

## **Nonlinear Transport in a Dilute Binary Mixture of Mechanically Different Particles**

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The hierarchy of moments of the Boltzmann equation for a binary mixture of mechanically different Maxwell molecules is exactly solved. The solution corresponds to a nonequilibrium homogeneous steady state generated by an external force that accelerates particles of each species (or "color") along opposite directions. As a consequence, macroscopic fluxes are induced in spite of the absence of concentration gradients. Explicit expressions for the fluxes of mass and momentum as functions of the field strength, the mass ratio, the molar fractions, and the interaction constant ratio are obtained. In particular, the color conductivity coefficient reduces to the mutual diffusion coefficient in the zero-field limit. Some physically interesting limiting cases are discussed. The maximum-entropy method is used to construct an approximate velocity distribution function from the exact knowledge of the mass and momentum fluxes. This distribution is exact up to second order in the color field and also in the limit of large color field.

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**KEY WORDS:** Boltzmann equation; Maxwell molecules; nonlinear transport; mutual diffusion.

### **1. INTRODUCTION**

The Boltzmann equation provides the appropriate framework for analyzing nonequilibrium states in dilute gases. Nevertheless, due to its mathematical intricacy, only a few exact solutions are known. The difficulties are much greater when the system is constituted by particles of different species, as one has to deal with a set of coupled Boltzmann equations. Further, the transport properties depend on the molar fractions, the mass ratios, and the size ratios. In order to get explicit results, one usually has to consider

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limit cases, such as the tracer limit, the Fokker–Planck limit, or the case of mechanically identical particles.

The aim of this paper is to obtain an exact solution of the set of Boltzmann equations for a binary mixture of mechanically distinguishable particles. Particles of different species are understood to possess different “color charges,” so that particles of different color can be distinguished even in the limit of mechanically identical particles. The system is driven out of equilibrium by the action of a constant external force. This color force acts on particles of each color along opposite directions, producing mutual diffusion in the absence of concentration gradients. In fact, the color force plays the role of a chemical potential gradient. A drag force is also introduced to achieve a steady state. In this problem, the ratio between the mass flux and the color force defines the most relevant transport coefficient, which will be referred to as the color conductivity coefficient. This coefficient reduces to the conventional mutual diffusion coefficient in the zero-field limit. This way of measuring the diffusion coefficient was the original motivation for introducing the color field method in molecular dynamics simulations.<sup>(1–3)</sup>

The exact solution reported here is obtained by recursively solving the moment hierarchy for the special case of Maxwell molecules (i.e., particles interacting via the inverse fifth power force). We derive explicit expressions for the moments corresponding to the mass and momentum fluxes. These expressions extend previous results obtained in the case of mechanically identical particles (i.e., equal masses and force constants).<sup>(4)</sup> Quite surprisingly, when one conveniently nondimensionalizes the field strength and the color conductivity coefficient, the latter is a nonlinear “universal” function, in the sense that it is independent of the parameters characterizing the mixture. On the other hand, the pressure tensor happens to be a function of the field strength that parametrically depends on the ratios of masses, molar fractions, and force constants. In particular, the trace of the pressure tensor gives the temperature, which is different for each species.

The organization of the paper is as follows. Section 2 concerns with the description of the color conductivity problem in a binary mixture. It is shown that the set of Boltzmann equations can be solved by the moment method for Maxwell molecules. The explicit calculation of the mass and momentum fluxes is carried out in Section 3. Some physically interesting limiting cases are discussed in Section 4. The maximum-entropy method is used in Section 5 to get an *approximate* expression for the velocity distribution functions from the knowledge of the *exact* mass and momentum fluxes. Section 6 offers a brief discussion of the results.

## 2. DESCRIPTION OF THE PROBLEM

Usually, mutual diffusion in a binary mixture takes place when concentration gradients are present. The phenomenological law linking the mass flux  $\mathbf{j}_r$  of species  $r$  to the gradient of molar fraction  $\nabla x_r$  is<sup>(5)</sup>

$$\mathbf{j}_r = -\frac{m_1 m_2 n^2}{\rho} D \nabla x_r, \quad r = 1, 2 \tag{1}$$

where  $m_r$  is the mass of a particle of species  $r$ ,  $n = n_1 + n_2$  is the total number density,  $n_r$  being the number density of species  $r$ ,  $\rho = \rho_1 + \rho_2 = m_1 n_1 + m_2 n_2$  is the total mass density, and  $x_r = n_r/n$  is the molar fraction of species  $r$ . The above relation defines the mutual diffusion coefficient  $D$ .

In the homogeneous color conductivity problem, an external force accelerates particles of different species (color) along opposite directions.<sup>(1)</sup> Consequently, mass fluxes are created in the absence of concentration gradients. The color force acting on particles of species  $r$  is constant and can be conveniently written as

$$\mathbf{F}_r = -k_B T \boldsymbol{\varepsilon}_r \tag{2}$$

where  $k_B$  is the Boltzmann constant,  $T$  is the temperature of the mixture, and  $\boldsymbol{\varepsilon}_r$  is a constant vector that mimics the role played by  $\nabla \ln n_r$  in a typical diffusion problem. The color force does work on the system. To reach a steady state, a drag force  $\mathbf{F}_r^{\text{drag}}$  must be introduced to compensate for the increase of temperature. It is given by

$$\mathbf{F}_r^{\text{drag}} = -\alpha m_r \mathbf{v} \tag{3}$$

$\alpha$  is a thermostat parameter, identical for all the particles. Its value is determined as a function of the color field strength by consistency.

In the general problem, the hydrodynamic balance equations are

$$\frac{\partial}{\partial t} \rho_r + \nabla \cdot \mathbf{j}_r = 0, \quad r = 1, 2 \tag{4}$$

$$\frac{\partial}{\partial t} \mathbf{j} + \nabla \cdot \mathbf{P} + k_B T (n_1 \boldsymbol{\varepsilon}_1 + n_2 \boldsymbol{\varepsilon}_2) + \alpha \mathbf{j} = 0 \tag{5}$$

$$\frac{\partial}{\partial t} \rho e + \nabla \cdot \mathbf{q} + k_B T \left( \boldsymbol{\varepsilon}_1 \cdot \frac{\mathbf{j}_1}{m_1} + \boldsymbol{\varepsilon}_2 \cdot \frac{\mathbf{j}_2}{m_2} + 3n\alpha \right) = 0 \tag{6}$$

where  $\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2$  is the total mass flux,  $\mathbf{P}$  is the total momentum flux,  $\rho e$  is the total energy density, and  $\mathbf{q}$  is the total energy flux, all of them measured in the laboratory frame. Now, we consider a steady, spatially homogeneous

state. If, without loss of generality, we take  $\mathbf{j} = 0$ , Eqs. (5) and (6) yield the constraints

$$n_1 \boldsymbol{\varepsilon}_2 + n_2 \boldsymbol{\varepsilon}_1 = 0 \quad (7)$$

$$\alpha = -\frac{\rho}{3nm_1\rho_2} \boldsymbol{\varepsilon}_1 \cdot \mathbf{j}_1 = -\frac{\rho}{3nm_2\rho_1} \boldsymbol{\varepsilon}_2 \cdot \mathbf{j}_2 \quad (8)$$

In this special state, the field strength  $\boldsymbol{\varepsilon}_1$  (or  $\boldsymbol{\varepsilon}_2$ ) represents the parameter measuring the distance from equilibrium. Near equilibrium, a linear law similar to Fick's law, Eq. (1), is expected to hold. Beyond this limit, a nonlinear color conductivity coefficient  $\sigma$  can be defined by

$$\mathbf{j}_r = -\frac{m_1 m_2 n}{\rho} \sigma n_r \boldsymbol{\varepsilon}_r, \quad r = 1, 2 \quad (9)$$

In general, the transport coefficient  $\sigma$  is a function of the field strength  $\boldsymbol{\varepsilon}_r$ . In accordance with the original spirit of the color field method, the color conductivity  $\sigma$  must reduce to the mutual diffusion coefficient  $D$  in the zero-field limit. Here, our goal is to go beyond the above limit and obtain the full dependence of  $\sigma$  on the color field.

In order to attack the problem, we will restrict ourselves to a low-density binary mixture. In that case, the adequate description is given by the set of two coupled Boltzmann equations.<sup>(6)</sup> In our problem, they read

$$\frac{1}{m_1} \frac{\partial}{\partial \mathbf{v}} \cdot [(\mathbf{F}_1 + \mathbf{F}_1^{\text{drag}}) f_1] = J_{11}[f_1, f_1] + J_{12}[f_1, f_2] \quad (10)$$

$$\frac{1}{m_2} \frac{\partial}{\partial \mathbf{v}} \cdot [(\mathbf{F}_2 + \mathbf{F}_2^{\text{drag}}) f_2] = J_{22}[f_2, f_2] + J_{21}[f_2, f_1] \quad (11)$$

where we have particularized to stationary, spatially homogeneous solutions. In Eqs. (10) and (11),  $f_r(\mathbf{v})$  is the one-particle velocity distribution function of species  $r$  and  $J_{rs}[f_r, f_s]$  is the Boltzmann collision term, which in standard notation is given by<sup>(6)</sup>

$$J_{rs}[f_r, f_s] = \int d\mathbf{v}_1 \int d\Omega |\mathbf{v} - \mathbf{v}_1| \sigma_{rs}(\mathbf{v} - \mathbf{v}_1, \theta) \\ \times [f_r(\mathbf{v}') f_s(\mathbf{v}'_1) - f_r(\mathbf{v}) f_s(\mathbf{v}_1)] \quad (12)$$

In terms of  $f_r$ , the number density and the mass flux are given by

$$n_r = \int d\mathbf{v} f_r \quad (13)$$

$$\mathbf{j}_r = \int d\mathbf{v} m_r \mathbf{v} f_r \quad (14)$$

In addition, the pressure tensor of species  $r$  can be defined as

$$P_r = \int d\mathbf{v} m_r \mathbf{v} \mathbf{v} f_r \tag{15}$$

The temperature  $T_r$  is introduced through the relation

$$p_r = n_r k_B T_r \tag{16}$$

where  $p_r = \frac{1}{3} \text{Tr} P_r$ . From a hydrodynamic point of view, the relevant quantities are the total pressure tensor  $\mathbf{P} = \mathbf{P}_1 + \mathbf{P}_2$  and the temperature of the mixture  $T = x_1 T_1 + x_2 T_2$ . At a kinetic level, however, there are two distribution functions and this justifies the convenience of introducing the partial quantities  $P_r$  and  $T_r$ . The first one measures the contribution to the total momentum flux associated with each species, while  $T_r$  measures the degree of unequal partition of the total energy between both species.

A general solution, valid for arbitrary interaction potentials, to the set of equations (10) and (11) could be obtained as a perturbation expansion in powers of the field strength, in the same spirit as in the well-known Chapman-Enskog method.<sup>(6)</sup> However, its applicability is restricted to states near equilibrium. Furthermore, a perturbation solution is not necessary if one considers the special case of Maxwell molecules (particles interacting via the potential  $\varphi_{rs} = \kappa_{rs} r^{-4}$ ). For this interaction, the Boltzmann equations (10) and (11) are solvable by means of the moment method. The key point is that a moment of order  $k$  of the collision operator only involves moments of order less than or equal to  $k$ . In particular,<sup>(7)</sup>

$$\int d\mathbf{v} m_r \mathbf{v} J_{rs}[f_r, f_s] = -\frac{\lambda_{rs}}{m_r m_s} (\rho_s \mathbf{j}_r - \rho_r \mathbf{j}_s) \tag{17}$$

$$\begin{aligned} \int d\mathbf{v} m_r \mathbf{v} \mathbf{v} J_{rs}[f_r, f_s] = & \frac{\lambda'_{rs}}{(m_r + m_s) m_r} \left[ \left( \rho_r p_s + \rho_s p_r - \frac{2}{3} \mathbf{j}_r \cdot \mathbf{j}_s \right) \mathbf{1} \right. \\ & \left. - (\rho_r \mathbf{P}_s + \rho_s \mathbf{P}_r) + (\mathbf{j}_r \mathbf{j}_s + \mathbf{j}_s \mathbf{j}_r) \right] \\ & - \frac{\lambda_{rs}}{(m_r + m_s) m_r} \left[ 2 \left( \frac{m_r}{m_s} \rho_s \mathbf{P}_r - \rho_r \mathbf{P}_s \right) \right. \\ & \left. + \left( 1 - \frac{m_r}{m_s} \right) (\mathbf{j}_r \mathbf{j}_s + \mathbf{j}_s \mathbf{j}_r) \right] \end{aligned} \tag{18}$$

where

$$\lambda_{rs} = 1.69\pi \left( \kappa_{rs} \frac{m_r m_s}{m_r + m_s} \right)^{1/2} \tag{19}$$

and

$$\lambda'_{rs} = 2.61\pi \left( \kappa_{rs} \frac{m_r m_s}{m_r + m_s} \right)^{1/2} \quad (20)$$

As shown in the next section, the use of these equations allows one to obtain explicitly the mass and momentum fluxes for arbitrarily large values of the field strength.

### 3. MASS AND MOMENTUM FLUXES

In the following, we will focus on the transport properties associated with species 1. Obviously, the transport properties of species 2 can be obtained just by the adequate change of indices. This is a direct consequence of the fact that the results derived in this paper apply to arbitrary ratios of masses, concentrations, and force constants. Multiplying both sides of Eq. (10) by  $m_1 \mathbf{v}$  and integrating, one gets

$$k_B T n_1 \boldsymbol{\varepsilon}_1 + \alpha \mathbf{j}_1 = - \frac{\lambda_{12}}{m_1 m_2} \rho \mathbf{j}_1 \quad (21)$$

where use has been made of Eq. (17). Inserting Eq. (8) into Eq. (21), we obtain a quadratic equation for  $\mathbf{j}_1$ . Its physical solution can be recast into the form (9) with the following expression for the color conductivity coefficient:

$$\sigma = \frac{3\lambda_{12} n_2 \rho}{2m_1 m_2 n_1} \varepsilon_1^{-2} \left[ \left( 1 + \frac{4m_1 m_2 n_1 k_B T}{3\lambda_{12}^2 n_2 n \rho} \varepsilon_1^2 \right)^{1/2} - 1 \right] \quad (22)$$

Equation (22) provides the exact explicit expression for the color conductivity coefficient for arbitrary values of the field strength  $\varepsilon_1$ , the masses  $m_1$  and  $m_2$ , the densities  $n_1$  and  $n_2$ , and the force constant  $\kappa_{12}$ . The above expression represents the main result of this paper. Since the color conductivity  $\sigma$  is independent of the species considered, as assumed in Eq. (9), it does not depend on  $\kappa_{11}$  and  $\kappa_{22}$ . If we take the limit  $\kappa_{12} \rightarrow 0$ , i.e., we ignore cross-collisions, the mass flux must be the same as in a collisionless gas, namely

$$\mathbf{j}_r = \rho_r \mathbf{u}_r^{\text{lim}} \quad (23)$$

where

$$\mathbf{u}_r^{\text{lim}} = - \frac{k_B T}{\alpha m_r} \boldsymbol{\varepsilon}_r \quad (24)$$

is the limit velocity, which is obtained when the drag force equals the color force. Obviously, the mean kinetic energy is  $\frac{1}{2}m_r(u_r^{\text{lim}})^2 = \frac{3}{2}k_B T_r$ . The constraint  $T = x_1 T_1 + x_2 T_2$  allows one to get  $\alpha$ . Substitution into Eq. (24) yields

$$\mathbf{u}_1^{\text{lim}} = -\left(\frac{3k_B T}{m_1}\right)^{1/2} \left(\frac{x_2}{x_1} \frac{nm_2}{\rho}\right)^{1/2} \hat{\boldsymbol{\varepsilon}}_1 \quad (25)$$

As a matter of fact, this result coincides with that obtained from Eqs. (9) and (22) by taking the limit  $\kappa_{12} \rightarrow 0$ .

Now we return to the nontrivial situation when  $\kappa_{12} \neq 0$ . In the zero-field limit, the color conductivity coefficient becomes

$$\lim_{\varepsilon_1 \rightarrow 0} \sigma = \frac{k_B T}{\lambda_{12} n} \quad (26)$$

As expected, this limit coincides with the expression for the mutual diffusion coefficient  $D$  of a binary mixture of Maxwell molecules.<sup>(6)</sup> This equivalence between  $D$  and the zero-field limit of  $\sigma$  has been verified in molecular dynamics simulations for dense fluids.<sup>(1,3,8)</sup>

In order to analyze the nonlinear transport properties in the system, it is convenient to introduce dimensionless quantities. We define the reduced color conductivity coefficient  $\sigma^* = \sigma/D$  and the reduced field strength

$$\varepsilon^* = \left(\frac{2}{3} \frac{k_B T m_1 m_2}{\lambda_{12}^2 n \rho} \frac{x_1}{x_2}\right)^{1/2} \boldsymbol{\varepsilon}_1 \quad (27)$$

In these units, Eq. (22) becomes

$$\sigma^*(\varepsilon^*) = \varepsilon^{*-2} [(1 + 2\varepsilon^{*2})^{1/2} - 1] \quad (28)$$

Written in reduced units, the field strength dependence of the color conductivity adopts a universal form, regardless of the values of the mass and concentration ratios. Consequently, Eq. (28) is exactly the same as the one derived in ref. 4 in the particular case of mechanically identical particles. The expansion of  $\sigma^*$  in powers of  $\varepsilon^*$  is convergent for  $\varepsilon^{*2} < 1/2$ . In the large-field limit,  $\sigma^* \approx \sqrt{2} |\varepsilon^*|^{-1}$ , so that the mass flux is again given by Eq. (23).

Let us now get the next moment, namely the pressure tensor. Multiplying both sides of Eq. (10) by  $m_1 \mathbf{v}\mathbf{v}$  and integrating, one obtains

$$\begin{aligned}
\frac{k_B T}{m_1} (\boldsymbol{\varepsilon}_1 \mathbf{j}_1 + \mathbf{j}_1 \boldsymbol{\varepsilon}_1) + 2\alpha P_1 = & \frac{\lambda'_{11}}{m_1^2} \left[ \left( \rho_1 p_1 - \frac{1}{3} j_1^2 \right) \mathbb{1} - \rho_1 \mathbf{P}_1 + \mathbf{j}_1 \mathbf{j}_1 \right] \\
& + \frac{\lambda'_{12}}{(m_1 + m_2) m_1} \left[ \left( \rho_1 p_2 + \rho_2 p_1 - \frac{2}{3} \mathbf{j}_1 \cdot \mathbf{j}_2 \right) \mathbb{1} \right. \\
& \left. - (\rho_1 \mathbf{P}_2 + \rho_2 \mathbf{P}_1) + (\mathbf{j}_1 \mathbf{j}_2 + \mathbf{j}_2 \mathbf{j}_1) \right] \\
& - \frac{\lambda_{12}}{(m_1 + m_2) m_1} \left[ 2 \left( \frac{m_1}{m_2} \rho_2 \mathbf{P}_1 - \rho_1 \mathbf{P}_2 \right) \right. \\
& \left. + \left( 1 - \frac{m_1}{m_2} \right) (\mathbf{j}_1 \mathbf{j}_2 + \mathbf{j}_2 \mathbf{j}_1) \right] \quad (29)
\end{aligned}$$

where use has been made of Eq. (18). An equation similar to Eq. (29) can be obtained for species 2. Taking the trace in both sides of Eq. (29) and taking into account that  $p_1 + p_2 = nk_B T$ , one gets a closed equation for the partial pressure  $p_1 = n_1 k_B T_1$ . In dimensionless form, its solution is

$$T_1^* \equiv \frac{T_1}{T} = \frac{1 + [(1 - \mu)/2(\mu\nu + 1)] \varepsilon^{*2} \sigma^{*2} + [(\mu + 1)/2\mu\nu] \varepsilon^{*2} \sigma^*}{1 + [(\mu + 1)(\mu\nu + 1)/2\mu(\nu + 1)] \varepsilon^{*2} \sigma^*} \quad (30)$$

where  $\mu \equiv m_1/m_2$  is the mass ratio and  $\nu \equiv n_1/n_2$  is the concentration ratio. The expression for  $T_2^*$  can be obtained from Eq. (30) by making the changes  $\mu \leftrightarrow \mu^{-1}$  and  $\nu \leftrightarrow \nu^{-1}$ . In contrast to what happens in the case of the reduced color conductivity coefficient, the reduced temperatures  $T_r^*$  are not universal functions of the field strength. On the other hand,  $T_r^*$  is independent of the force constant ratios. In the limit of small field strengths, the behavior of the temperature is

$$T_1^* \approx 1 - \tau_1 \varepsilon^{*2} \quad (31)$$

where

$$\tau_1 = \frac{\mu^3 \nu^3 + \mu^2 \nu^2 (\nu + 2) - \mu(2\nu + 1) - 1}{2\mu\nu(\mu\nu + 1)(\nu + 1)} \quad (32)$$

In this small-field region, at a given value of  $\nu$ ,  $T_1^* > 1$  if  $\mu$  is smaller than a certain value  $\mu'(v)$ . For instance,  $\mu' = 2.54$  and  $0.39$  for  $\nu = 0.5$  and  $2$ , respectively. For large field strengths the behavior is

$$T_1^* \approx \frac{\nu + 1}{\nu(\mu\nu + 1)} \quad (33)$$



In this region,  $T_1^* > 1$  if  $\mu$  is smaller than a certain value  $\mu''(v) = v^{-2}$ . Consequently,  $T_1^*$  is a monotonic function of  $\varepsilon^*$  if and only if, at a given value of  $v$ ,  $\mu < \min\{\mu', \mu''\}$  or  $\mu > \max\{\mu', \mu''\}$ . In the equimolar case ( $v = 1$ ), the behavior is always monotonic, since  $\mu' = \mu'' = 1$ . Figure 1 shows the color field dependence of  $T_1^*$  for  $v = 0.5$  and  $v = 2$  and several values of  $\mu$ . It is observed that, for the cases considered in the figure,  $T_1 > T$  if  $n_1 = \frac{1}{2}n_2$ , whereas the opposite happens if  $n_1 = 2n_2$ . This means that particles of the defect species have a larger mean kinetic energy than particles of the excess species. Further, at given values of  $v$  and  $\varepsilon^*$ , the mean kinetic energy per particle of species 1 increases as the mass ratio  $m_1/m_2$  decreases. In the limit of  $\varepsilon^*$  going to infinity, Eqs. (23) and (33) show that  $\langle v \rangle^2 = \langle v^2 \rangle$  for each species. This means that in the limit of very large fields, the system behaves as a collisionless gas. Therefore,

$$\lim_{|\varepsilon^*| \rightarrow \infty} f_r(\mathbf{v}) = n_r \delta(\mathbf{v} - \mathbf{u}_r^{\text{lim}}) \tag{34}$$

In order to analyze the transition from the equilibrium distribution (with zero average velocity) to the  $\delta$ -distribution (34), it is instructive to consider

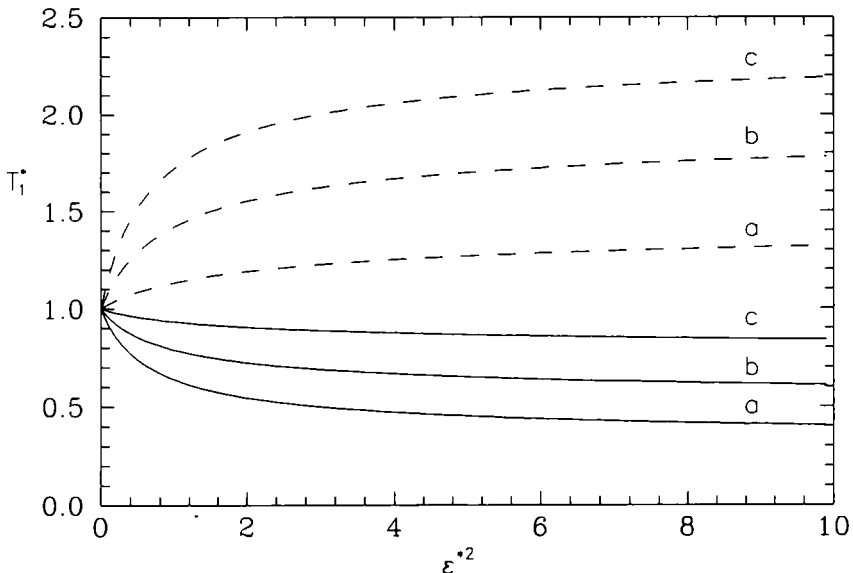


Fig. 1. Plot of the reduced temperature  $T_1^* \equiv T_1/T$  as a function of  $\varepsilon^{*2}$  for  $v \equiv n_1/n_2 = 2$  (solid line) and  $v = 0.5$  (dashed line) and the following values of  $\mu \equiv m_1/m_2$ : (a)  $\mu = 2$ , (b)  $\mu = 1$ , and (c)  $\mu = 0.5$ .

the color field dependence of  $\chi \equiv 1 - \langle v \rangle^2 / \langle v^2 \rangle$ . In the case of species 1, one gets

$$\chi_1 = 1 - \frac{\nu + 1}{2\nu(\mu\nu + 1)} \frac{\sigma^{*2} \varepsilon^{*2}}{T_1^*} \tag{35}$$

The quantity  $\chi_1$  is plotted in Fig. 2 for the same cases as in Fig. 1. We observe that the species with a smaller molar fraction tends more rapidly toward the  $\delta$ -distribution as the field strength increases.

Once  $p_1$  and  $p_2$  are known, a closed equation for  $P_1$  can be obtained by eliminating  $P_2$  between Eq. (29) and its counterpart for species 2. The solution can be written as

$$P_1^* \equiv \frac{P_1}{n_1 k_B T} = P_{1,\perp}^* \mathbb{1} + (P_{1,\parallel}^* - P_{1,\perp}^*) \widehat{\varepsilon}^* \widehat{\varepsilon}^* \tag{36}$$

where

$$P_{1,\parallel}^* = 3T_1^* - 2P_{1,\perp}^* \tag{37}$$

$$P_{1,\perp}^* = \frac{1}{2(\mu\nu + 1)} \frac{\left( A_1 \varepsilon^{*4} \sigma^{*3} + A_2 \varepsilon^{*2} \sigma^{*2} + A_3 \varepsilon^{*2} \sigma^* T_1^* \right) + A_4 \varepsilon^{*2} \sigma^* + A_5 T_1^* + A_6}{A_7 \varepsilon^{*4} \sigma^{*2} + A_8 \varepsilon^{*2} \sigma^* + A_9} \tag{38}$$

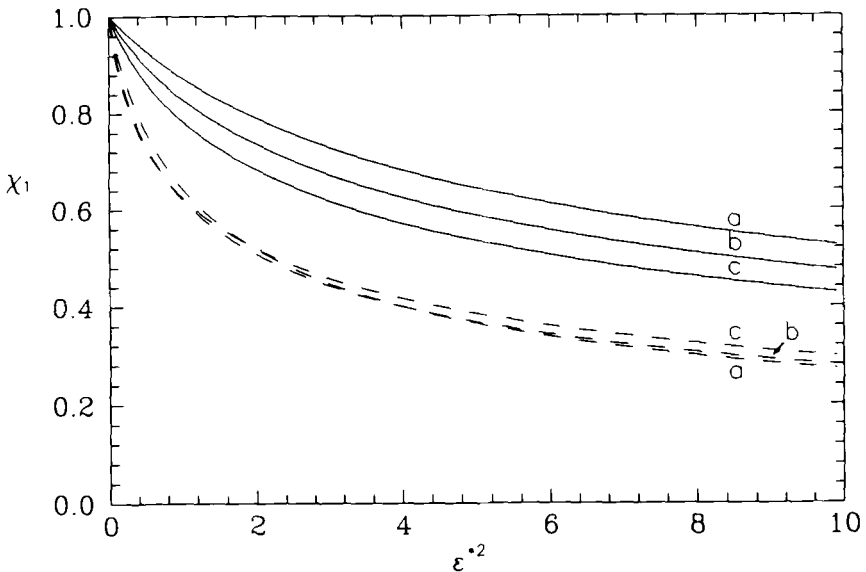


Fig. 2. Plot of the quantity  $\chi \equiv 1 - \langle v \rangle^2 / \langle v^2 \rangle$  for species 1 and for the same cases as in Fig. 1.

where the coefficients  $A_i$  depend on the parameters characterizing the mixture, namely  $\mu$ ,  $\nu$ , and the force constant ratios. Their expressions are given in the appendix. The element  $P_{1,\perp}^*$  of the reduced pressure tensor is plotted in Fig. 3 as a function of  $\varepsilon^{*2}$  for the same cases as in the previous figures. We have chosen for the force constants the relationship  $\kappa_{rs} \propto (m_r m_s)^{1/2}$ , which has been proposed to model the mass dependence of the cross section observed in disparate-mass binary mixtures.<sup>(9)</sup> We observe that, in general,  $P_{1,\perp}^*$  monotonically decreases as the field strength increases. However, at a given value of the concentration ratio  $\nu$ , there exists a threshold value of the mass ratio  $\mu_{th}$  such that if  $\mu < \mu_{th}$ , then  $P_{1,\perp}^*$  has a maximum in the region of small field strengths. In particular,  $\mu_{th} = 0.773$  for  $\nu = 0.5$  and  $\mu_{th} = 0.123$  for  $\nu = 2$ .

By following the same scheme, one could get explicit expressions for higher-order moments. This would require the knowledge of the corresponding moments of the Boltzmann collision operator. Nevertheless, due to the intricacy of the algebra involved, we restrict ourselves in this paper to the mass and momentum fluxes. In the special case of mechanically equivalent particles, the total energy flux was explicitly evaluated in ref. 4.

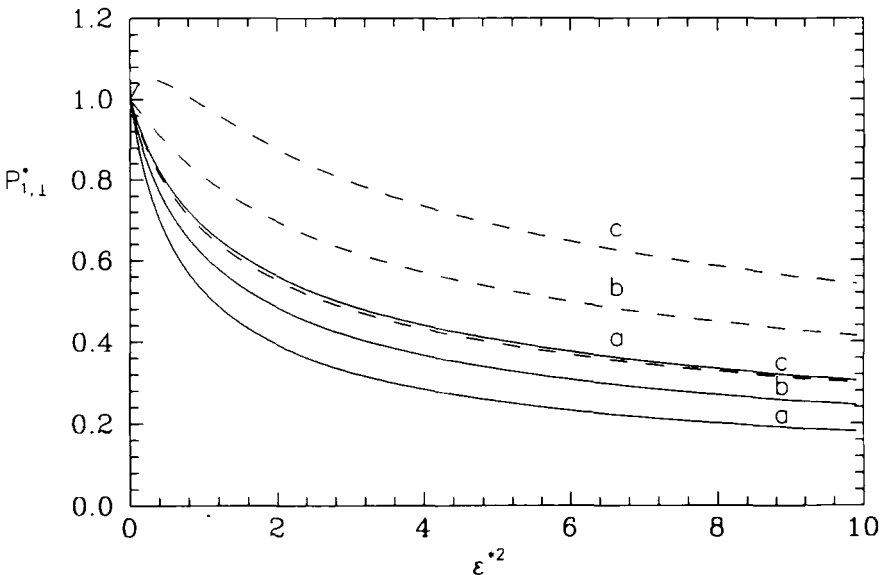


Fig. 3. Plot of  $P_{1,\perp}^*$  for the same cases as in Fig. 1. We have chosen for the force constants the relationship  $\kappa_{rs} \propto (m_r m_s)^{1/2}$ .

#### 4. SOME INTERESTING LIMITING CASES

The results derived in the previous section are general, in the sense that they apply to arbitrary mass, concentration, and force constant ratios. This allows us to consider some physically interesting particular cases. For the sake of brevity we focus here on the behavior of the reduced temperatures  $T_r^*$ . Further, we shall assume that  $\varepsilon^* \neq 0$ .

##### 4.1. Equal Masses

This is the simplest case. By substituting  $\mu = 1$  into Eq. (30), one gets

$$T_1^* = \frac{1 + v^{-1} \varepsilon^{*2} \sigma^*}{1 + \varepsilon^{*2} \sigma^*} \quad (39)$$

This result was already obtained in ref. 4 in the particular case of mechanically identical particles. Notice that Eq. (39) applies even in the case of unequal force constants.

##### 4.2. Disparate Masses

Let us consider now that one of the species, say species 1, is much lighter than the other one, their concentrations being otherwise comparable. Taking the limit  $\mu \rightarrow 0$  in Eq. (30) as well as in its counterpart for species 2, one obtains

$$T_1^* = 1 + v^{-1} = 1/x_1 \quad (40)$$

$$T_2^* = 2(v + 1)[\varepsilon^{*-2} \sigma^{*-1} + \frac{1}{2}v(1 - \sigma^*)]\mu \quad (41)$$

Thus, the heavy particles have a mean kinetic energy much less than that of the light particles. This is related to the fact that both species have the same mass flux, so that the mean velocity of species 2,  $u_2$ , is  $\mu v$  times that of species 1,  $u_1$ .

##### 4.3. Tracer Limit

When one of the species, say species 1, has a vanishing molar fraction, it acts as a tracer species. Let us assume first that the masses  $m_1$  and  $m_2$  are comparable. Then, taking the limit  $v \rightarrow 0$ , we get

$$T_1^* = \left(1 + \frac{2\mu}{\mu + 1} \varepsilon^{*-2} \sigma^{*-1}\right)^{-1} v^{-1} \quad (42)$$

$$T_2^* = \left(1 + \frac{\mu + 1}{2\mu} \varepsilon^{*2} \sigma^*\right)^{-1} \quad (43)$$

The mean kinetic energy of the tracer particles goes to infinity, although their total kinetic energy remains finite.

**4.3.1. Lorentz Gas.** If further we assume that the tracer particles are much lighter than the bath particles, we arrive at the so-called Lorentz gas. The temperatures of each species can easily be obtained by taking the limit  $v \rightarrow 0$  in Eqs. (40) and (41) or, equivalently, the limit  $\mu \rightarrow 0$  in Eqs. (42) and (43). The result is

$$T_1^* = v^{-1} \tag{44}$$

$$T_2^* = 2\varepsilon^{*-2}\sigma^{*-1}\mu \tag{45}$$

This means that practically the total kinetic energy of the mixture belongs to the tracer species.

**4.3.2. Rayleigh Limit.** Let us assume now that the tracer particles are much heavier than the bath particles. If, in addition,  $n_1 m_1 \ll n_2 m_2$ , then the average velocity of the tracer species is much larger than that of the bath particles ( $u_1 \gg u_2$ ). After taking the limit  $\mu \rightarrow \infty$ , Eqs. (42) and (43) become, respectively,

$$T_1^* = (1 + 2\varepsilon^{*-2}\sigma^{*-1})^{-1} v^{-1} \tag{46}$$

$$T_2^* = (1 + \frac{1}{2}\varepsilon^{*2}\sigma^*)^{-1} \tag{47}$$

Obviously, the mean kinetic energy of a tracer particle is much larger than that of a bath particle, but the total kinetic energy of both species are of the same order.

#### 4.4. Brownian Limit

In this limit, species 1 has a vanishing molar fraction, is much heavier than species 2, and the ratio between the average velocities  $u_1/u_2$  is of order  $(m_2/m_1)^{1/2}$ . In our units, the Brownian limit corresponds to  $v \rightarrow 0$ ,  $\mu \rightarrow \infty$ , and  $v^2\mu = \text{const}$ . Under these conditions, one gets

$$T_1^* = \frac{1 - \sigma^*}{v^2\mu} \tag{48}$$

$$T_2^* = 1 \tag{49}$$

The fact that  $T_2^*$  takes the value corresponding to a collisionless gas, cf. Eq. (33), shows that the state of the bath particles is practically not disturbed by the presence of the Brownian particles. On the other hand,

although the mean kinetic energy of the Brownian and the bath particles are different, they are of the same order.

#### 4.5. $n_1 \ll n_2$ , $m_1 \gg m_2$ , $n_1 m_1 \sim n_2 m_2$

In this situation, the average velocities of both species are comparable. This case can be considered to lie in between the Rayleigh and the Brownian limits. Taking the limits  $v \rightarrow 0$ ,  $\mu \rightarrow \infty$ , with  $\mu v = \text{const}$ , one has

$$T_1^* = \frac{\frac{1}{2}\varepsilon^{*2}\sigma^*(1/\mu v - \sigma^*/(\mu v + 1))}{1 + \frac{1}{2}(\mu v + 1)\varepsilon^{*2}\sigma^*} \mu \quad (50)$$

$$T_2^* = \frac{1 + \frac{1}{2}\mu v \varepsilon^{*2}\sigma^*(1 + \sigma^*/(\mu v + 1))}{1 + \frac{1}{2}(\mu v + 1)\varepsilon^{*2}\sigma^*} \quad (51)$$

Although the mean kinetic energy of the heavy particles is much larger than that of the light particles, the total kinetic energies of both species are comparable.

## 5. MAXIMUM-ENTROPY METHOD

Because of the mathematical complexity of the Boltzmann equation, we have not been able to find a closed expression for the velocity distribution functions in this problem. However, as said in Section 3, the recursive solution of the moment hierarchy would allow one, *in principle*, to obtain all the velocity moments. In that case, the velocity distribution functions can be represented as expansions in a complete set of orthogonal functions. For instance,

$$f_r(\mathbf{v}) = f_r^0(\mathbf{v}) \sum_{k,l} C_r^{k,l} \Psi_{k,l}(\xi) \quad (52)$$

where

$$f_r^0(\mathbf{v}) = n_r \left( \frac{m_r}{2\pi k_B T} \right)^{3/2} \exp \left( - \frac{m_r v^2}{2k_B T} \right) \quad (53)$$

is the equilibrium distribution,

$$\xi = \left( \frac{m_r}{2k_B T} \right)^{1/2} \mathbf{v} \quad (54)$$

is the velocity relative to the equilibrium thermal velocity, and

$$\Psi_{k,l}(\xi) = N_{k,l} \xi^l L_k^{l+1/2}(\xi^2) P_l(\hat{\xi} \cdot \hat{\varepsilon}^*) \quad (55)$$

In Eq. (55),  $L_k^{l+1/2}$  are Laguerre polynomials,  $P_l$  are Legendre polynomials, and  $N_{k,l}$  are normalization constants. The coefficients  $C_r^{k,l}$  are orthogonal moments of  $f_r$ . Except for  $C_r^{0,0} = \text{const}$ , they are nonlinear functions of  $\varepsilon^*$  that vanish at  $\varepsilon^* = 0$ . By taking moments in Eqs. (10) and (11) for the special case of Maxwell molecules, it is easy to check that the coefficients  $C_r^{k,l}$  are at least of order  $\varepsilon^{*2k+l}$ .

The moments we have explicitly derived in this paper, namely  $\mathbf{j}_r$  and  $\mathbf{P}_r$ , are directly related to the coefficients  $C_r^{0,1}$ ,  $C_r^{0,2}$ , and  $C_r^{1,0}$ . It is clear that the knowledge of these moments does not provide a complete information about the distribution functions. A possible way of constructing approximate distributions consists of truncating the series (52):

$$f_r(\mathbf{v}) \approx f_r^0(\mathbf{v}) [1 + C_r^{0,1} \Psi^{0,1} + C_r^{0,2} \Psi^{0,2} + C_r^{1,0} \Psi^{1,0}] \tag{56}$$

Although this approximation contains all the orders in the color field strength, it is only exact up to second order. The relevant question is whether Eq. (56) provides the “best” approximation compatible with the exact knowledge of the mass and momentum fluxes. According to the maximum-entropy method,<sup>(10)</sup> the “less biased” distribution is the one that maximizes the entropy

$$S_r = -k_B \int d\mathbf{v} f_r(\mathbf{v}) \ln f_r(\mathbf{v}) \tag{57}$$

subject to the constraints given by Eqs. (13)–(15). The result is

$$f_r^{\text{ME}}(\mathbf{v}) = n_r \pi^{-3/2} (\det \Gamma_r)^{1/2} \exp \left[ -\Gamma_r : \left( \mathbf{v} - \frac{\mathbf{j}_r}{\rho_r} \right) \left( \mathbf{v} - \frac{\mathbf{j}_r}{\rho_r} \right) \right] \tag{58}$$

where

$$\Gamma_r = \frac{1}{2} \rho_r \left( \mathbf{P}_r - \frac{1}{\rho_r} \mathbf{j}_r \mathbf{j}_r \right)^{-1} \tag{59}$$

Obviously, the coefficients  $C_r^{0,1}$ ,  $C_r^{0,2}$ , and  $C_r^{1,0}$  in the expansion of  $f_r^{\text{ME}}$  in terms of the complete set  $\{\Psi_{k,l}\}$  coincide with the exact ones. Consequently, the maximum-entropy distribution is exact up to second order in the color field, as happens with the approximation (56). However, in contrast to Eq. (58), the approximation (56) is not a positive-definite function for arbitrary values of the field strength.

It is interesting to notice that Eq. (58) satisfies the exact property (34). As a consequence, the maximum-entropy distribution becomes exact in the limits of small and large color fields. Thus, one can expect that Eq. (58) provides a reasonably good estimate of the actual distribution function for

arbitrary values of the color field. By inserting Eq. (58) into Eq. (57), one gets an upper estimate of the entropy. The result for species 1 is

$$S_1^{\text{ME}} = S_1^0 + \frac{1}{2} n_1 k_B \ln \left[ (P_{1,\perp}^*)^2 \left( P_{1,\parallel}^* - \frac{3}{2} \frac{nm_2 n_2}{\rho n_1} \varepsilon^{*2} \sigma^{*2} \right) \right] \quad (60)$$

where  $S_1^0$  is the equilibrium entropy. In the limit of small  $\varepsilon^*$ , one has

$$\begin{aligned} \Delta S_1^* &\equiv \frac{S_1^{\text{ME}} - S_1^0}{\frac{3}{2} n_1 k_B} \\ &\approx - \left( \tau_1 + \frac{1}{2} \frac{nm_2 n_2}{\rho n_1} \right) \varepsilon^{*2} \\ &= - \frac{\mu v^2 (\mu + 1) + \mu v - 1}{2\mu v (\nu + 1)} \varepsilon^{*2} \end{aligned} \quad (61)$$

where in the last step use has been made of Eq. (32). This behavior coincides exactly with that of the actual entropy for species 1. It is instructive to realize that  $\Delta S_1^*$  can be positive if  $\tau_1$  is (sufficiently) negative, i.e., if  $T_1$

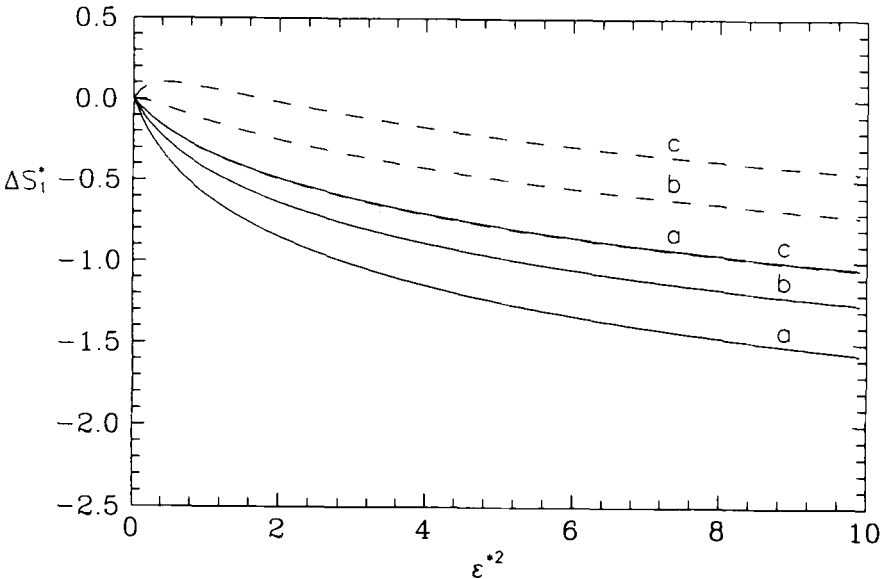


Fig. 4. Plot of the reduced excess entropy  $\Delta S_1^*$  obtained from the maximum-entropy method for the same cases as in Fig. 3.



is (sufficiently) larger than  $T$ . Of course, this does not violate the second law of thermodynamics, since the *total* entropy behave as

$$S = S_1 + S_2 \approx S^0 - \frac{3}{4}nk_B\epsilon^{*2} \quad (62)$$

Figure 4 shows  $\Delta S_1^*$  for the same cases as in the previous figures. In agreement with Eq. (61),  $\Delta S_1^*$  is positive in the small-color-field region for the case  $\mu = 0.5$ ,  $\nu = 0.5$ . Except in that region, the entropy always decreases with the color field. Notice that  $\Delta S_1^*$  is practically the same in the cases  $\mu = 2$ ,  $\nu = 0.5$  and  $\mu = 0.5$ ,  $\nu = 2$ .

## 6. DISCUSSION

In this paper, we have studied the nonlinear mass and momentum transport across a binary mixture of mechanically different Maxwell molecules in the low-density regime. The system is driven to a non-equilibrium homogeneous steady state by the action of an external “color” force that creates mutual diffusion in the absence of concentration gradients. The main transport coefficient is the color conductivity coefficient, which is defined as the ratio between the mass flux and the color field strength. This method to produce diffusion has been proposed in molecular dynamics simulations as a means to evaluate the mutual diffusion coefficient in the zero-field limit. Nevertheless, we have gone beyond the linear limit to analyze the nonlinear response of the system to arbitrary values of the field.

It must be emphasized that no approximations have been considered, except the restriction to the Maxwell interaction. In that case, the infinite hierarchy of moment equations for the color conductivity problem can be recursively solved in an exact way. We have explicitly obtained the color conductivity coefficient and the pressure tensor for each species as functions of the color field, the molar fractions, the particle masses, and the interaction constants. The generality of the results allows one to specialize to some physically interesting limit cases, such as the Lorentz gas, the Rayleigh gas, or the Brownian motion.

One of the outcomes of our solution is that the *reduced* color conductivity coefficient is a function of the *reduced* field strength, which is independent of the characteristic parameters of the mixture. This “universal” character disappears when one considers higher-order moments. In particular, the reduced temperature of each species depends on the concentration and the mass ratios. As functions of the field strength, the temperatures exhibit monotonic or nonmonotonic behaviors, depending on the values of the concentration and the mass ratios. In addition to the

previous parameters, the normal stresses also depend on the values of the interaction constants. In the limit of large color fields, the system behaves as a collisionless gas, so that the velocity distribution functions become  $\delta$ -distributions.

Since we have not been able to find an explicit exact expression for the distribution functions, we have resorted to the maximum-entropy method for constructing *approximate* distributions consistent with the *exact* mass and momentum fluxes. These maximum-entropy functions are exact up to second order in the color field, as well as in the large-field. The corresponding entropies are upper bounds of the exact ones and are expected to give a fair picture of their real behavior for arbitrary values of the field strength. In order to test the reliability of the maximum-entropy method in this problem, it would be interesting to perform numerical simulations of the Boltzmann equation.

The problem we have analyzed in this paper can be considered as a rather academic one. Nevertheless, we think that the results reported here are a first step toward the understanding of nonlinear *electrical* conductivity in a Coulombic system at low density.<sup>(11)</sup> We plan to explore the possibility of interpreting the color charge as an electrical charge and introducing the Coulombic interaction in a perturbation way.

## APPENDIX

In this appendix we list the expressions for the coefficients  $A_i$  appearing in Eq. (38). They are

$$A_1 = -\gamma_{12}[\mu(\gamma_{11} - 2) + \gamma_{11}](\mu v + 1)(v + 1) \quad (\text{A1})$$

$$A_2 = -\mu\{v[\mu^2\gamma_{22}(2\gamma_{12} - 1) + \mu(\gamma_{11} - 4\gamma_{12}) + 2\gamma_{11}\gamma_{12}] + \mu\gamma_{22}(\gamma_{11} - 2) + \gamma_{11}\gamma_{22}\}(v + 1) \quad (\text{A2})$$

$$A_3 = 2\gamma_{12}\{v[\mu(\gamma_{11} - 1) + \gamma_{11}] + 1\}(\mu v + 1)^2 \quad (\text{A3})$$

$$A_4 = 2\mu\gamma_{12}[v^3\mu^2 + v^2\mu(\mu + 2) + v(2\mu + 1) + 1] \quad (\text{A4})$$

$$A_5 = 2\mu(\mu v + 1)\{v^2[\mu(\gamma_{11} - 2\gamma_{12}) + 2\gamma_{11}\gamma_{12}] + v[\mu\gamma_{22}(\gamma_{11} - 2\gamma_{12}) + \gamma_{11}\gamma_{22} + 2\gamma_{12}] + \gamma_{22}\} \quad (\text{A5})$$

$$A_6 = 4\mu^2\gamma_{12}(\mu v + 1)(v + \gamma_{22})(v + 1) \quad (\text{A6})$$

$$A_7 = \gamma_{12}^2(\mu + 1)(\mu v + 1)^2 \quad (\text{A7})$$

$$A_8 = \gamma_{12}(\mu\nu + 1) \{ v[\mu^2 + \mu(\gamma_{11} + 2\gamma_{12}) + \gamma_{11}] + \mu^2\gamma_{22} + \mu(2\gamma_{12} + \gamma_{22}) + 1 \} \quad (A8)$$

$$A_9 = \mu[v^2\gamma_{11}(\mu + 2\gamma_{12}) + v(\gamma_{11}\gamma_{22} + 2\gamma_{12})(\mu + 1) + \gamma_{22}(2\mu\gamma_{12} + 1)] \quad (A9)$$

In these equations,  $\gamma_{11} \equiv \lambda'_{11}/\lambda'_{12}$ ,  $\gamma_{22} \equiv \lambda'_{22}/\lambda'_{12}$ , and  $\gamma_{12} \equiv \lambda_{12}/\lambda'_{12} = 0.648$ . The parameters  $\gamma_{11}$  and  $\gamma_{22}$  depend on the force constant ratios  $\kappa_{11}/\kappa_{12}$  and  $\kappa_{22}/\kappa_{12}$ , respectively. With the choice  $\kappa_{rs} \propto (m_r m_s)^{1/2}$ , one gets  $\gamma_{11} = \mu^{-1/4}[(1 + \mu)/2]^{1/2}$  and  $\gamma_{22} = \mu^{-3/4}[(1 + \mu)/2]^{1/2}$ .

According to Eq. (38), the behaviors of  $P_{i,\perp}^*$  in the limits of small and large field strengths are, respectively,

$$P_{i,\perp}^* \approx 1 - \left( \frac{A_8}{A_9} - \frac{A_2 + A_3 + A_4 - A_5\tau_1}{A_5 + A_6} \right) \varepsilon^{*2} \quad (A10)$$

$$P_{i,\perp}^* \approx \frac{2A_1 + A_3[(\nu + 1)/\nu(\mu\nu + 1)] + A_4}{2\sqrt{2}(\mu\nu + 1)A_7} |\varepsilon^*|^{-1} \quad (A11)$$

In Eq. (A10),  $\tau_1$  is given by Eq. (32).

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