

TRANSPORT THEORY OF BINARY MIXTURE
WITH ONE TRACE COMPONENT OF DISPARATE MASS

Wokyung Sung

Department of Physics
State University of New York at Stony Brook
Long Island, New York 11974

and

G. Stell

Departments of Mechanical Engineering and Chemistry
State University of New York at Stony Brook
Long Island, New York 11974

Report #353
October, 1980

ABSTRACT

We develop a simple but novel method for calculating transport coefficients for binary hard-sphere mixtures with one trace component of extreme mass disparity (Lorentzian and Rayleighian mixtures). The results are exact on the Enskog theory level, within the framework of the Chapman-Enskog solution. Such mixtures allow us to expand the solute-solvent collision integral in powers of the mass ratio and thereby to reduce it to a differential form, from which we can in principle calculate directly velocity moments of various orders relevant to the fluxes instead of determining the distribution function. Here we mainly concern ourselves with determination of the transport coefficients through the first-order in the mass ratio. Our results for the transport coefficients are compared with those obtained from the lowest Sonine polynomial approximation. We find this approximation becomes exact in a Rayleighian mixture while it is at its worst in the Lorentz limit. We give a brief comparative analysis of shear viscosity, bulk viscosity and thermal conductivity in the Lorentz and Rayleigh limits.

I. INTRODUCTION

Before Chapman and Enskog¹ presented a comprehensive transport theory based on the Boltzmann equation in 1916 - 1917, there had been some attempts to calculate transport coefficients, in special cases. Among them, the model Lorentz² considered to describe the transport of electron in metal provides an exactly solvable case. Lorentz noted that the problem is similar to that of a binary mixture in which the molecule of one component has a negligible mass compared to that of the other. Ignoring the mutual collisions between the particles of the lighter component, whose motions are therefore affected only by their collision with that of the heavy component which are regarded as quasi-stationary, he could calculate the thermal and electrical conductivity and diffusivity of the light particle, without having to determine the velocity distribution function. Since it does not involve any approximations, his results provide a standard or benchmark to test the approximation method, i.e. the use of Sonine polynomial approximation.³

An extension of this model to include the effect of nonnegligible response of the heavy component (gas) was attempted by Pidduck⁴ in his study of ions in gases. He made use of Hilbert's transformation⁵ of the Boltzmann equation, in which the collision integral is reduced to a form resembling the left-hand side of an integral equation, and he expanded the resulting collisional term for a hard-sphere interaction up through the first order in the mass

ratio, which included the Lorentz collision term as the lowest order, thereby yielding the first-order mass ratio correction to the Lorentz results for the diffusivity. He also considered the opposite limiting case, i.e. heavy ions in lighter gas molecules (which we shall refer as Rayleighian mixtures). In this case he showed that the Boltzmann equation can be reduced to the Focker-Planck equation, through which the diffusivity could be evaluated directly. Although his treatment is limited to the case of a gas in equilibrium and ions in steady state, his results proved to be identical to the more rigorous results of Kihara⁶ and Mason,⁷ which are based on the Chapman-Enskog solution^{1,8} of the Boltzmann equation.

A more recent extension of the "Almost-Lorentzian" gas made by Mason et al.⁹ is based on the Chapman-Enskog solution. To improve the nature of convergence in the Sonine-polynomial series expansion for the solution of the Boltzmann equation, which is at its worst for such mixtures, Mason et al. developed for almost-Lorentzian mixtures a perturbation scheme which exploits the exact results available in the Lorentz limit. Since their evaluation of the transport coefficients is made through the use of the Sonine polynomial expansion, their results can also be utilized in the case of a larger region of solute composition. Thus, this work is different from the work of Pidduck in spirit, but less straightforward with regard to affecting the mass correction for the trace-binary mixture in which the lighter solute particle is

extremely dilute.

The transport coefficients previously considered in the Lorentzian mixtures have been the diffusivity (binary and thermal) and thermal conductivity. For Rayleighian mixture, the binary diffusivity has been the only transport coefficient that was calculated exactly.^{6,7} The method of evaluating the transport coefficients in the Lorentz limit (well described in the monographs of Chapman-Cowling⁸ and Ferzigen-Kaper¹⁰) is not capable of yielding--in its strict sense of a binary mixture--the transport coefficients such as the shear viscosity and the thermal conductivity since the treatment is concerned only with the motion of the light particle deflected by the stationary solvent particle. Here we present a method of calculating, within the context of Chapman-Enskog theory, all the transport coefficients of the Rayleighian and Lorentzian mixtures in which the more massive solvent particle is also mobile. To consider a wider range of solvent density we also go beyond the Boltzmann-equation description. We use as the starting point the revised Enskog equation,¹¹ which is the only simple kinetic theory of dense fluid available that permits analytic expression for the transport coefficients of dense fluid. Among other things, the Enskog-theory treatment yields the bulk viscosity which in the Lorentz limit has an interesting physical implication. This work was motivated by our study of the shear and bulk viscosities in dilute suspension (trace binary

mixture) for the solute particle of arbitrary mass and size,¹² where the problem posed is how far the lowest Sonine polynomial approximations that we used remain reliable. As the result of this work, we find they are reasonably accurate as long as the mass of the solute particle is not much smaller than that of the solvent particle, and in particular they are exact in the limit of large solute particle mass.

In section II, we present a brief sketch of the standard materials on which our subsequent developments are based: The hydrodynamic equations constructed from the kinetic (revised Enskog) equation and Chapman-Enskog's hydrodynamic (normal) solution of the revised Enskog equation. In section III, we develop a theory of transport in trace-binary mixture of mass disparity by expanding the solute-solvent collision integral in terms of the mass ratio taken as a small parameter. We calculate the transport coefficients without solving the equation for the distribution function by determining the appropriate (peculiar) velocity moments. Our results are compared with the results of the lowest Sonine polynomial approximation used in solving the distribution function. Some comparative analysis of shear and bulk viscosities and thermal conductivity in both limits are made. Our conclusions are summarized in section IV.

II. HYDRODYNAMIC SOLUTION OF THE REVISED ENSKOG THEORY OF A BINARY
HARD-SPHERE MIXTURE

Our starting point is the revised Enskog equation¹¹ that reads

$$\left(\frac{\partial}{\partial t} + \tilde{V}_i \cdot \tilde{\nabla} \right) f_i(\tilde{r}, \tilde{V}_i, t) = \sum_j J_{ij} \quad (i, j = 1, 2) \quad (2-1)$$

with the collision integral

$$\begin{aligned} J_{ij} = & \sigma_{ij}^2 \int d\tilde{V}_j d\tilde{\sigma} (\tilde{\sigma} \cdot \tilde{V}_{ji}) \Theta(\tilde{\sigma} \cdot \tilde{V}_{ji}) \\ & \times [g_{ij}(\tilde{r}, \tilde{r} + \tilde{\sigma}_{ij} \tilde{\sigma}) f_i(\tilde{r}, \tilde{V}_i', t) f_j(\tilde{r} + \tilde{\sigma}_{ij} \tilde{\sigma}, \tilde{V}_j', t) \\ & - g_{ij}(\tilde{r}, \tilde{r} - \tilde{\sigma}_{ij} \tilde{\sigma}) f_i(\tilde{r}, \tilde{V}_i, t) f_j(\tilde{r} - \tilde{\sigma}_{ij} \tilde{\sigma}, \tilde{V}_j, t)] \end{aligned} \quad (2-2)$$

where f_i is one particle distribution function (DF) of the species i , σ_{ij} is the contact distance between the center of the particle i and j , $\tilde{V}_{ji} = \tilde{V}_j - \tilde{V}_i$, the primes in the velocity denotes the post collisional values, $\tilde{\sigma}$ is the unit vector along the apse line in such a direction that the Heaviside step function $\Theta(\tilde{\sigma} \cdot \tilde{V}_{ji})$ imposes the condition of the collision. g_{12} is local equilibrium pair distribution function at contact which depends functionally on the local density fields.¹¹

Our interest here lies mainly in the hydrodynamic transport properties of binary mixture which are considered as a homogeneous continuum specified by the local hydrodynamic variables regardless of any molecular disparity in the constituent molecules.

The adequate description for this situation is provided by a contraction of the full kinetic description via (2-1) into the hydrodynamic description for the lowest first five moments of f_i :

$$\rho(\underline{r}, t) = \sum_i \int dV_i m_i f_i \quad (2-3a)$$

$$\rho \underline{u}(\underline{r}, t) = \sum_i \int dV_i m_i V_i f_i \quad (2-3b)$$

$$\frac{3}{2} n(\underline{r}, t) k_B T(\underline{r}, t) = \sum_i \int dV_i \frac{1}{2} m_i [V_i - \underline{u}(\underline{r}, t)]^2 f_i \quad (2-3c)$$

Here n , ρ , \underline{u} , T are the local number density, fluid mass density, hydrodynamic velocity, and the temperature of the fluid mixture. k is the Boltzmann constant. Applying the above definition to the kinetic equation (2-1), one obtains the hydrodynamic equations for the change of mass momentum, and energy:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \underline{u} = 0 \quad (2-4a)$$

$$\frac{\partial}{\partial t} \rho \underline{u} + \nabla \cdot (\rho \underline{u} \underline{u} + \underline{P}) = 0 \quad (2-4b)$$

$$\frac{3}{2} nk \left(\frac{\partial T}{\partial t} + \underline{u} \cdot \nabla T \right) + \nabla \cdot \underline{J}_T + \underline{P} \cdot \nabla \underline{u} = 0 \quad (2-4c)$$

where the momentum flux and energy flux is shown to consist of streaming part and collisional part.¹³

$$\underline{P} = \underline{P}^S + \underline{P}^C \quad (2-5)$$

$$\underline{P}^S = \sum_i \int f_i m_i (V_i - \underline{u})(V_i - \underline{u}) dV_i$$

$$\begin{aligned}
P_{ij}^C &= \sum_{i,j} \frac{1}{2} \sigma_{ij}^3 \int dV_j dV_i d\sigma \Theta(\sigma \cdot V_{ji}) (\sigma \cdot V_{ji}) \sigma (m_i V_i' - m_i V_i) \\
&\quad \times \int_0^1 d\alpha g_{ij}(r - \alpha \sigma_{ij} \sigma, r + (1-\alpha) \sigma_{ij} \sigma) f_i(r - \alpha \sigma_{ij} \sigma, V_i, t) \\
&\quad \times f_j[r + \sigma_{ij} \sigma (1-\alpha), V_j, t]
\end{aligned} \tag{2-6}$$

$$\begin{aligned}
J_T &= J_T^S + J_T^C \\
J_T^S &= \sum_i \int f_i \frac{1}{2} m_i (V_i - u) (V_i - u)^2 dV_i \\
J_T^V &= \sum_{i,j} \frac{1}{2} \sigma_{ij}^3 \int dV_j dV_i d\sigma \Theta(\sigma \cdot V_{ji}) (\sigma \cdot V_{ji}) \sigma \\
&\quad \times \left\{ \frac{1}{2} m_i (V_i' - u)^2 - \frac{1}{2} m_i (V_i - u)^2 \right\} \int_0^1 d\alpha g_{ij}[r - \alpha \sigma_{ij} \sigma, r + (1-\alpha) \sigma_{ij} \sigma] \\
&\quad \times f_i(r - \alpha \sigma_{ij} \sigma, V_i, t) f_j[r + \sigma_{ij} \sigma (1-\alpha), V_j, t]
\end{aligned} \tag{2-7}$$

In addition, we are interested in the process of the diffusion of the one species to the other, which is described by the equation

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot J_M^{(i)} = 0 \tag{2-8}$$

where the mass density and the mass flux are defined by

$$\rho_i = \int dV_i m_i f_i \tag{2-9}$$

$$J_M^{(i)} = \int dV_i m_i V_i f_i \tag{2-10}$$

To give specific expressions for the fluxes, f_i generally should be solved. On the other hand, in phenomenological theory

these are given by the linear constitutive relations between the fluxes and gradients in the hydrodynamic variables, which are

i) Newton's law of friction

$$\underline{\underline{P}} = - P \underline{\underline{I}} + \eta [\underline{\underline{\nabla}} \underline{\underline{u}} + (\underline{\underline{\nabla}} \underline{\underline{u}})^+ - \frac{2}{3} \underline{\underline{\nabla}} \cdot \underline{\underline{u}} \underline{\underline{I}}] + \kappa (\underline{\underline{\nabla}} \cdot \underline{\underline{u}} \underline{\underline{I}}) \quad (2-11)$$

ii) Fourier law of heat conduction

$$\underline{\underline{J}}_T = -\lambda \underline{\underline{\nabla}} T \quad (2-12)$$

iii) Fick's law of diffusion

$$\underline{\underline{J}}_M^{(1)} = -\rho \mathcal{D}_{12} \underline{\underline{\nabla}} (\rho_1 / \rho). \quad (2-13)$$

Here η , κ , λ , \mathcal{D}_{12} is the shear viscosity, bulk viscosity, thermal conductivity and diffusivity and P is the local hydrostatic pressure. With these relations the hydrodynamic equations (2-4a-c) are closed. The rigorous kinetic-theoretic foundation for this contracted description is provided by Chapman-Enskog procedure¹ of normal solution for equation (2-1), which we shall sketch briefly below. This solution yields empirical relations (2-11), (2-12), (2-13) as well as the expressions for the transport coefficients in terms of the molecular parameters.

In the time and length scale relevant to hydrodynamic description (t_h, ℓ_h) which is far larger than the molecular scales (t_c, ℓ_c : the mean collision time and length), the molecules undergo an extremely large number of collisions and the state of fluid is brought very close to the local equilibrium. Thus, we look for the solution

$$f_i = f_i^0 + f_i^1 = f_i^0(1 + \Phi_i) \quad (2-14)$$

where

$$f_i^0 = n_i \left(\frac{m_i}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m_i [V_i - u(\underline{r}, t)]^2}{2kT(\underline{r}, t)} \right] \quad (2-15)$$

is the local equilibrium distribution function. Substituting this into the eq. (2-1), we observe that LHS of the equation is characterized by the scales t_h , λ_h , over which the hydrodynamic fields varies. On the other hand, the collisional term is characterized by t_c , λ_c . Hence we find $\Phi_i = f_i^1/f_i^0$ is in the order of the smallness parameter $\epsilon = t_c/t_h = \lambda_c/\lambda_h \ll 1$, consistent with our ansatz of local-equilibrium form as the lowest order approximation. Noting that

$$\lambda_c \nabla \sim 0(\epsilon) \quad t_c \frac{\partial}{\partial t} \sim 0(\epsilon)$$

and equating the coefficients of the equal powers in ϵ in RHS and LHS of the eq. (2-1), we obtain to the order ϵ^0 , ϵ^1 .

$$\epsilon^0; 0 = \sum_j \sigma_{ij}^2 Y_{ij} \int dV_j d\sigma (\sigma \cdot V_{ji}) \Theta(\sigma \cdot V_{ji}) (f_i^{0'} f_j^{0'} - f_i^0 f_j^0) \quad (2-16)$$

$$\begin{aligned} \epsilon^1; \left(\frac{\partial}{\partial t} + \underline{v}_i \cdot \nabla \right) f_i &= \sum_j \sigma_{ij}^2 Y_{ij} \int dV_j d\sigma \Theta(\sigma \cdot V_{ji}) (\sigma \cdot V_{ji}) \\ &\times [(f_i^{0'} f_j^{1'} + f_i^{1'} f_j^{0'} - f_i^0 f_j^1 - f_i^1 f_j^0) \\ &- \sigma_{ij} f_i^{0'} \sigma \cdot \nabla f_j^{0'} - \sigma_{ij} f_j^0 \sigma \cdot \nabla f_i^0 \\ &+ f_i^0 f_j^0 \sum_\ell \int d\underline{r}_\ell |\underline{r}_\ell - \underline{r}| \nabla n_\ell(\underline{r}, t) \{ H_{ij\ell}(|\underline{r}_\ell - \underline{r}_i|, |\underline{r}_\ell - \underline{r}_i - \sigma_{ij} \sigma|) \\ &- H_{ij\ell}(|\underline{r}_\ell - \underline{r}_i|, |\underline{r}_\ell - \underline{r}_i + \sigma_{ij} \sigma|) \}] \end{aligned} \quad (2-17)$$

$$f_i^n = f_i^n(\tilde{r}, \tilde{v}_i, t), f_i^{n'} = f_i^{n'}(\tilde{r}, \tilde{v}_i', t)$$

$$H_{ij\ell}(|\tilde{r}_\ell - \tilde{r}_i|, |\tilde{r}_\ell - \tilde{r}_j|) \equiv \frac{\delta g_{ij}}{\delta n_\ell} \Big|_{n_\ell = n_\ell(\tilde{r}, t)}$$

ℓ is 1 or 2, and Y_{ij} is the equilibrium pair distribution function at contact.

Equation (2-16) is automatically fulfilled by (2-15) due to conservation of momentum and energy in binary collision. Multiplied by the collisional invariants m_i , $m_i V_i$, $\frac{1}{2} m_i C_i^2$, integrated over the velocity \tilde{v}_i and summed over all species indices ($i=1,2$), (2-17) yields the lowest order hydrodynamic equation (the Euler equation)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \tilde{u} = 0 \quad (2-18a)$$

$$\rho \left(\frac{\partial \tilde{u}}{\partial t} + \tilde{u} \cdot \nabla \tilde{u} \right) + \nabla P = 0 \quad (2-18b)$$

$$\frac{3}{2} nk \left(\frac{\partial T}{\partial t} + \tilde{u} \cdot \nabla T \right) + P \nabla \cdot \tilde{u} = 0 \quad (2-18c)$$

where the hydrostatic pressure P is given by

$$P = kT \left(n + \frac{2\pi}{3} \sum_{ij} \sigma_{ij}^3 n_i n_j Y_{ij} \right). \quad (2-19)$$

Using these equations to reduce the time derivatives on the LHS of (2-17) in terms of the gradients and using the fact that the last term in (2-17) is reduced to^{11,14}

$$f_i^0(\tilde{r}, \tilde{v}_i, t) C_i [\nabla \ell m_i(\tilde{r}, t) - \nabla \mu_i + \sum_{\ell} \frac{4\pi}{3} \sigma_{i\ell}^3 Y_{i\ell}(\sigma_{i\ell}) \nabla n_\ell]$$

where μ_i is the chemical potential of the species i , we arrive at

an integral equation for Φ_i

$$\begin{aligned}
\sum_j I_{ij}(\Phi_i + \Phi_j) &= \sum_j I_{ij}(\Phi_i) + \sum_j I_{ij}(\Phi_j) \\
&\equiv \sum_j \sigma_{ij}^2 Y_{ij} f_i^0 \int dV_j f_j^0 \int d\sigma \Theta(\sigma \cdot \tilde{v}_{ji}) (\sigma \cdot \tilde{v}_{ji}) \\
&\quad \times [\Phi_i(\tilde{r}, \tilde{v}'_i, t) + \Phi_j(\tilde{r}, \tilde{v}'_j, t) - \Phi_i(\tilde{r}, \tilde{v}_j, t) - \Phi_j(\tilde{r}, \tilde{v}_j, t)] \\
&= f_i^0 \left\{ 2 \mathcal{C}_i^0 \mathcal{C}_i : \nabla u (1 + \gamma_i) + \left(\frac{2}{3} \mathcal{C}_i^2 - 1 \right) \nabla \cdot u (1 + \beta_i) \right. \\
&\quad \left. + C_i \left\{ \frac{n}{n_i} d_i + \frac{\nabla T}{T} \left(\mathcal{C}_i^2 - \frac{5}{2} \right) (1 + \alpha_i) \right\} \right\} \\
&\equiv J_i. \tag{2-20}
\end{aligned}$$

Here $\tilde{C}_i = \tilde{v}_i - u$ is the peculiar velocity, $\mathcal{C}_i \equiv (m_i/2kT)^{1/2} \tilde{C}_i$, the circle over the second-order tensor denotes its symmetric, traceless component, e.g.

$$\mathcal{C}_i^0 \mathcal{C}_i \equiv (\mathcal{C}_i \mathcal{C}_i - \frac{1}{3} \mathcal{C}_i^2 \mathbf{I}),$$

d_i is the thermodynamic driving force given by

$$d_i \equiv \frac{n_i}{n} \left\{ \frac{1}{kT} \nabla \mu_i - \frac{m_i}{\rho kT} \nabla P + \frac{\nabla T}{T} \left\{ 1 + \frac{5}{8} \gamma_i \right\} \right\} \tag{2-21}$$

and

$$\alpha_i = \left(\frac{8\pi}{15} \sum_j \sigma_{ij}^3 Y_{ij} n_j \frac{m_j}{M_{ij}} \right) \tag{2-22a}$$

$$\beta_i = - \frac{P}{nkT} + \frac{4\pi}{3} \sum_j \sigma_{ij}^3 Y_{ij} n_j \frac{m_j}{M_{ij}} \tag{2-22b}$$

$$\gamma_i = \frac{8\pi}{15} \sum_j \sigma_{ij}^3 Y_{ij} n_j \frac{\mu_{ij}}{M_{ij}} \tag{2-22c}$$

Since I_{ij} is a isotropic operator which retains the tensorial character of the argument Φ , we may write as a solution of (2-20),

$$f_i = f_i^0 + f_i^{A+D} + f_i^B + f_i^H \quad (2-23)$$

with

$$f_i^{A+D} = f_i^0 \bar{\Phi}_i^{A+D}, \quad f_i^B = f_i^0 \bar{\Phi}_i^B, \quad f_i^H = f_i^0 \bar{\Phi}_i^H$$

$$\bar{\Phi}_i^{A+D} = -A_i (\mathcal{E}_i^2) C_i \cdot \frac{\nabla T}{T} \quad (2-23a)$$

$$\bar{\Phi}_i^B = -B_i (\mathcal{E}_i^2) \mathcal{E}_i^0 \mathcal{E}_i : \nabla u \quad (2-23b)$$

$$\bar{\Phi}_i^H = H_i (\mathcal{E}_i^2) \nabla \cdot u \quad (2-23c)$$

where each component satisfies the integral equations

$$\sum_j I_{ij} (\bar{\Phi}_i^{A+D} + \bar{\Phi}_j^{A+D}) = f_i^0 C_i \cdot \left\{ \frac{n}{n_i} d_i + \nabla \ln T (\mathcal{E}_i^2 - \frac{5}{2}) \right\} (1 + \alpha_i) \equiv J_i^{A+D} \quad (2-24a)$$

$$\sum_j I_{ij} (\bar{\Phi}_i^B + \bar{\Phi}_j^B) = f_i^0 \left\{ 2 \mathcal{E}_i^0 \mathcal{E}_i : \nabla u \right\} (1 + \gamma_i) \equiv J_i^B \quad (2-24b)$$

$$\sum_j I_{ij} (\bar{\Phi}_i^H + \bar{\Phi}_j^H) = f_i^0 \left\{ (\frac{2}{3} \mathcal{E}_i^2 - 1) \nabla \cdot u \right\} (1 + \beta_i) \equiv J_i^H \quad (2-24c)$$

Determination of $\bar{\Phi}_i$ by the above equations should be subject to the conditions (2-9), (2-3b), (2-3c).

Being satisfied by f_i^0 , the local equilibrium, these conditions are reduced to

$$\int dC_i f_i^0 \Phi_i^H = \int dC_i (f_i - n_i) = 0 \quad (25-a)$$

$$\sum_i \int dC_i f_i^0 \Phi_i^{A+D} m_i C_i = \sum_i \int dC_i f_i m_i C_i = 0 \quad (25-b)$$

$$\sum_i \int dC_i f_i^0 \Phi_i^H \frac{1}{2} m_i C_i^2 = \sum_i \int dC_i f_i \left(\frac{1}{2} m_i C_i^2 - \frac{3}{2} kT \right) = 0 \quad (25-c)$$

III. TRANSPORT PROPERTIES OF BINARY MIXTURE WITH ONE TRACE COMPONENT OF DISPARATE MASS

To identify the linear transport coefficients, the fluxes should be expressed in terms of the gradients in hydrodynamic and thermodynamic variables. One can show from (2-6) and (2-7) that the momentum and energy fluxes can be given in the forms^{13,15}

$$\begin{aligned} \tilde{P} = & \sum_i (1+\gamma_i) \int m_i C_i C_i f_i dC_i + \frac{1}{2} \sum_i \gamma_i \int m_i C_i^2 f_i dC_i \\ & - \left(\frac{6}{5} \tilde{\nabla}^0 u + \tilde{\nabla} \cdot u \tilde{I} \right) \sum_{i,j} \frac{4}{9} \sigma_{ij}^4 Y_{ij} n_i n_j (2\pi k T \mu_{ij})^{1/2} \end{aligned} \quad (3-1)$$

$$\begin{aligned} \tilde{J}_T = & \sum_i (1+\alpha_i) \int \frac{1}{2} m_i C_i^2 C_i f_i dC_i - kVT \sum_{i,j} \frac{4}{3} \sigma_{ij}^4 Y_{ij} n_i n_j \\ & \times (2\pi k T \mu_{ij})^{1/2} M_{ij}^{-1}. \end{aligned} \quad (3-2)$$

The mass flux was given by (2-10). To calculate the (peculiar) velocity moments of various tensorial character pertaining to the fluxes, one generally has to find the solution of f_i , i.e. Φ_i , for the integral equation (2-20) or (2-24).

However, in certain situations, one can avoid the procedure of solving Φ_i and proceed directly to a determination of the various velocity moments. The binary mixture of extreme mass and concentration disparity that we shall study here serves as such an example. We consider a situation in which the impurity (solute) particles (of the species 2) are dispersed in a solvent fluid (species 1) of arbitrary density (n_1) at such low dilution (n_2) that we can

reasonably neglect the collisions among themselves. Being mainly concerned with finding the effect of the impurity on the transport property through the order ξ_2/ξ_1 where $\xi_i = \frac{\pi}{6} n_i \sigma_{ii}^3$ is the volume fraction, we start with the integral equation in the form

$$I_{11}(\Phi_1 + \Phi_1) + I_{12}(\Phi_1 + \Phi_2) = J_1 \quad (3-3a)$$

$$I_{21}(\Phi_2 + \Phi_1) = J_2 \quad (3-3b)$$

As we shall see, $I_{21}(\Phi_2)$ plays a primary role in determining the diffusivity of the impurity and its contribution to the transport properties such as the viscosity and thermal conductivity. Physically this represents a change of distribution of solute caused by the collision with the solvent particles at local equilibrium. In its mathematical form, however, it is identical (apart from the additional factor Y_{12} in our case) to the collision integral of the Boltzmann equation for the solute distribution function f_2 when the solvent is at absolute equilibrium. Thus, we shall utilize as follows the results^{4,16} of analysis already made on the Boltzmann equation level for our study involving $I_{21}(\Phi_2)$ simply by taking into consideration the multiplicative factor Y_{12} in $I_{12}(\Phi_2)$. In addition, it should be borne in mind that V_2 appearing in this Boltzmann equation expression of $I_{21}(\Phi_2)$ should be replaced by C_2 , the peculiar velocity, since we are concerned with the relaxation into local equilibrium (2-15).

In the case in which the solute particle is much more massive than the solvent particle ($m_1 \ll m_2$) the velocity of a

heavier solute particle undergoes a very small change during its encounter with a solvent particle. In this process, the small change, $C_2' - C_2$ can be regarded as a natural smallness parameter which enables us to expand $\Phi_2' - \Phi_2$ as

$$\Phi_2' - \Phi_2 = \frac{\partial \Phi_2}{\partial C_2} \cdot (C_2' - C_2) + \frac{1}{2} \frac{\partial}{\partial C_2} \frac{\partial \Phi_2}{\partial C_2} : (C_2' - C_2) (C_2' - C_2) + \dots \quad (3-4)$$

According to the calculation done by Uhlenbeck and Wang-Chang¹⁶ on the Boltzmann-level equation, the above expression up through the second order leads to the form for $I_{21}(\Phi_2)$:

$$\begin{aligned} I_{21}^R(\Phi_2) &= \sigma_{12}^2 Y_{12} f_2^0 \int dV_1 f_1^0 \int d\sigma (\sigma \cdot V_{12})^\Theta (\sigma \cdot V_{12}) (\Phi_2' - \Phi_2) \\ &= \frac{8}{3} \left(\frac{m_1}{m_2} \right) n_1 \left(\frac{2\pi kT}{m_1} \right)^{\frac{1}{2}} \sigma_{12}^2 Y_{12} f_1^0 \left(-C_2 \cdot \frac{\partial \Phi_2}{\partial C_2} + \frac{kT}{m_2} \frac{\partial}{\partial C_2} \cdot \frac{\partial \Phi_2}{\partial C_2} \right) \\ &= \frac{\xi_R}{m_2} \frac{\partial}{\partial C_2} \cdot \left(C_2 + \frac{kT}{m_2} \frac{\partial}{\partial C_2} \right) f_2 \\ &\equiv \frac{m_1}{m_2} R_2^{(1)} f_2 \end{aligned} \quad (3-5)$$

$$\xi_R = \frac{8}{3} n_1 (2\pi m_1 kT)^{\frac{1}{2}} \sigma_{12}^2 Y_{12} \quad (3-6)$$

where

$$R_2^{(1)} = \frac{8}{3} n_1 \left(\frac{2\pi kT}{m_1} \right)^{\frac{1}{2}} \sigma_{12}^2 Y_{12} \frac{\partial}{\partial C_2} \cdot \left(C_2 + \frac{kT}{m_2} \frac{\partial}{\partial C_2} \right) \quad (3-7)$$

We find (3-5) takes the form of Focker-Planck collision term with the friction coefficient ξ_R , which describes the Brownian motion of the particle in the bath of the lighter fluid particles. This case of a binary mixture has been studied by a good many authors,^{7,16,17,18} and shall be referred¹⁹ as Reyleighian for a

historical reason; specifically for the situation described by the equation (3-5) we denote by R_1 since it corresponds to the expansion in terms of m_1/m_2 up through the first order. Higher order expansion will result in introducing R_2 , R_3 , etc. Though the calculations of R_2 , R_3 are apparently straightforward and not difficult, we shall here confine ourselves to R_1 only.

Multiplying (3-5) by C_2 , $C_2^0 C_2$, C_2^2 , and $C_2^2 C_2$, respectively, and integrating over C_2 , we are led to

$$\int I_{21}^R(\Phi_2) C_2 dC_2 = -\frac{\xi_R}{m_2} \int f_2 C_2 dC_2 \quad (3-8a)$$

$$\int I_{21}^R(\Phi_2) C_2^0 C_2 dC_2 = -\frac{2\xi_R}{m_2} \int (C_2^0 C_2) f_2 dC_2 \quad (3-8b)$$

$$\int I_{21}^R(\Phi_2) C_2^2 dC_2 = -\frac{2\xi_R}{m_2} \int \left(C_2^2 - \frac{3kT}{m_2} \right) f_2 dC_2 \quad (3-8c)$$

$$\int I_{21}^R(\Phi_2) C_2^2 C_2 dC_2 = \frac{\xi_R}{m_2} \int \left(\frac{12kT}{m_2} C_2 - 3C_2^2 C_2 \right) f_2 dC_2 \quad (3-8d)$$

The case opposite that of a Rayleighian mixture is the Lorentzian mixture, in which the mass of the impurity particle is negligibly light compared to the solvent particle. The smallness parameter that exists in this situation is $\frac{1}{2}m_2(C_2'^2 - C_2^2)$ (the change of the kinetic energy induced by collision with the heavier particle) or the mass ratio m_2/m_1 . The limit $m_2/m_1 \rightarrow 0$ corresponds to the so-called Lorentz limit in which a light particle is elastically scattered by a quasi-stationary solvent particle with its kinetic energy preserved. In considering the case of small but nonvanishing $C_2'^2 - C_2^2$ or m_2/m_1 , one may seek the expansion of $\Phi_2' - \Phi_2$ in terms of

$C_2'^2 - C_2^2$ in a manner analogous to that which we have done for the case of Rayleighian mixture. However, it appears that such a procedure is not so straightforward here except when Φ_2 is an isotropic function of \underline{C}_2 , i.e. $\Phi_2(\underline{C}) = \Phi_2(C_2)$. Thus, it turns out to be more tractable to start with Hilbert's version⁵ of the Boltzmann collision term, in which $\Phi_2' - \Phi_2$ is already integrated out over the angle σ and the collision term appears in a form resembling the left-hand side of an integral equation. According to Pidduck's generalization⁴ of Hilbert's form to the case of binary mixture, $I_{21}(\Phi_2)$ reads

$$I_{21}(\Phi_2) = \int K(\underline{C}_2, \underline{C}_2') f_2(\underline{C}_2') d\underline{C}_2' - k(C_2) f_2(C_2) \quad (3-9)$$

$$K(\underline{C}_2, \underline{C}_2') = \left(\frac{m_1}{2\pi kT} \right)^{1/2} \frac{\sigma_{12}^2 n_1 Y_{12}}{8\mu_1^2 R} \exp \left[- \frac{m_1}{8\mu_1^2 R^2 kT} \{ 4Q^2 \mu_1^2 + 4\mu_1 (2\mu_1 - 1) QR^2 + (2\mu_1 - 1)^2 R^4 \} \right] \quad (3-10)$$

$$k(C_2) = 2\pi^{1/2} n_1 \sigma_{12}^2 \frac{kT}{m_1 C_2} \psi \left\{ \left(\frac{m_1}{2kT} \right)^{1/2} C_2 \right\} \quad (3-11)$$

where

$$\psi(x) = x e^{-x^2} + (2x^2 + 1) \int_0^x e^{-y^2} dy$$

$$R = |\underline{C}_2' - \underline{C}_2|, \quad Q = \underline{C}_2 \cdot (\underline{C}_2' - \underline{C}_2), \quad \mu_1 = \frac{m_1}{m_1 + m_2}.$$

Pidduck proceeded to an expansion of $I_{21}(\Phi_2)$ up through linear order in m_2/m_1 , yielding

$$I_{21}^L(\hat{\Phi}_2) = \pi n_1 \sigma_{12}^2 Y_{12} C_2 \left[\frac{1}{4\pi} \hat{\Phi}_2 d\hat{1}_2 - \hat{\Phi}_2 + \frac{m_1}{m_2} \left\{ \frac{1}{4\pi} d\hat{1}_2 \right. \right. \\ \left. \left. \left\{ 2\hat{\Phi}_2 + (1 - \hat{1}_2 \cdot \hat{1}_2) \left(-2\hat{\Phi}_2 + \left(\frac{3}{2\mathcal{E}_2} - \frac{\mathcal{E}_2}{2} \right) \frac{\partial \hat{\Phi}_2}{\partial \mathcal{E}_2} + \frac{1}{2} \frac{\partial^2 \hat{\Phi}_2}{\partial \mathcal{E}_2^2} \right) \right\} \right] \quad (3-12)$$

where the superscript $\hat{}$ denotes the quantity that the particle 2 assumes after elastic collision (i.e. at Lorentz limit) which rotates $C_2 = C_2 \hat{1}_2$ into $\hat{C}_2 = C_2 \hat{1}_2$, e.g. $\hat{\Phi}_2 = \Phi_2(\hat{C}_2)$, $d\hat{1}_2$ is element of the solid angle in the direction of the unit vector $\hat{1}_2$.

Defining a projection operator P_2 ; $P_2^2 = P_2$, by

$$P_2[\] \equiv \frac{1}{4\pi} \int d\hat{1}_2 [\hat{}] = \frac{1}{4\pi} \int d\hat{1}_2 [\] \quad (3-13)$$

(which projects $[\]$ onto its isotropic component, e.g. $P_2 \Phi_2 = \Phi_2^H$) and inserting $f_2 = f_2^0(1 + \Phi_2)$, we find our version of eq. (3-12):

$$I_{21}^L(\Phi_2) = L_2 f_2 \\ L_2 = L_2^{(0)} + \left(\frac{m_2}{m_1} \right) L_2^{(1)} \quad (3-14)$$

$$L_2^{(0)} = \lambda_{21}^{-1} C_2 (P_2 - 1) \quad (3-14a)$$

$$L_2^{(1)} = \lambda_{21}^{-1} C_2 \left\{ 2P_2 + (P_2 - \hat{1}_2 \cdot P_2 \hat{1}_2) \right. \\ \left. \left\{ 2 + \left(\mathcal{E}_2 + \frac{3}{2\mathcal{E}_2} \right) \frac{\partial}{\partial \mathcal{E}_2} + \frac{1}{2} \frac{\partial^2}{\partial \mathcal{E}_2^2} \right\} \right\} \quad (3-14b)$$

where

$$\lambda_{21} \equiv (\pi n_1 \sigma_{12}^2 Y_{12})^{-1} \quad (3-15)$$

is the mean free path of the impurity particle in collision with the surrounding solvent particles. Here $L_2^{(0)}$ is identified as the collision operator corresponding to the Lorentz limit $m_2/m_1 \rightarrow 0$.

$L_2^{(1)}$ reflects the nonvanishing response of the solvent particle to the impact of the solute because of its finite mass. Derivation of higher order collision operator from (3-9) is straightforward, but we shall not pursue further here. Decomposition of f_2 onto its various components yields

$$I_{21}^L(\Phi_2^{A+D}) = -\lambda_{21}^{-1} C_2 \left\{ 1 + \frac{1}{3} \frac{m_2}{m_1} (\mathcal{D}_2 - 2) \right\} f_2^{A+D} \quad (3-16a)$$

$$I_{21}^L(\Phi_2^B) = -\lambda_{21}^{-1} C_2 f_2^B \quad (3-16b)$$

$$I_{21}^L(\Phi_2^H) = \lambda_{21}^{-1} \left(\frac{m_2}{m_1} \right) C_2 \mathcal{D}_2 f_2^H \quad (3-16c)$$

where the differential operators \mathcal{D}_2 is defined by

$$\mathcal{D}_2 = 4 + \left(\mathcal{C}_2 + \frac{3}{2\mathcal{C}_2} \right) \frac{\partial}{\partial \mathcal{C}_2} + \frac{1}{2} \frac{\partial^2}{\partial \mathcal{C}_2^2}. \quad (3-17)$$

The differential equation (3-16c) is identical to the result of Andersen and Schuler²⁰ who considered the distribution function as a function of the scalar variable (\mathcal{C}_2^2) only. To find the velocity moments in this case analogous to (3-8a,b,c,d), we multiply 1_2 , C_{21}^0 , C_2 , and C_{21}^2 and integrate over \mathcal{C}_2 . We obtain

$$\int I_{21}^L(\Phi_2) 1_2 d\mathcal{C}_2 = -\lambda_{21}^{-1} \left(1 - \frac{2}{3} \frac{m_2}{m_1} \right) \int C_2 f_2 d\mathcal{C}_2 \quad (3-18a)$$

$$\int I_{21}^L(\Phi_2) C_{21}^0 d\mathcal{C}_2 = -\lambda_{21}^{-1} \int C_2^0 C_2 f_2 d\mathcal{C}_2 \quad (3-18b)$$

$$\int I_{21}^L(\Phi_2) C_2 d\mathcal{C}_2 = -\left(\frac{m_1}{m_2} \right) \lambda_{21}^{-1} \int \left(C_2^2 - \frac{3kT}{m_2} \right) f_2 d\mathcal{C}_2 \quad (3-18c)$$

$$\int I_{21}^L(\Phi_2) C_{21}^2 d\mathcal{C}_2 = -\lambda_{21}^{-1} \left\{ \left(1 - \frac{4}{3} \frac{m_2}{m_1} \right) \int C_2^2 C_2 f_2 d\mathcal{C}_2 + \frac{8kT}{3m_2} \left(\frac{m_2}{m_1} \right) \int C_2 f_2 d\mathcal{C}_2 \right\}. \quad (3-18d)$$

Before proceeding to the problem of calculating transport coefficients, we investigate the implications that the conditions (2-25a-c) have for possible simplification in our development.

We note that these conditions imply

$$\phi_1^{A+D}/\phi_2^{A+D} = O\left(\frac{n_2}{n_1}\right) \quad (3-19a)$$

and

$$\phi_1^H/\phi_2^H = O\left(\frac{n_2}{n_1}\right) \quad (3-19b)$$

which allow us to neglect ϕ_1^{A+D} and ϕ_1^H compared to ϕ_2^{A+D} and ϕ_2^H as long as we deal with the extreme disparity in concentration. The equation (3-3b) for the particle 2 corresponding to these components are now put as

$$I_{21}(\phi_2^{A+D}) = J_2^{A+D} \quad (3-20a)$$

$$I_{21}(\phi_2^H) = J_2^H. \quad (3-20b)$$

We shall find this simplification along with (2-25b) and (2-25c) enables us to evaluate the exact mass and thermal diffusivity, and bulk viscosity up to the level R_1 and L_1 . For the shear viscosity and thermal conductivity, where such simplifying conditions are not fully feasible, the exact results are to be obtained only through the level L_0 and R_1 within the context of our neglect of the collision terms other than $I_{21}(\phi_2)$ and $I_{11}(\phi_1 + \phi_{\underline{1}})$.

1) Binary Diffusion and Thermal Diffusion

There are several definitions²¹ for the coefficient of mass diffusion depending upon the experimental situation. The diffusivity of concern to us here is not the so-called "center of mass mutual diffusion" defined by eq. (2-13) but binary diffusion given by

$$\bar{v}_1 - \bar{v}_2 = - \frac{n^2}{n_1 n_2} (D_{12} d_{1\sim} + D_T \nabla \ln T) \quad (3-21)$$

which also defines D_T , the thermal diffusivity. The diffusion velocity difference can be expressed as

$$\begin{aligned} \bar{v}_1 - \bar{v}_2 &= \bar{c}_1 - \bar{c}_2 \quad (3-22) \\ &= \frac{1}{n_1} \int dC_{1\sim} f_1^{A+D} C_{1\sim} - \frac{1}{n_2} \int dC_{2\sim} f_2^{A+D} C_{2\sim} \\ &= - \frac{1}{n_2} \left(1 + \frac{n_2 m_2}{n_1 m_1} \right) \int dC_{2\sim} f_2^{A+D} C_{2\sim} \end{aligned}$$

where the condition for f_1^{A+D} (2-25b) is utilized.

(A) $m_1 \gg m_2$ (Lorentzian, $L_0 + L_1$)

From (3-20a), (3-18a) and (2-24a), we find

$$\begin{aligned} -\lambda_{21}^{-1} \left(1 - \frac{2}{3} \frac{m_2}{m_1} \right) \int dC_{2\sim} f_2 dC_{2\sim} &= \int dC_{2\sim} f_2^0 C_{2\sim} \cdot \left\{ \frac{n}{n_2} d_{2\sim} \right. \\ &\quad \left. + (1 + \alpha_2) \left[\frac{2}{3} - \frac{5}{2} \right] \nabla \ln T \right\} \\ &= \frac{1}{3} \left(\frac{2kT}{\pi m_2} \right)^{\frac{1}{2}} [2n_1 d_{2\sim} - n_2 (1 + \alpha_2) \nabla \ln T]. \quad (3-23) \end{aligned}$$

By virtue of the relations (3-21) and (3-22), we readily identify, by noting that $d_{1\sim} = -d_{2\sim}$,

$$\begin{aligned}
D_{12}^L &= \frac{2}{3} \lambda_{21}^{-1} \left(\frac{2kT}{\pi m_2} \right)^{\frac{1}{2}} \left(1 + \frac{2}{3} \frac{m_2}{m_1} \right) \\
&= \frac{2}{3\pi} \left(\frac{2kT}{\pi m_2} \right)^{\frac{1}{2}} \frac{1}{n_1 \sigma_{12}^2 Y_{12}} \left(1 + \frac{2}{3} \frac{m_2}{m_1} \right)
\end{aligned} \tag{3-24}$$

$$D_T^L = \frac{1}{2} \frac{n_2}{n_1} (1 + \alpha_2^L) D_{12}^L. \tag{3-25}$$

(B) $m_1 \ll m_2$ (Rayleighian, R_1)

From (3-20a), (3-8a) and (2-24a), we find

$$\begin{aligned}
-\frac{\xi_R}{m_2} \int dC_{\sim 2} f_{\sim 2}^{A+D} C_{\sim 2} &= \int dC_{\sim 2} f_{\sim 2}^0 C_{\sim 2} C_{\sim 2} \cdot \left\{ \frac{n}{n_2} \frac{d}{\sim 2} + (1 + \alpha_2) \left(\frac{d^2}{\sim 2} - \frac{5}{2} \right) \nabla \ell n T \right\} \\
&= -\frac{kT}{m_2} n_{\sim 1}^d.
\end{aligned} \tag{3-26}$$

In a similar manner, (3-21) and (3-22) leads us to

$$D_{12}^R = \frac{kT}{\xi_R} = \frac{3}{8} \left(\frac{2\pi kT}{m_1} \right)^{\frac{1}{2}} \frac{1}{n_1 \sigma_{12}^2 Y_{12}} \tag{3-27}$$

$$D_T^R = 0. \tag{3-28}$$

In the low-solvent density limit (Boltzmann limit) in which $Y_{12} = 1$, the diffusivity (3-24) and (3-27) are reduced to the results of Pidduck.⁴ Kihara⁶ and Mason's⁷ results are also identical with $Y_{12} = 1$ to (3-27).

2) Bulk Viscosity

The bulk viscosity is to be identified from the constitutive relation

$$\underline{\underline{P}} = \underline{\underline{P}}_I - 2\eta \underline{\underline{\nabla}} \cdot \underline{\underline{u}} - \kappa \underline{\underline{\nabla}} \cdot \underline{\underline{u}} \underline{\underline{I}} \tag{2-11}$$

and (3-1). We find

$$-\kappa \nabla \cdot \mathbf{u} = \sum_i \left\{ \frac{1}{3}(1+\gamma_i) + \frac{1}{2} \gamma_i \right\} \int m_i C_i^2 f_i^H dC_i - \nabla \cdot \mathbf{u} \sum_{i,j} \frac{4}{9} \sigma_{ij}^4 Y_{ij} n_i n_j (2\pi k T \mu_{ij})^{\frac{1}{2}}, \quad (3-29)$$

which is simplified a great deal by the condition (2-25c) to

$$-\kappa \nabla \cdot \mathbf{u} = \frac{5}{6}(\gamma_2 - \gamma_1) \int m_2 C_2^2 f_2^H dC_2 - \nabla \cdot \mathbf{u} \sum_{i,j} \frac{4}{9} \sigma_{ij}^4 Y_{ij} n_i n_j (2\pi k T \mu_{ij})^{\frac{1}{2}} \quad (3-30)$$

where $\int m_2 C_2^2 f_2^H dC_2$ emerges as the only quantity to be evaluated.

(A) $m_1 \gg m_2$ (Lorentzian, L_1).

The relations (3-20b), (3-18c) and (2-24c) allow us to write

$$-\left(\frac{m_2}{m_1}\right) \ell_{21}^{-1} \int C_2^2 f_2^H dC_2 = (1+\beta_2) \int f_2^0 \left(\frac{2}{3} \mathcal{E}_2^2 - 1\right) C_2 dC_2 = \frac{2}{3}(1+\beta_2) \left(\frac{2kT}{\pi m_2}\right)^{\frac{1}{2}} n_2 \nabla \cdot \mathbf{u}. \quad (3-31)$$

Here the contribution from the lowest order (L_0 , Lorentzian limit) collision term to LHS is found to be null; the leading contribution is in the order $O(m_2/m_1)$. Contribution of (3-31) to κ is

$$\begin{aligned} \kappa_{21}^L &= \frac{5}{9} n_2 (\gamma_2^L - \gamma_1^L) m_1 \ell_{21} (1+\beta_2^L) \left(\frac{2kT}{\pi m_2}\right)^{\frac{1}{2}} \\ &= \frac{8\pi}{81} n_1 n_2 \frac{1}{Y_{12}} (\sigma_{11}^3 Y_{11} - 2\sigma_{12}^3 Y_{12})^2 \frac{1}{\sigma_{12}^2} \left(\frac{m_1}{m_2}\right)^{\frac{1}{2}} \left(\frac{2m_1 kT}{\pi}\right)^{\frac{1}{2}}. \end{aligned} \quad (3-32)$$

The total bulk viscosity is written by taking only the terms up through linear in n_2 :

$$\begin{aligned} \kappa^L = & \frac{4}{9} \sigma_{11}^4 Y_{11} n_1^2 (\pi k T m_1)^{\frac{1}{2}} + \frac{8}{9} \sigma_{12}^4 Y_{12} n_1 n_2 \left(\frac{m_2}{m_1}\right)^{\frac{1}{2}} (2\pi k T m_1)^{\frac{1}{2}} \\ & + \frac{8\pi}{81} n_1 n_2 \frac{1}{Y_{12}} (\sigma_{11}^3 Y_{11} - 2\sigma_{12}^3 Y_{12})^2 \left(\frac{m_1}{m_2}\right)^{\frac{1}{2}} \left(\frac{2m_1 k T}{\pi}\right)^{\frac{1}{2}}. \end{aligned} \quad (3-33)$$

Introducing $\check{\eta}_1 = \frac{5}{16} \left(\frac{m_1 k T}{\pi}\right)^{\frac{1}{2}} \frac{1}{\sigma_{11}^2}$ (the shear viscosity of the low density solvent calculated by the lowest Sonine polynomial approximation from the Boltzmann equation) as the appropriate unit of viscosities, (3-33) is expressed as

$$\begin{aligned} \kappa^L = & \left[\frac{256}{5\pi} \xi_1^2 Y_{11} + \xi_2 \left(\frac{32\sqrt{2}}{5\pi} p^{-\frac{1}{2}} q^{-1} (1+q)^4 \xi_1 Y_{12} \right. \right. \\ & \left. \left. + \frac{2048\sqrt{2}}{45\pi} p^{\frac{1}{2}} q^5 (1+q)^{-2} \xi_1 \frac{1}{Y_{12}} ([Y_{11} - \frac{1}{4} q^{-3} (1+q)^3 Y_{12}]^2) \right] \check{\eta}_1 \end{aligned}$$

where

$$q = \sigma_{11}/\sigma_{22}, \quad p = m_1/m_2. \quad (3-34)$$

(B) $m_1 \ll m_2$ (Rayleighian, $R_0 + R_1$)

From (3-20b), (3-8c) and (2-24c), we find

$$\begin{aligned} \frac{2\xi_R}{m_2} \int C_2^2 f_2^H d\tilde{C} &= \nabla \cdot \tilde{u} (1+\beta_2) \int f_2^0 \left(\frac{2}{3} \mathcal{C}_2^2 - 1 \right) C_2^2 d\tilde{C}_2 \\ &= \nabla \cdot \tilde{u} \frac{2n_2 k T}{m_2} (1+\beta_2) \end{aligned} \quad (3-35)$$

which enable us to calculate the bulk viscosity

$$\begin{aligned} \kappa_{21}^R &= \frac{5}{6} (\gamma_2^R - \gamma_1^R) \frac{n_2 m_2 k T}{\xi_R} (1+\beta_2^R) \\ &= \frac{\pi}{36} n_1 n_2 (\sigma_{11}^3 Y_{11} - 2\sigma_{12}^3 Y_{12} \frac{m_1}{m_2})^2 \left(\frac{m_1}{m_2}\right) \frac{(2\pi m_1 k T)^{\frac{1}{2}}}{\sigma_{12}^2 Y_{12}}. \end{aligned} \quad (3-36)$$

We find the total bulk viscosity

$$\begin{aligned}
\kappa^R &= \frac{4}{9} \sigma_{11}^4 Y_{11} n_1^2 (\pi k T m_1)^{\frac{1}{2}} + \frac{8}{9} \sigma_{12}^4 Y_{12} n_1 n_2 (2\pi k T m_1)^{\frac{1}{2}} \\
&\quad + \frac{\pi}{36} n_1 n_2 \left(\sigma_{11}^3 Y_{11} - 2\sigma_{11}^3 Y_{12} \frac{m_1}{m_2} \right)^2 \left(\frac{m_2}{m_1} \right) \frac{(2\pi m_1 k T)^{\frac{1}{2}}}{\sigma_{12}^2 Y_{12}} \\
&= \left[\frac{256}{5\pi} \xi_1^2 Y_{11} + \xi_2 \left(\frac{32}{5\pi} q^{-1} (1+q)^4 \xi_1 Y_{12} + \frac{64\sqrt{2}}{5} p^{-1} q^5 (1+q)^{-2} \right. \right. \\
&\quad \left. \left. \times \xi_1 \frac{1}{Y_{12}} \left\{ Y_{11} - \frac{1}{4} q^{-3} (1+q)^3 p \right\}^2 \right) \right] \tilde{\eta}_1. \tag{3-37}
\end{aligned}$$

3) Shear Viscosity

Shear viscosity is identified from the traceless component of (3-1) and (2-11):

$$\begin{aligned}
-2\eta \tilde{\nabla}^0 \tilde{u} &= \sum_i (1+\gamma_i) \int m_i C_i C_i f_i^B dC_i \\
&\quad - \frac{8}{15} \tilde{\nabla}^0 \tilde{u} \sum_{i,j} \sigma_{ij}^4 Y_{ij} n_i n_j (2\pi k T \mu_{ij})^{\frac{1}{2}}. \tag{3-38}
\end{aligned}$$

Since Φ_i^B or f_i^B lack such simplifying conditions as (2-25b), (2-25c), we have to include collision integrals left out of the foregoing analysis. Among these, $I_{12}(\Phi_1)$ is simply obtained from $I_{21}(\Phi_2)$ by exchanging the species indices. To avoid the complexities involved in calculating $I_{12}(\Phi_2)$ and $I_{21}(\Phi_1)$ in detail, we shall concern ourselves with only L_0 (the Lorentz limit $m_2/m_1 \rightarrow 0$) in the Lorentzian mixture ($m_2/m_1 \ll 1$). Also we note that in contemplating such a mixture as Rayleighian in which the solute particle is much more massive than the solvent particle it is natural to regard the solute particle as also much larger than the solvent particle for any realizable solute suspended in a solvent. Such limit as L_0 and our

where the exact value of the Boltzmann shear viscosity is known from the Sonine-polynomial expansion:

$$\eta_1^B = 1.016\check{\eta}_1. \quad (3-43)$$

On the other hand, for the distribution of particle 2, we find

$$I_{21}^L(\Phi_2^B) = L_2^{(0)} f_2^B = -\ell_{21}^{-1} C_2 f_2^B = J_2^B, \quad (3-44)$$

in which we have neglected $I_{21}(\Phi_1)$ by observing the fact that $\Phi_1' - \Phi_1$ is expanded in powers of $\mathcal{E}_2' - \mathcal{E}_2$, which is of the order $(m_2/m_1)^{1/2}$. From (3-44) the following is derived via (3-18b) and (2-24b)

$$\begin{aligned} -\ell_{21}^{-1} \int dC_2 f_2^B C_2^0 C_2 &= 2(1+\gamma_2) \int dC_2 f_2^0 C_2^0 C_2^1 \mathcal{E}_2^0 \mathcal{E}_2 : \nabla u \\ &= \frac{4}{15} (1+\gamma_2) \nabla^0 u \int f_2^0 \mathcal{E}_2^3 dC_2 \\ &= \frac{16}{15} (1+\gamma_2) \left(\frac{2kT}{\pi m_2} \right)^{1/2} \nabla^0 u. \end{aligned} \quad (3-45)$$

When inserted into (3-38), this is found to contribute to the shear viscosity the term

$$\eta_{21}^L = \frac{8\sqrt{2}}{15\pi} \frac{n_2}{n_1} \frac{1}{Y_{12}} (1+\gamma_2)^2 \left(\frac{m_2 kT}{\pi} \right)^{1/2} \frac{1}{\sigma_{12}^2} \quad (3-46)$$

whose low density limit ($n_1 \rightarrow 0$; $\gamma_2 \rightarrow 0$, $Y_{12} \rightarrow 1$) is identical to the result given in Chapman and Cowling.⁸

The total viscosity is written as

$$\begin{aligned} \eta^L = & \frac{1}{Y_{11}}(1+\gamma_1^L)^2 \eta_1^B + \frac{4}{15} \left\{ \sigma_{11}^3 Y_{11} n_1^2 (\pi k T m_1)^{\frac{1}{2}} \right. \\ & \left. + 2\sigma_{12}^3 Y_{12} n_1 n_2 \left(\frac{m_2}{m_1}\right)^{\frac{1}{2}} (2\pi k T m_1)^{\frac{1}{2}} \right\} \\ & + \frac{1}{Y_{12}}(1+\gamma_2^L)^2 \frac{8\sqrt{2}}{15\pi} \frac{n_2}{n_1} \left(\frac{m_2}{m_1}\right)^{\frac{1}{2}} \left(\frac{m_1 k T}{\pi}\right)^{\frac{1}{2}} \frac{1}{\sigma_{12}^2} \end{aligned} \quad (3-47)$$

However, self-consistency in neglecting the terms $I_{12}^L(\Phi_1^B)$, $I_{12}^L(\Phi_2^B)$ requires us to retain only

$$\eta^L = \left\{ 1.016 \frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11}\right)^2 + \frac{768}{25\pi} \xi_1^2 Y_{11} \right\} \eta_1^B. \quad (3-48)$$

This is in a form apparently identical to the Enskog shear viscosity for a single-component fluid. It should be noted, however, that Y_{11} and ξ_1 in the presence of the solute are different from those quantities in the pure solvent and therefore (3-48) is different from the viscosity of pure solvent. This difference could not have been obtained from the Boltzmann equation, where the shear viscosity of a single component fluid is density-independent. The lack of appreciable direct contribution from the impurity particles as expressed in (3-48) supports the obvious observation that the light impurity particles give a negligible contribution with regards to shearing momentum transport.

$$(B) \quad m_1/m_2 \ll 1, \quad \sigma_{11}/\sigma_{22} \ll 1 \quad (\text{Rayleighian, } R_0 + R_1)$$

We first estimate the order of magnitude for some collisional terms

$$I_{21}^R(\Phi_1^B) \sim L_1^{(0)} f_1^B = -\ell_{21}^{-1} f_1^B \sim 0 \left(\frac{n_2 \sigma_{12}^2}{n_1 \sigma_{11}^2} \right) \ll 1 \quad (3-49)$$

$$I_{12}^R(\Phi_2^B) = 0 \left(\frac{n_2 \sigma_{12}^2}{n_1 \sigma_{11}^2} \left(\frac{m_2}{m_1} \right)^\alpha \right) \ll 1 \quad (3-50)$$

Equation (3-49) is due to the fact that $\frac{n_1 \sigma_{12}^2}{n_1 \sigma_{11}^2} = \frac{\xi_2}{\xi_1} q$ is negligibly small if we consider only the nonnegligible term linear in ξ_2 .

Thus, we may write

$$I_{11}^R(\Phi_1^B + \Phi_2^B) = J_1^B \quad (3-51)$$

which leads us to the expression similar to (3-42):

$$\int f_{1m_1}^B C_{1\sim 1} C_{1\sim 1} dC_{1\sim 1} = -\frac{1}{Y_{11}} (1 + \gamma_1^R) 2\eta_1^B \nabla_{\sim 1}^0 u.$$

For the component 2, we retain the form

$$I_{21}^R(\Phi_2^B) + I_{21}^R(\Phi_1^B) = J_2^B \quad (3-52)$$

with $I_{21}^R(\Phi_2^B) = \frac{m_1}{m_2} R_2^{(1)} f_2^B$. The calculation of $I_{21}^R(\Phi_1^B)$ through the order (m_1/m_2) comparable to $I_{21}^R(\Phi_2^B)$ is a formidable task. Rather than embarking on the exact calculation based on Hilbert's transformation, we can employ the lowest Sonine polynomial approximation Φ_1^B , which is presumably good enough (possibly exact) to give an accurate order-of-magnitude estimate. Inserting

$$\Phi_1^B = b_0^{(1)} S_{5/2}^{(0)}(\mathcal{C}_{1\sim 1}^2) \mathcal{C}_{1\sim 1}^0 : \nabla u = b_0^{(1)} \mathcal{C}_{1\sim 1}^0 \mathcal{C}_{1\sim 1}^0 : \nabla u \quad (3-53)$$

to $I_{21}^R(\Phi_1^B)$, multiplying by $\mathcal{C}_{1\sim 1}^0 \mathcal{C}_{1\sim 1}^0$ and performing integration over $C_{1\sim 1}$ we find

$$b_0^{(1)} = \frac{5}{8} (1 + \gamma_1)^2 m_1 (\pi m_1 kT)^{-1/2} (\sigma_{11}^2 Y_{11} n_1)^{-1}. \quad (3-54)$$

Performing a similar procedure for (3-52) by using this, i.e.

$$\int dC_2 \left\{ \frac{m_1}{m_2} R_2^{(1)} f_2^B + I_{21}(-b_0^{(1)} \mathcal{C}_{11} : \nabla u) \right\} \mathcal{C}_{22}^0 = \int J_{22}^B \mathcal{C}_{22} dC_2 \quad (3-55)$$

we are led to the identity by using (3-8b):

$$\int dC_2 m_2 C_2^0 f_2^B = -\frac{n_2}{n_1} \left(\frac{m_1 kT}{\pi} \right)^{\frac{1}{2}} \left\{ \frac{3\sqrt{2}}{16} \left(\frac{m_2}{m_1} \right) \frac{1}{Y_{12}} (1+\gamma_2) \right. \\ \left. \times \frac{1}{\sigma_{12}^2} + \frac{1}{4} \frac{1}{Y_{11}} (1+\gamma_1) \frac{1}{\sigma_{11}^2} \right\} \nabla u \quad (3-56)$$

Via (3-38), this brings us to the expression of the viscosity contributed directly by the solute particle as

$$\eta_{21}^R = \frac{6\sqrt{2}}{5} \frac{\xi_2}{\xi_1} q^5 p^{-1} (1+q)^{-2} \frac{1}{Y_{12}} (1+\gamma_2^R) \frac{2}{\eta_1} \quad (3-57)$$

where the second term in the bracket in (3-56) (originated from $I_{21}(\Phi_1^B)$ which we calculated with the lowest Sonine polynomial) is neglected on the basis of the conditions (3-49) and (3-50).

Summing up all the contributions, we find

$$\eta^R = \left\{ \left[1.016 \times \frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11} \right)^2 + \frac{768}{25\pi} \xi_1^2 Y_{11} \right] \right. \\ \left. + \xi_2 \left[\frac{4}{5} \frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11} \right) (1+q)^3 Y_{12} \right. \right. \\ \left. \left. + \xi_1^{-1} \frac{6\sqrt{2}}{5} p^{-1} q^5 (1+q)^{-2} \left\{ 1 + \frac{2}{5} \xi_1 p q^{-3} (1+q)^2 Y_{12} \right\}^2 \right. \right. \\ \left. \left. + \frac{96\sqrt{2}}{25\pi} \xi_1 q^{-1} (1+q)^4 Y_{12} \right] \right\} \frac{2}{\eta_1} \quad (3-58)$$

Among the various terms in the order of ξ_2 , the first term is from the motion of the solvent particle caused by the solute particle, and the second is from the Brownian motion of the solute particle, the last being from the mutual collisional transfer

$$\begin{aligned}
& -\ell_{21}^{-1} \int C_2^2 C_2 f_2^{A+D} dC_2 + \left(\frac{m_2}{m_1} \right) \frac{8kT}{3m_2} \int C_2 f_2^{A+D} dC_2 \\
& = \int dC_2 f_2^{A+D} C_2 C_2 C_2 \cdot \left\{ \frac{n}{n_2} d_2 + (1+\alpha_2) \left(\frac{2}{2} - \frac{3}{2} \right) \Sigma \ell n T \right\}. \quad (3-62)
\end{aligned}$$

Since thermal conductivity is defined in the situation devoid of mass diffusion, i.e. $\bar{C}_2 = 0$ or $d_1 = \frac{D_T}{D_{12}} \nabla \ell n T$ (from 3-21), (3-62) is reduced to

$$\begin{aligned}
& \frac{1}{2} \int m_2 C_2^2 C_2 f_2^{A+D} dC_2 \\
& = -\frac{2}{3} \left(\frac{2kT}{\pi m_2} \right)^{3/2} \frac{n_2}{n_1 \sigma_{12}^2 Y_{12}} \left\{ \frac{n D_T}{n_2 D_{12}} + \frac{1}{2} (1+\alpha_2) \right\} \nabla \ell n T \\
& = -\frac{2}{3} \left(\frac{2kT}{\pi m_2} \right)^{3/2} \frac{n_2}{n_1 \sigma_{12}^2 Y_{12}} (1+\alpha_2) \nabla \ell n T. \quad (3-63)
\end{aligned}$$

The last equality is due to the result (3-25). The contribution to thermal conductivity found from (3-2) is

$$\lambda_{21}^L = \frac{4}{3\pi} \frac{n_2}{n_1} \left(\frac{m_1}{m_2} \right)^{1/2} \left(\frac{2k^3 T}{\pi m_1} \right)^{1/2} \frac{1}{\sigma_{12}^2 Y_{12}} (1+\alpha_2^L)^2, \quad (3-64)$$

which is identical to the result in Chapman and Cowling⁸ in the low density limit.

The total thermal conductivity is

$$\begin{aligned}
\lambda^L & = \frac{1}{Y_{11}} (1+\alpha_1^L)^2 \lambda_1^B + \frac{2}{3} \sigma_{11}^4 Y_{11} n_1^2 \left(\frac{\pi k^3 T}{m_1} \right)^{1/2} \\
& \quad + \frac{4}{3\pi} \frac{n_2}{n_1} \left(\frac{m_1}{m_2} \right)^{1/2} \left(\frac{2k^3 T}{\pi m_1} \right)^{1/2} \frac{1}{\sigma_{12}^2 Y_{12}} (1+\alpha_2)^2 \\
& = \left[1.025 \times \frac{1}{Y_{11}} \left(1 + \frac{12}{5} \xi_1 Y_{11} \right)^2 + \frac{512}{25\pi} \xi_1^2 Y_{11} \right. \\
& \quad \left. + \frac{\xi_2}{\xi_1} \left(\frac{1024}{225\pi} \sqrt{2} q^5 (1+q)^{-2} p^{1/2} \frac{1}{Y_{12}} \left(1 + \frac{2}{5} \xi_1 q^{-3} (1+q)^3 Y_{12} \right) \right) \right] \lambda_1. \quad (3-65)
\end{aligned}$$

(B) $m_1/m_2 \ll 1$, $\sigma_{11}/\sigma_{22} \ll 1$ (Rayleighian, $R_0 + R_1$)

For the particle 1, $I_{12}^R(\Phi_1^{A+D})$ and $I_{12}^R(\Phi_2^{A+D})$ are neglected on ground identical to those in the case of shear viscosity and thus we find

$$\lambda_1^R = \frac{1}{Y_{11}}(1+\alpha_1^R)^2 \lambda_1^B + \frac{2}{3} \sigma_{11}^4 Y_{11} n_1^2 \left(\frac{\pi k^3 T}{m_1} \right)^{\frac{1}{2}}. \quad (3-66)$$

For the particle 2, we find

$$\lambda_{21}^R = \frac{5\sqrt{2}}{4} \frac{n_2}{n_1} \left(\frac{k^3 T}{\pi m_1} \right)^{\frac{1}{2}} \frac{1}{\sigma_{12}^2 Y_{12}} (1+\alpha_2^R)^2 \quad (3-67)$$

by using the argument also similar to the case of the shear viscosity.

The total thermal conductivity is found to be

$$\begin{aligned} \lambda^R &= \frac{1}{Y_{11}}(1+\alpha_1^R)^2 \lambda_1^B + \frac{2}{3} \sigma_{11}^4 Y_{11} n_1^2 \left(\frac{\pi k^3 T}{m_1} \right)^{\frac{1}{2}} \\ &\quad + \frac{8}{3} \sigma_{12}^4 Y_{12} n_1 n_2 (2\pi k T m_1)^{\frac{1}{2}} m_2^{-1} \\ &\quad + \frac{5\sqrt{2}}{4} \frac{n_2}{n_1} \left(\frac{k^3 T}{\pi m_1} \right)^{\frac{1}{2}} \frac{1}{\sigma_{12}^2 Y_{12}} (1+\alpha_2^R)^2 \\ &= \left[1.025 \times \frac{1}{Y_{11}} \left(1 + \frac{12}{5} \xi_1 Y_{11} \right)^2 + \frac{512}{25\pi} \xi_1^2 Y_{11} \right. \\ &\quad + \xi_2 \frac{108\sqrt{2}}{25\pi} \xi_1 q^{-1} (1+q)^4 p + \frac{64\sqrt{2}}{25} \xi_1 q^5 (1+q)^{-2} \bar{Y}_{12} \\ &\quad \left. \times \left(1 + \frac{2}{5} \xi_1 p q^{-3} (1+q)^3 \right) \right]^2 \lambda_1^R. \end{aligned} \quad (3-68)$$

Comparison of Our Results with the Lowest Sonine Polynomial Approximation.

Since exact solution of the integral equations (2-20) is not generally feasible, an approximation method must be used--the method of series expansion being the most obvious choice. Among the various possibilities, the expansion in terms of Sonine polynomials is often found to be the most convenient method. The lowest order terms of these expansions yield the exact solutions for the case of Maxwellian molecules in which the intermolecular potential is $\phi(r) = \kappa r^{-4}$; expansions with a few terms have been found to be surprisingly good approximations for the hard-sphere fluid. In fact, in regards to the transport coefficients of a single component hard-sphere fluid, the use of the lowest sonine polynomials is good enough to produce remarkably accurate results.

Here we compare, for the case of the binary mixtures we consider herein, the results of diffusion coefficient, bulk viscosity and shear viscosity obtained from the lowest Sonine polynomial approximations, with the exact results we obtained. The lowest Sonine polynomials appropriate to D_i , B_i , H_i , respectively, are^{23,24}

$$D_i = d_0^{(i)} S_{3/2}^0(\mathcal{C}_i^2) = d_0^{(i)} \quad (3-68a)$$

$$B_i = b_0^{(i)} S_{5/2}^0(\mathcal{C}_i^2) = b_0^{(i)} \quad (3-68b)$$

$$H_i = h_1^{(i)} S_{1/2}^{(1)}(\mathcal{C}_i^2) = h_1^{(i)} (\frac{1}{2} + 1 - \mathcal{C}_i^2). \quad (3-68c)$$

With these expressions inserted into the equations (2-24) and (2-25) we find the condition for the coefficients $d_0^{(i)}$, $b_0^{(i)}$, and $h_1^{(i)}$, from which these are to be determined. The results of our calculations for the coefficient of binary diffusion, bulk and shear viscosity are

$$D_{12} = \frac{3}{8} \frac{1}{n_1 \sigma_{12}^2 Y_{12}} \left(\frac{kT}{2\pi\mu_{12}} \right)^{\frac{1}{2}} \quad (3-70)$$

$$\begin{aligned} \kappa = & \left[\frac{256}{5\pi} \xi_1^2 Y_{11} + \xi_2 \left\{ \frac{32}{5\pi} \left(\frac{2\mu_{12}}{m_1} \right)^{\frac{1}{2}} q^{-1} (1+q)^4 \xi_1 Y_{12} \right. \right. \\ & \left. \left. + \frac{64\sqrt{2}}{5} \left(\frac{\mu_{12}}{m_1} \right)^{3/2} p^{-1} q^5 (1+q)^{-2} Y_{12}^{-1} \left(Y_{11} - \frac{1}{4} q^{-3} (1+q)^3 p \frac{\mu_{12}}{m_1} \right)^2 \right\} \right] \check{\eta}_1 \end{aligned} \quad (3-71)$$

$$\begin{aligned} \eta = & \left[\frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11} \right)^2 + \frac{768}{25\pi} \xi_1^2 Y_{11} + \xi_2 \left\{ \frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11} \right) \right. \right. \\ & \times \left(\frac{2}{5} (1+q)^3 \left(1 + \frac{\mu_{12}}{m_1} \right) Y_{12} \right) + \frac{96}{25\pi} \left(\frac{2\mu_{12}}{m_1} \right)^{\frac{1}{2}} (1+q)^4 q^{-1} \xi_1 Y_{12} \\ & + \xi_1^{-1} \left(1 + \frac{2}{3} \frac{\mu_{12}}{m_1} \right)^{-1} \frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11} \right) \left\{ \frac{2}{3} q^3 \frac{\mu_{12}}{m_1} - \frac{5}{12} q (1+q)^3 \right. \\ & \times \left. \left(\frac{2\mu_{12}}{m_1} \right)^{\frac{1}{2}} \frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11} \right) Y_{12} + \frac{2}{5} \left(\frac{\mu_{12}}{m_1} - 1 \right) (1+q)^3 \xi_1 Y_{12} \right\} \\ & + \xi_1^{-1} \left(1 + \frac{2}{3} \frac{\mu_{12}}{m_1} \right)^{-1} \left\{ \frac{2}{3} \frac{\mu_{12}}{m_1} \frac{1}{Y_{11}} q^3 \left(1 + \frac{8}{5} \xi_1 Y_{11} \right) + 4 \left(\frac{2\mu_{12}}{m_1} \right)^{-\frac{1}{2}} \right. \\ & \times \left. p^{-1} q^5 Y_{12}^{-1} \left(1 + \frac{2}{5} (1+q)^2 q^{-3} p \frac{\mu_{12}}{m_1} \xi_1 Y_{12} \right) \right\} \\ & \left. \times \left(1 + \frac{2}{5} (1+q)^3 q^{-3} p \frac{\mu_{12}}{m_1} \xi_1 Y_{12} \right) \right] \check{\eta}_1. \end{aligned} \quad (3-72)$$

The diffusivity (3-70) corresponds to $\frac{9\pi}{32} = 88\%$ of the exact result (3-24) in the Lorentz limit while it proves to be exact [identical to (3-27)] in the Rayleighian limit. For bulk viscosity

we find in the case of the Lorentzian mixture,

$$\begin{aligned} \kappa^L = & \left[\frac{256}{5\pi} \xi_1^2 Y_{11} + \xi_2 \left\{ \frac{32}{5\pi} \sqrt{2} p^{-\frac{1}{2}} q^{-1} (1+q)^4 \xi_1 Y_{12} \right. \right. \\ & \left. \left. + \frac{64\sqrt{2}}{5} p^{\frac{1}{2}} q^5 (1+q)^{-2} Y_{12}^{-1} \left(Y_{11} - \frac{1}{4} q^{-3} (1+q)^3 \right)^2 \right\} \right] \check{\eta}_1. \end{aligned} \quad (3-73)$$

which only differs from (3-34) in κ_{21}^L (the last term) that corresponds to $\frac{9\pi}{32} = 88\%$ (the ratio identical to the case of diffusivity). On the other hand, the expression (3-71) for the Rayleighian regime is identical to (3-37). The Lorentz limit of the shear viscosity is reduced to

$$\left(\frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11} \right)^2 + \frac{768}{25\pi} \xi_1^2 Y_{11} \right) \check{\eta}_1, \quad (3-74)$$

which differs from (3-48) only slightly and implies that the approximation given by the lowest Sonine polynomial for the shear viscosity is very good for the case of the single component. As was briefly mentioned below Eq. (3-48), this should not be regarded as the viscosity of the pure solvent, however. If one focuses only on η_{21}^L , the direct contribution of the solute, which was neglected in (3-74) in comparison with solvent viscosity) as the treatments Chapman-Cowling and the Ferzigen-Kaper do on the Boltzmann level, one finds the term in (3-72) pertaining to η_{21}^L is just $\frac{75\pi}{256} = 92\%$ of the exact (3-46). In the opposite case, $p \ll 1$, $q \ll 1$, the result (3-72) is seen to be exact [identical to (3-58)]. Thus, we have found here that the lowest Sonine polynomial approximation yields the exact results for the Rayleighian mixture for all transport coefficients, although not in the Lorentz limit. Since (3-70), (3-73),

(3-72) are reduced to the expression of the single component at $q = 1$, $p = 1$, which is accurate, we can conclude that the lowest Sonine polynomial approximation generally gives reliable results in the region as long as the solute particle is not much lighter than the solvent particle.

Comparison of the Contribution of the Solute to κ , η , λ in the Lorentzian Mixture.

The effect of the solute on the transport in the whole fluid system is multiple as we have seen. One aspect is the relaxation of the solute particles toward local equilibrium by a streaming motion that involves collision with the solvent particles; another is the mutual collisional transfer between the solute and solvent particles at local equilibrium. The additional indirect effects via the change of the structure and thermodynamic properties of the solvent will not be discussed here.

In the Lorentzian limit the contribution of the solute in relaxation toward local equilibrium is predominant over the local equilibrium contribution. As is obvious from the observation that the lighter particle is more effective in transporting energy but less efficient in transporting momentum, it is found that λ_{21}^L is larger than η_{21}^L by a factor of p . Accordingly, in the Rayleighian mixture the opposite result is found, i.e. η_{21}^R is larger than λ_{21}^R by a factor of p^{-1} . However, our result for bulk viscosity seems to defy such a simple

explanation. We discover here that the light solute particle in the Lorentzian mixture is as effective in its contribution to the bulk viscosity (κ_{21}^L) as in its contribution to the thermal conductivity! The possible reason for this is as follows: Through its time-correlation function²⁵ expression the bulk viscosity is related to the fluctuation of the pressure of total fluid system. (This is also reflected through the pressure term β_1 (2-21b) in our kinetic theory). In contrast to the thermal conductivity or the shear viscosity of the light particles scattered by the heavy stationary object envisioned by Lorentz, one cannot focus on the relaxation of the light particles without considering simultaneously the response of the heavy solvent particles which also contribute to the pressure. Thus, the mechanism of the momentum transport here is entirely different; it is implemented purely by the collisional transfer instead of via the streaming motion of the light particle.

R_1 and R_0 Limit

The direct contributions to the bulk and shear viscosity due to the Brownian motion of the solute particles which are much heavier than the surrounding fluid particles are given by the expressions for κ_{21}^R and η_{21}^R in Eqs. (3-32) and (3-57). We note that the effect of Brownian motion is pronounced as long as the mass ratio p and size ratio q are related by $p = q^\alpha$ with α larger than 5. That is, Brownian motion of solute particles with mass density far larger

than that of the surrounding solvent particle is more effective in the transport of momentum as the limit $p \rightarrow 0$, $q \rightarrow 0$ is approached.

Conversely, in the case $p = q^\alpha$ with $1 < \alpha < 5$, these effect of the solute particle on the viscosity tends to vanish as $p \rightarrow 0$, $q \rightarrow 0$. In this limit, the heavy solute particle does not undergo Brownian motion (diffusion) but drifts with the local hydrodynamic velocity \underline{u} (i.e. $\bar{C}_2 = 0$). This is the situation with which the usual hydrodynamic treatments²⁶ of suspension are concerned and is described by the limiting level of approximation denoted as R_0 by us. In the R_0 limit, we find

$$\kappa = \left(\frac{256}{5\pi} \xi_1^2 Y_{11} + \xi_2 \left\{ \frac{32}{5\pi} q^{-1} \xi_1 Y_{12} \right\} \right) \check{\eta}_1 \quad (3-75)$$

$$\eta = \left[\left\{ 1.016 \times \frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11} \right)^2 + \frac{768}{25\pi} \xi_1^2 Y_{11} \right\} + \xi_2 \left[\frac{4}{5} \frac{1}{Y_{11}} \left(1 + \frac{8}{5} \xi_1 Y_{11} \right) \right] Y_{12} + \frac{96\sqrt{2}}{25\pi} \xi_1 q^{-1} Y_{12} \right] \check{\eta}_1 \quad (3-76)$$

$$\lambda = \left(1.025 \times \frac{1}{Y_{11}} \left(1 + \frac{12}{5} \xi_1 Y_{11} \right)^2 + \frac{512}{25\pi} \xi_1^2 Y_{11} \right) \check{\lambda}_1 \quad (3-77)$$

where the local equilibrium contribution of solute to λ is absent since as long as $p = q^\alpha$, $1 < \alpha < 5$, the heavy particle is ineffective in conducting energy.

IV. CONCLUSION AND COMMENTS

By using the solute-solvent collision integrals expanded in terms of mass ratio (through linear order), we have developed a simple method of calculating the transport coefficients of trace-binary mixtures with extreme mass disparity on the Enskog-theory level. Our results have been compared with the results obtained from the lowest Sonine polynomial approximation. In the Lorentz limit, these show the largest (but still reasonably small) deviation from our exact results while in the opposite limit (Rayleighian) they are found to be exact (i.e. identical to ours), which supports some earlier comparisons made of the Boltzmann-equation level. Our method presumably can be extended for low density application to various other models of intermolecular potentials with which the Boltzmann equation can cope. More detailed analysis including higher-order expansion of the collision integral is also straightforward and is capable of yielding expressions for the transport coefficients under more general conditions.

Throughout this work, we have not given explicit expressions for the indirect effect that the solute may have on the transport coefficients as the result of the thermodynamic change of the solvent; e.g. Y_{11} and ξ_1 in the presence of solute are different from those in the pure solvent. One has to specify the mixing condition if one wants to compare these two. Thus, the terms in our expressions of κ , η , λ corresponding to the order ξ_2 do not

fully represent the effect of the solute. This feature could not have been obtained in the Boltzmann-theory description. We shall come back to this problem in the next paper.¹²

Although the resulting transport coefficients in the limit $\sigma_{22}/\sigma_{11} \rightarrow \infty$, $m_2/m_1 \rightarrow \infty$ are exact within the framework of the Enskog theory, we note that they lead to singular physical behaviors in comparison with the hydrodynamic results that are exact in this limit; the results of D_{12} , κ , η in (3-27), (3-77) and (3-78) manifest a singularity that goes like σ_{22}/σ_{11} in contrast to the hydrodynamic results (obtained using slip boundary condition), such as

$$D_{12} = kT/2\pi\eta\sigma_{22}, \quad \lim_{\xi_2 \rightarrow 0} \frac{\eta - \eta_{10}}{\xi_2 \eta_{10}} = 1$$

(η_{10} is pure solvent viscosity). These anomalous results of Enskog theory are due to its assumption of velocity chaos (i.e. the lack of velocity correlation between two particles about to collide) which breaks down in this limit. These problems of modifying the Enskog theory by including the collective effects will be the topics of our subsequent investigations.²⁷

ACKNOWLEDGMENTS

Acknowledgment is made to the National Science Foundation, to the Donors of Petroleum Research Fund, administered by the American Chemical Society, for support of this research. G.S. further acknowledges the support of the Office of Basic Energy Science, Department of Energy, during the period over which this manuscript was written.

REFERENCES

1. S. Chapman, Phil. Trans. R. Soc. A 216, 279 (1916).
D. Enskog, Inaugural Dissertation, Uppsala, 1917.
2. H. A. Lorentz, Proc. Amst. Acad. 7, 438, 585, 684 (1905).
3. D. Burnett, Proc. Lond. Math. Soc. 39, 385 (1935).
4. F. B. Pidduck, Proc. Lond. Math. Soc. 15, 89 (1915).
5. D. Hilbert, Math. Ann. 72, 562 (1912).
6. T. Kihara, Imperfect Gases (U.S. Office of Air Research, Wright-Patterson Air Base).
7. E. A. Mason, J. Chem. Phys. 27, 782 (1957).
8. S. Chapman, T. G. Cowling, The Mathematical Theory of Nonuniform Gases (Cambridge Univ. Press, Cambridge, England, 1952).
9. S. I. Sandler, E. A. Mason, J. Chem. Phys. 12, 71 (1969).
E. A. Mason, F. J. Smith, J. Chem. Phys. 44, 3100 (1966).
10. J. H. Ferziger, H. G. Kaper, Mathematical Theory of Transport Processes in Gases (North-Holland, Amsterdam, 1972).
11. H. Van Beijeren, M. H. Ernst, Physica 68, 437 (1973); *ibid.* 70, 225 (1973).
12. Part I, Sec. B of this thesis
13. J. T. O'Toole, J. S. Dahler, J. Chem. Phys. 32, 1097 (1960).
14. J. Karkheck, Ph.D. Thesis (December 1978) SUNY-Stony Brook.
15. L. Barajas, L. S. Garcia-Colin, E. Pinã, J. of Stat. Phys. 7, 161 (1973).

16. G. E. Uhlenbeck, C. S. Wang Chang in Transport Processes in Statistical Mechanics, I. Prigogine, ed. (Interscience Publishers, Inc., New York, 1958).
17. Lord Rayleigh, Phil. Mag. 32, 424 (1891).
18. M. S. Green, J. Chem. Phys. 19, 1036 (1951).
19. This was also referred as quasi Lorentzian by E. A. Mason (ref. 7).
20. K. Andersen, K. E. Shuler, J. Chem. Phys. 40, 633 (1964).
21. R. B. Bird, W. E. Stewart and E. N. Lightfoot, Selected Topics in Transport Phenomena, Chem. Eng. Progress Symposium Series, #58, Vol. 61, AIChE, New York (1965).
22. K. Kumar, Ann. Phys. (NY) 37, 113 (1966).
23. M. J. Tham, K. E. Gubbins, J. Chem. Phys. 55, 268 (1971).
24. J. Karkheck, G. Stell, J. Chem. Phys. 71, 3620 (1979).
25. E. Helfand, Phys. Rev. 119, 1 (1960).
26. G. K. Batchelor, J. T. Green, J. Fluid Mech. 56, 401 (1972).
27. Part II, Sections A and B of this thesis.