i T_j / 8p\sigma_{ij}) \cdot (\pi/2\mu_{ij}k_B T_{ij})^{1/2}$. In the special case of equal component temperatures, equation (47) reduces to precisely the expression for D_{ij} obtained from FOCE theory [3]. This agreement is not unexpected, as it was previously obtained by Furry [1] in the case of binary mixtures. It is nevertheless remarkable that the elementary theory predicts D_{ij} to such high accuracy. The theory does not, however, provide thermal diffusion coefficients β_{ij} of comparable accuracy, for the simple reason that b_{ij} involves an inherently approximate collision time whereas a_{ij} does not.

Since the β_{ij} are inherently approximate in any case, it may be of interest to consider a further approximation in which they reduce to a considerably simpler form. This approximation consists in replacing u^2 in equation (34) by its mean value $\int du f_{oi}(u)\, u^2 = 3/2\gamma_i$. When this is done, it follows from equations (33) and (34) that $b_{ij} = -(\tau_i/2\gamma_i^2)\, a_{ij}$, which combines with equations (45)–(47) to yield

$$\beta_{ij} = \frac{\alpha_{ij}\tau_j}{2\gamma_j} = \frac{8\tau_j}{3\gamma_i} n_i n_j \mu_{ij} \Omega_{ij}^{(1)}(1, T_{ij}) = \frac{p z_i z_j \tau_j}{2\gamma_j D_{ij}}. \tag{48}$$

In this approximation, therefore, β_{ij} is related to D_{ij} in a direct and very simple way.

4. Single-temperature systems

Here we specialize the general results of the preceding sections to the case in which the individual component temperatures are all equal; i.e., $T_i = T$ for all i. This is of course the most common situation of interest. In this case the pressure fractions z_i reduce to the mole fractions $x_i = n_i/n$ (where $n = \Sigma_i n_i$ is the total number density), and as previously noted the D_{ij} reduce to the usual single-temperature binary diffusivities. The Stefan-Maxwell relations of equation (8) then become

$$\sum_j \frac{x_i x_j}{D_{ij}} (\bar{u}_j - \bar{u}_i) = \nabla x_i + (x_i - y_i) \nabla \ln p - \frac{1}{p} \left(\varrho_i F_i - y_i \sum_j \varrho_j F_j \right) - \frac{1}{p} \sum_j (\beta_{ij} - \beta_{ji}) \nabla \ln T . \tag{49}$$

Equation (49) is identical to the standard Stefan-Maxwell equations [3], if we make the identification

$$\frac{1}{p} \sum_j (\beta_{ji} - \beta_{ij}) = \sum_j \frac{x_i x_j}{D_{ij}} \left(\frac{D_i^T}{\varrho_i} - \frac{D_j^T}{\varrho_j} \right) \tag{50}$$

where the D_k^T are the conventional multicomponent thermal diffusion coefficients for a single-temperature system [3], which are constrained by

$$\sum_k D_k^T = 0 . \tag{51}$$

Equations (50) and (51) constitute a simultaneous linear system of equations which determine the D_k^T in terms of the β_{ij}.

The solution of this system is greatly simplified when the β_{ij} are approximated by equation (48). Equation (50) then takes the form

$$k_B T \sum_j \frac{x_i x_j}{D_{ij}} \left(\frac{\tau_i}{m_i} - \frac{\tau_j}{m_j} \right) = \sum_j \frac{x_i x_j}{D_{ij}} \left(\frac{D_i^T}{\varrho_i} - \frac{D_j^T}{\varrho_j} \right) \tag{52}$$

which may be solved by inspection to give $D_i^T/\varrho_i = k_B T \tau_i/m_i + C$, where C is a constant independent of i. This constant may be determined from equation (51), and we thereby obtain

$$D_i^T = k_B T (n_i \tau_i - y_i \sum_j n_j \tau_j) \tag{53}$$

which provides a remarkably simple approximation for the thermal diffusion coefficients in a multicomponent gas mixture.

5. Binary mixtures

In a binary mixture of components 1 and 2, equations (4), (8), and (10) combine to yield

$$J_1 = -\frac{\varrho_1 \varrho_2 D_{12}}{\varrho z_1 z_2} \left[\nabla z_1 + (z_1 - y_1) \nabla \ln p + \frac{\varrho_1 \varrho_2}{\varrho p} (F_2 - F_1) + \frac{1}{p} (\beta_{21} \nabla \ln T_1 - \beta_{12} \nabla \ln T_2) \right]. \tag{54}$$

In the special case of equal temperatures ($T_1 = T_2 = T$), z_i reduces to $x_i = n_i/n$ and equation (54) further reduces to

$$J_1 = -\frac{n^2}{\varrho} m_1 m_2 D_{12} [d_1 + \frac{1}{p} (\beta_{21} - \beta_{12}) \nabla \ln T] \tag{55}$$

where $d_1 = \nabla x_1 + (x_1 - y_1) \nabla \ln p + (\varrho_1 \varrho_2 / \varrho p)(F_2 - F_1)$. Moreover, in a binary mixture equations (50) and (51) combine to yield

$$D_1^T = \frac{n^2}{\varrho p} m_1 m_2 D_{12} (\beta_{21} - \beta_{12}) \tag{56}$$

so that equation (55) becomes

$$J_1 = -\frac{n^2}{\varrho} m_1 m_2 D_{12} d_1 - D_1^T \nabla \ln T = -\frac{n^2}{\varrho} m_1 m_2 D_{12} (d_1 + k_T \nabla \ln T) \tag{57}$$

where the thermal diffusion ratio k_T is defined by [3],

$$k_T = \frac{\varrho D_1^T}{n^2 m_1 m_2 D_{12}}. \tag{58}$$

Combining equations (46), (56), and (58), we obtain

$$k_T = \frac{8}{3} n x_1 x_2 \mu_{12}^2 \left(\frac{\tau_1}{m_1^2} - \frac{\tau_2}{m_2^2} \right) [5 \Omega_{12}^{(1)}(1, T) - 2 \Omega_{12}^{(1)}(2, T)]. \tag{59}$$

It is of interest to compare this result with that of Furry [1], which he obtained by a somewhat different approach. Furry adopts a different sign convention, according to which his k_T is the negative of ours. With this in mind, we find that our equation (59) agrees with Furry's equation (97) if we identify $\bar{c}_i \lambda_i$ with $2 k_B T \tau_i / m_i$, where $\bar{c}_i$ and λ_i are respectively the mean speed and mean free path for molecules of type i in Furry's treatment. This identification is indeed sensible, as can be seen by estimating $\lambda_i = \bar{c}_i \tau_i$ so that $\bar{c}_i \lambda_i = \bar{c}_i^2 \tau_i = 8 k_B T \tau_i / \pi m_i$. This differs from the desired identification by only a factor of $4/\pi = 1.27$, which is just the sort of discrepancy that one often encounters in simplified kinetic theories. The present theory is therefore in essential agreement with Furry in the special case of binary mixtures with equal temperatures.

6. Self-consistent effective binary diffusion approximation

The multicomponent Stefan-Maxwell relations of equation (8), together with equation (4), constitute a simultaneous linear system of equations for the diffusion velocities. Effective binary diffusion approximations are sometimes used to avoid solving this system. A self-consistent effective binary diffusion approximation for single-temperature gas mixtures was described in reference [13]. Here we generalize this approximation to the case of multiple component temperatures.

Let $\boldsymbol{G}_i$ denote the entire right member of equation (8). This equation then becomes identical in form to equation (1) of reference [13], but with x_i replaced by z_i. With this replacement, the entire development of reference [13] may then be followed through with no further modifications. The resulting self-consistent approximation to the diffusion fluxes is

$$\boldsymbol{J}_i = -\left(\frac{pM_iD_i}{R_gT_i}\right)\boldsymbol{G}_i + y_i\sum_j\left(\frac{pM_jD_j}{R_gT_j}\right)\boldsymbol{G}_j \tag{60}$$

where the effective binary diffusivities D_i are given by

$$D_i = \left(1 - \frac{w_i}{w}\right)\left(\sum_{j \neq i}\frac{z_j}{D_{ij}}\right)^{-1}. \tag{61}$$

Here the w_i are weighting factors and w is their sum [13]. In the case of equal temperatures (i.e., $T_i = T$ for all i), z_i reduces to x_i, D_{ij} and $\boldsymbol{G}_i$ reduce to their single-temperature forms, p/R_gT_i reduces to the total molar concentration c, and equations (60) and (61) reduce to equations (16) and (15) of reference [13], respectively. We remark that the self-consistent effective binary diffusion approximation becomes exact in a binary mixture, regardless of the choice of the weighting factors w_i.

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Appendix: collision frequencies and times

The total number of collisions per unit time experienced by a single molecule of type i may be written as

$$\nu_i = \frac{1}{n_i} \sum_j \int d\nu_{ij} = \sum_j n_j \sigma_{ij} \int d\boldsymbol{u}\, d\boldsymbol{u}' f_{oi}(\boldsymbol{u}) f_{oj}(\boldsymbol{u}') \, |\boldsymbol{u} - \boldsymbol{u}'| \tag{A1}$$

where the summation extends over all species in the mixture, including species i, and $f_k(\boldsymbol{u})$ in equation (15) has been replaced by $f_{ok}(\boldsymbol{u})$ in accordance with the linearization of equation (22). The integral in equation (A1) may be evaluated by transforming to new integration variables $(\boldsymbol{v}, \boldsymbol{w})$, just as in equation (33) of the main text. We thereby obtain

$$\nu_i = 2 \sum_j \frac{n_j \sigma_{ij}}{\sqrt{\pi \gamma_{ij}}} . \tag{A2}$$

The collision time τ_i is then simply the reciprocal of ν_i,

$$\tau_i = \frac{1}{\nu_i} = \frac{1}{2} \left(\sum_j \frac{n_j \sigma_{ij}}{\sqrt{\pi \gamma_{ij}}} \right)^{-1} . \tag{A3}$$

References

[1] Furry, W. H., On the Elementary Explanation of Diffusion Phenomena in Gases, Am. J. Phys., 16 (1948), 63.
[2] Williams, F. A., Elementary Derivation of the Multicomponent Diffusion Equation, Am. J. Phys., 26 (1958), 467.
[3] Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., Molecular Theory of Gases and Liquids, Wiley, New York, 1964.
[4] Chapman, S., Cowling, T. G., The Mathematical Theory of Non-Uniform Gases, 3rd ed., Cambridge University Press, Cambridge, 1970.
[5] Ferziger, J. H., Kaper, H. G., Mathematical Theory of Transport Processes in Gases, North-Holland, Amsterdam, 1972.
[6] Truesdell, C., Mechanical Basis of Diffusion, J. Chem. Phys., 37 (1962), 2336.
[7] Williams, F. A., Combustion Theory, 2nd ed., Benjamin/Cummings, Menlo Park, CA, 1985, Sect. E.2.1.
[8] Chmieleski, R. M., Ferziger, J. H., Transport Properties of a Nonequilibrium Partially Ionized Gas, Phys. Fluids, 10 (1967), 364
[9] Daybelge, U., Unified Transport Theory of Partially Ionized Nonisothermal Plasmas, J. Appl. Phys., 41 (1970), 2130.
[10] Kruger, C. H., Mitchner, M., Kinetic Theory of Two-Temperature Plasmas, Phys. Fluids., 10 (1967), 1953.
[11] Mitchner, M., Kruger, C. H., Partially Ionized Gases, Wiley-Interscience, New York, 1973.
[12] Ramshaw, J. D., Brownian Motion in a Flowing Fluid, Phys. Fluids, 22 (1979), 1595.
[13] Ramshaw, J. D., Self-Consistent Effective Binary Diffusion in Multicomponent Gas Mixtures, J. Non-Equilib. Thermodyn., 15 (1990), 295.

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