Kinetic theory of binary gas mixtures with large mass disparity

J. Fernández de la Mora and R. Fernández-Feria
Department of Mechanical Engineering, Yale University, Box 2159 Y. S., New Haven, Connecticut 06520

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The Boltzmann equations for a binary mixture of gases are considered in the asymptotic limit when their molecular weight ratio and the light gas Knudsen number are small quantities. A first mass-ratio expansion reduces the cross-collision operator of the light gas Boltzmann equation to a Lorentz form, uncoupling its kinetic behavior from that of the heavy gas. The light gas distribution function is then determined to first order in the Knudsen number, independently of the degree of nonequilibrium characterizing the heavy gas, whose influence is felt only through its hydrodynamic quantities. All transport coefficients arising are determined variationally for arbitrary interaction potentials using Sonine polynomial expansions as trial functions. A remarkable feature of this analysis is that it yields binary transport information (i.e., diffusion and thermal diffusion coefficients) from considering only the Boltzmann equation for the light gas. A second mass expansion reduces the cross-collision operator of the heavy gas equation to a Fokker–Planck form. The corresponding coefficients involve integrals over the light gas distribution function determined previously and are evaluated explicitly in terms of the hydrodynamic quantities and transport coefficients of the light gas. The heavy gas distribution function can be determined by solving a Fokker–Planck equation at dilutions large enough to make heavy–heavy collisions negligible, or by a new Knudsen number expansion when the molar fraction of the heavy gas is of order 1. In this latter case, the heavy gas kinetic behavior is independent of the light gas, being characterized by the same transport coefficients of the pure heavy gas. The problem is then reduced to a set of two-fluid hydrodynamic equations.

I. INTRODUCTION

The behavior of binary mixtures whose constituents have widely different molecular masses ($m_p \gg m$) differs considerably from that of ordinary gas mixtures because of the presence of disparate relaxation times governing the approach to equilibrium of the various degrees of freedom. In pure gases or mixtures with similar masses, the departure from equilibrium conditions may be measured in terms of a single Knudsen number ($\mathrm{Kn} \equiv \omega\mu/p$), or the ratio between the microscopic and the macroscopic times, μ/p and ω^{-1}, respectively, where μ and p are the gas viscosity and pressure. However, in mixtures involving disparate masses, the energy interchanged in collisions among different molecules is much smaller than in collisions involving equal molecules by a factor of the order of the ratio of masses $M \equiv m/m_p$ between the light and the heavy gas. Therefore, one may roughly characterize the process of equilibration of disparate-mass mixtures with three different relaxation times: two for self-equilibration, $\tau_i = \mu_i/p_i$ (based on the viscosity coefficients and partial pressures of each gas individually; $i = 1,2$), and a third one, τ, associated with the slower process of interspecies equilibration. Typically, when the number concentrations n_i (thus the partial pressures p_i) of the two gases are of the same order, because the coefficients of viscosity are roughly mass independent,[1] the two self-relaxation times are comparable ($\tau_1 n_1 \approx \tau_2 n_2$) and much smaller than the interspecies energy relaxation time τ by a factor of order $M = m/m_p$. Accordingly, the standard hydrodynamic equations based on the Chapman–Enskog theory[2] apply to disparate-mass mixtures only under the very restrictive conditions when the macroscopic time ω^{-1} is much larger than the slow energy relaxation time τ ($\omega\tau \ll 1$). In the range where the system is perturbed within a characteristic time ω^{-1} comparable to or smaller than τ, but still larger than the fast relaxation times μ_i/p_i ($\omega\tau \ll m_p/m$), some rather interesting relaxation phenomena arise.[3–6] These phenomena may still be described at a hydrodynamical level by means of generalized two-fluid equations.[7–11]

The starting point for the present work is the observation that the same mass disparity that enriches and complicates the physics of the problem can be used to simplify its mathematical description. Indeed, it was this simplifying feature that led to the theory of the Lorentz gas[12] well before the Chapman–Enskog theory on ordinary gases. Yet the construction of systematic perturbation approaches based on the small parameter $M = m/m_p$ has evolved slowly. A key step was taken in 1969 by Bernstein[13] who obtained a generalized Lorentz (Bernstein) operator by expansion of the corresponding Boltzmann collision integral up to first order in m/m_p, though his formalism may be extended to any order. The approach is based on a double expansion where (1) the finite recoil velocity of the heavy gas upon collision with the light gas is one small parameter (of order m/m_p), and (2) the velocity distribution function f_p of the heavy gas is treated as a delta function to lowest order, while still accounting for its finite width [of order $(m/m_p)^{1/2}$]. The integrals in velocity space involving the heavy gas distribution function f_p may then be carried out explicitly so that the Boltzmann equation for the light gas depends on f_p only through its moments $n_p, \mathbf{U}_p$, etc., and the light gas is kinetically uncoupled from the heavy gas to any order in m/m_p. Such a remarkable feature will play an essential role in the present work.

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Similar systematic theories for the "Brownian limit" of a heavy gas moving in a light fluid have also appeared.[14,15] As a result, one has reduced forms for the two Boltzmann integrals involving collisions of the light with the heavy gas (Lorentz–Bernstein operator) and of the heavy gas with the light gas (Fokker–Planck operator). Therefore, the Boltzmann equations for a binary disparate-mass mixture may now be attacked under circumstances broader than contemplated in either the Chapman–Enskog theory or two-fluid theories, as we propose to do in the present work by further exploiting the smallness of the parameter m/m_p.

The structure of the paper is as follows. We consider the case where the distribution function f of the light gas is nearly Maxwellian, while the heavy component is allowed to be arbitrarily far from equilibrium yet with a temperature of the order of the light gas temperature (notice that this condition on the temperature is compatible with a strongly non-Maxwellian distribution function f_p). After deriving the Lorentz operator from its corresponding Boltzmann integral it is seen that f is kinetically uncoupled from f_p, implying that its corresponding kinetic equation may be solved without additional assumptions on the heavy gas. As in the Chapman–Enskog theory for a pure gas, the method of solution is based on expansion in a Knudsen number $\omega\mu/p$ around an equilibrium Maxwellian. To first order in m/m_p, the heavy gas is seen to perturb the distribution function f only through its moments, number density n_p, mean velocity $\mathbf{U}_p$, and pressure tensor $\underline{\mathbf{P}}_p$. The dependence of the light gas Boltzmann equation on n_p and $\underline{\mathbf{P}}_p$ is straightforward and linear; however, $\mathbf{U}_p$ enters through complicated functions of the difference $\mathbf{U}-\mathbf{U}_p$ in mean velocities between the two gases. Therefore the theory is also linearized in $\mathbf{U}-\mathbf{U}_p$, thus being additionally constrained by the condition that the group $|\mathbf{U}-\mathbf{U}_p|/(2kT/m)^{1/2}$ be small compared to unity ($\mathbf{U}$ and T are the mean velocity and the temperature of the light gas; k is Boltzmann's constant). An interesting new feature of the governing integral equation arises from the nonconservation of momentum for the light gas alone, which results in a modified (nonsymmetric) integral operator. Such a behavior leads to the appearance of a new "collision invariant" that provides freedom to assign different mean speeds to the two gases. Also, all the transport coefficients arising may be calculated variationally in spite of the lack of symmetry of the collision operator, and are determined for general interaction potentials.

Once the light gas distribution function is found, it is used to derive an extended expression for the Fokker–Planck collision operator governing the evolution of the heavy gas and including the effects of the nonequilibrium interaction between the two species. Further reduction in the problem of determining the distribution function f_p is possible only in two limits. When the ratio of number densities n_p/n is of order unity or larger, the heavy gas is also near equilibrium, and a new (heavy gas) Knudsen number expansion results in a two-fluid theory valid for arbitrary interaction potentials. When the heavy gas is dilute $[n_p/n = 0(m/m_p)]$, the near-equilibrium expansion leads to the same difficulties as the CE theory (it is only valid for the very restrictive limit $\omega\tau \ll 1$), because both self-collisions and collisions with the light gas become slow compared with $\mu\omega/p$. Nevertheless, if the dilution is sufficient to make heavy–heavy collisions negligible, the process of equilibration of the heavy gas is governed by the Fokker–Planck operator only, reducing significantly the kinetic equation governing the evolution of f_p. However, the problem cannot be reduced to a hydrodynamic level in the region of interest where $\omega\tau \approx O(1)$.

II. LORENTZ COLLISION OPERATOR

The change in the light gas distribution function as a result of collisions with the heavy molecules is given by Boltzmann's collision integral

$$J_{12} = \int d^3u_p\, d\Omega\, g\sigma(g,\theta)\,[f_p(\mathbf{u}_p')f(\mathbf{u}') - f_p(\mathbf{u}_p)f(\mathbf{u})], \quad (1)$$

where $\mathbf{u}$ and $\mathbf{u}_p$ denote the independent variables of f and f_p, and their primed counterparts are the postcollision velocities; σ is the differential scattering cross section, $d\Omega = \sin\theta\, d\theta\, d\phi$ (Fig. 1), and $\mathbf{g} = \mathbf{u}_p - \mathbf{u}$. The reduction of expression (1) to a Lorentz operator involves carrying the integration explicitly over $\mathbf{u}_p$ space by exploiting the small value of the parameters

$$M_1 \equiv m/(m+m_p) \quad (2a)$$

and

$$M \equiv m/m_p. \quad (2b)$$

The integration to lowest order is straightforward because $\mathbf{u}_p' \simeq \mathbf{u}_p$ and the width of f_p is negligibly small [in the relevant scale $(2kT/m)^{1/2}$ or, in other words, the heavy species thermal speed is small compared to that of the light species] so that it can be treated as a Delta function. Retaining higher order corrections requires taking account of the finite width of f_p and of the small recoil of the heavy particles upon collision with a light molecule. In the systematic perturbation scheme introduced by Bernstein,[13] the $\mathbf{u}_p$ dependence of the integrand in (1) is reduced to products of $f_p(\mathbf{u}_p)$ with pow-

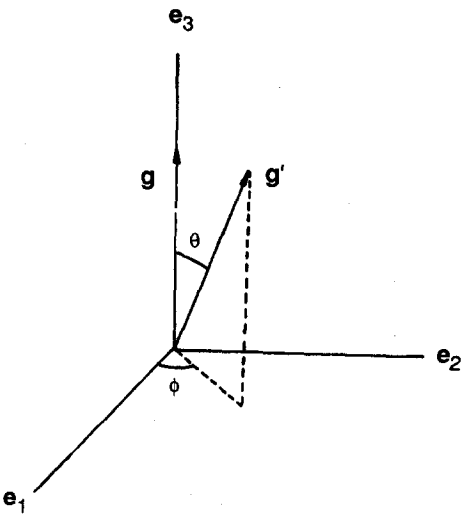

FIG. 1. Reference system.

ers of $\mathbf{u}_p - \mathbf{U}_p$ by Taylor expansion around the mean velocity $\mathbf{U}_p$ of the heavy gas. The expansion is justified because $\mathbf{u}_p - \mathbf{U}_p$ is of the order of $(2kT/m)^{1/2}M^{1/2}$ within the range where f_p is not negligibly small (unless T_p/T becomes a large quantity). The integration in $\mathbf{u}_p$ space may thus be completed and all the dependence left on f_p is through its moments n_p, $\mathbf{U}_p$, and the pressure tensor $\underline{\mathbf{P}}_p$ (to first order in M_1). We will sketch Bernstein's derivation here in order to introduce the notation, and also because the subsequent analysis is simplified by using a slightly different reference frame not necessarily tied to the heavy gas.

From the dynamics of elastic two-body collisions, we can write

$$\mathbf{u}_p' = \mathbf{u}_p + M_1 \Delta\mathbf{g}, \tag{3}$$

$$\mathbf{u}' = \mathbf{u} - \Delta\mathbf{g} + M_1 \Delta\mathbf{g}, \tag{4}$$

where

$$\Delta\mathbf{g} = \mathbf{g}' - \mathbf{g}, \quad \mathbf{g}' = \mathbf{u}_p' - \mathbf{u}', \tag{5}$$

and as a result of energy conservation ($g' = g$), $\mathbf{g}'$ is obtained by rotation of the vector $\mathbf{g}$ from its position in the polar axis into the solid angle Ω (Fig. 1). We thus introduce the rotation operator $\underline{\Omega}$

$$\mathbf{g}' = \underline{\Omega}\mathbf{g}. \tag{6}$$

The expansion of $f_p(\mathbf{u}_p')$ and $f(\mathbf{u}')$ in powers of M_1 yields

$$\begin{aligned} f_p(\mathbf{u}_p')f(\mathbf{u}') - f_p(\mathbf{u}_p)f(\mathbf{u}) &= f_p(\mathbf{u}_p)[f(\mathbf{u}-\Delta\mathbf{g}) - f(\mathbf{u})] \\ &\quad + M_1 \Delta\mathbf{g}\cdot\nabla_u [f_p(\mathbf{u}_p) f(\mathbf{u}-\Delta\mathbf{g})] + \cdots, \end{aligned} \tag{7}$$

where ∇_u is the gradient in $\mathbf{u}$ space. We now exploit the fact that the ranges of the thermal velocity of the heavy species $\mathbf{c}_p = \mathbf{u}_p - \mathbf{U}_p$ and the light gas thermal velocity $\mathbf{c} = \mathbf{u} - \mathbf{U}$ scale quite differently, being in a ratio of order $(T_p/T)M^{1/2} = O(M^{1/2})$. The analysis is simplest in the reference frame used by Bernstein[13] in which the heavy gas has zero mean velocity. However, subsequent computations are simplified with the choice of a reference frame moving at a speed slightly different from that of the heavy gas, so that $\mathbf{U}_p$ is a small quantity compared to $(2kT/m)^{1/2}$. We are thus left with the freedom to select a reference frame moving with the light gas.

Defining

$$\mathbf{k} \equiv \underline{\Omega}\mathbf{u} \quad \text{and} \quad \mathbf{k}_p \equiv \underline{\Omega}\mathbf{u}_p, \tag{8}$$

we have

$$\mathbf{u} - \Delta\mathbf{g} = \mathbf{k} - \mathbf{k}_p + \mathbf{u}_p, \tag{9}$$

and $f(\mathbf{u} - \Delta\mathbf{g})$ can be expanded as

$$f(\mathbf{u} - \Delta\mathbf{g}) = f(\mathbf{k}) + (\mathbf{u}_p - \mathbf{k}_p)\cdot\nabla_k f(\mathbf{k}) + \tfrac{1}{2}(\mathbf{u}_p - \mathbf{k}_p)(\mathbf{u}_p - \mathbf{k}_p):\nabla_k\nabla_k f(\mathbf{k}) + \cdots. \tag{10}$$

Similarly, since $\underline{\Omega}$ is a rotation operator we have

$$g \equiv |\mathbf{g}| = |\underline{\Omega}\mathbf{g}| = |\underline{\Omega}\mathbf{u} - \underline{\Omega}\mathbf{u}_p| = |\mathbf{k} - \mathbf{k}_p|, \tag{11}$$

and the expansion of

$$g\sigma(g,\theta) \equiv S(\mathbf{k} - \mathbf{k}_p) \tag{12}$$

in powers of $\mathbf{k}_p$ yields

$$S(\mathbf{k} - \mathbf{k}_p) = S(\mathbf{k}) - \mathbf{k}_p\cdot\nabla_k S(\mathbf{k}) + \tfrac{1}{2}\mathbf{k}_p\mathbf{k}_p:\nabla_k\nabla_k S(\mathbf{k}) + \cdots. \tag{13}$$

Introducing expansions (7) and (13) into the integral (1) and using the properties $|\mathbf{k}| = |\mathbf{u}|$, $\mathbf{k}_p\cdot\nabla_k\phi = \mathbf{u}_p\cdot\nabla_u\phi$, one obtains

$$\begin{aligned} S(g)[f(\mathbf{u}-\Delta\mathbf{g}) - f(\mathbf{u})] &= S(u)[f(\mathbf{k}) - f(\mathbf{u})] + \mathbf{u}_p\cdot(S(u)[\nabla_k f(\mathbf{k}) \\ &\quad - \nabla_u f(\mathbf{u})] - \nabla_u\{S(u)[f(\mathbf{k}) - f(\mathbf{u})]\}) \\ &\quad + \mathbf{u}_p\mathbf{u}_p:(\tfrac{1}{2}\nabla_u\nabla_u S(u)[f(\mathbf{k}) - f(\mathbf{u})] \\ &\quad + \nabla_u\{S(u)[\nabla_u f(\mathbf{u}) - \nabla_k f(\mathbf{k})]\} \\ &\quad + [S(u)/2][\nabla_k\nabla_k f(\mathbf{k}) - \nabla_u\nabla_u f(\mathbf{u})]) + \cdots. \end{aligned}$$

The $\mathbf{u}_p$ integration can now be carried explicitly in (1), and in terms of the moments

$$n_p = \int d^3u_p\, f_p, \quad n_p\mathbf{U}_p = \int d^3u_p\, \mathbf{u}_p f_p,$$

$$n_p\mathbf{U}_p\mathbf{U}_p + \underline{\mathbf{P}}_p/m_p = \int d^3u_p\, \mathbf{u}_p\mathbf{u}_p f_p,$$

where $\underline{\mathbf{P}}_p$ is the heavy gas pressure tensor, we obtain for the Lorentz operator

$$\begin{aligned} J_{12} &= N + \mathbf{U}_p\cdot(\mathbf{L} - \nabla_k N) \\ &\quad + (k\underline{\mathbf{T}}_p/m_p + \mathbf{U}_p\mathbf{U}_p):[\nabla_u(-\mathbf{L} + \nabla_u N/2) \\ &\quad - \underline{\mathbf{Y}}/2] + M\nabla_u\cdot\mathbf{R} + \cdots. \end{aligned} \tag{14}$$

In this expression, $\underline{\mathbf{T}}_p = \underline{\mathbf{P}}_p/n_p k$ and

$$N \equiv \int d\Omega\, \nu[f(\mathbf{k}) - f(\mathbf{u})], \tag{15a}$$

$$\mathbf{L} \equiv \int d\Omega\, \nu[\nabla_k f(\mathbf{k}) - \nabla_u f(\mathbf{u})], \tag{15b}$$

$$\mathbf{R} \equiv \int d\Omega\, \nu(\mathbf{u} - \mathbf{k}) f(\mathbf{k}), \tag{15c}$$

$$\underline{\mathbf{Y}} \equiv \int d\Omega\, \nu[\nabla_k\nabla_k f(\mathbf{k}) - \nabla_u\nabla_u f(\mathbf{u})], \tag{15d}$$

where $\nu = n_p u\sigma(u,\theta)$ is the frequency for heavy–light collisions. Again we remark that f_p apears in J_{12} (and hence in the light species Boltzmann equation) only through its moments n_p, $\mathbf{U}_p$, $\underline{\mathbf{P}}_p$,... .

III. LIGHT GAS VELOCITY DISTRIBUTION FUNCTION f

A. Lowest order solution

The Boltzmann equation for the light gas may be written symbolically as

$$Df = J_{11}(f) + J_{12}(f, f_p), \tag{16}$$

where $J_{12}(f, f_p)$ is the Lorentz operator discussed above, Df is the streaming operator, and J_{11} the Boltzmann collision integral accounting for the light–light collisions. Since J_{12} depends on f_p only through its moments, Eq. (16) may be

solved for f in terms of the quantities n_p, $\mathbf{U}_p$, $\underline{\mathbf{P}}_p$, etc. In an expansion in powers of the Knudsen number, the mass ratio and the slip velocity parameter

$$\mathbf{v} \equiv (\mathbf{U} - \mathbf{U}_p)/(2kT/m)^{1/2}, \tag{17}$$

Eq. (16) admits a Maxwellian distribution as its lowest order solution centered at an arbitrary mean velocity $\mathbf{U}$ and temperature T provided that $\mathbf{v}$ is indeed small. We may thus write

$$f = f_0(1 + \phi + \cdots), \tag{18}$$

where ϕ contains first-order corrections in Kn, M, and $\mathbf{v}$, and is the function that we wish to determine, while f_0 is

$$f_0 = n(2\pi kT/m)^{-3/2}\exp[-m|\mathbf{u} - \mathbf{U}|^2/2kT]. \tag{19}$$

The fact that ϕ is a first-order quantity in these three parameters results from a reasoning identical to that used in the Chapman–Enskog (CE) theory for a pure gas, together with Eq. (14) for J_{12}. All terms except N in Eq. (14) are of order $\mathbf{v}$ or M. Here N itself is the standard Lorentz operator of order νf, while ν has the same order of magnitude as the inverse of the light gas relaxation time when $n_p/n = 0(1)$. Therefore $N(f)$ and J_{11} are comparable. Furthermore, in the reference frame where the light gas is at rest ($\mathbf{U} = \mathbf{0}$), f_0 is spherically symmetric and $N(f_0) = 0$. The lowest order equation

$$0 = J_{11}(f_0) + N(f_0)$$

is thus satisfied by a Maxwellian function. Notice also that our choice of a reference frame in which $\mathbf{U} = \mathbf{0}$ requires substituting $\mathbf{U}_p$ for $\mathbf{U}_p - \mathbf{U}$ in Eq. (14) for J_{12}.

B. Governing integral equation for ϕ

Let us use the notation

$$J(\phi) \equiv J_{12}(f_0\phi), \tag{20a}$$

$$K(\phi) \equiv J_{11}(f_0\phi), \tag{20b}$$

$$J_0(\phi) \equiv N(f_0\phi). \tag{20c}$$

Then, Boltzmann's equation becomes to first order in Kn, M, and $\mathbf{v}$

$$Df_0 - J(1) = K(\phi) + J_0(\phi). \tag{21}$$

Introducing the inner product

$$[f,g] = \int d^3u\, fg, \tag{22}$$

it can be shown (see, for instance, Ref. 2, Sec. 4.4) that the operator K is symmetric and nonpositive, that is,

$$[\chi,K\phi] = [\phi,K\chi] \quad \text{and} \quad [\phi,K\phi] < 0,$$

the equality holding for the second expression above only when ϕ is a linear combination of the functions 1, $\mathbf{u}$, and u^2 (notice that our linear collision operator K is equal to $-n^2I$ of Ref. 2). Similarly, as shown in Appendix A, J_0 is also a symmetric and nonpositive operator.

Using the independent variable in $\mathbf{u}$ space relative to the mean value $\mathbf{U}$,

$$\mathbf{c} \equiv \mathbf{u} - \mathbf{U}, \tag{23}$$

the conservation equations resulting from taking moments in the Boltzmann equation for the light gas are

$$\partial_t n + \nabla\cdot(n\mathbf{U}) = 0, \tag{24}$$

$$\partial_t(n\mathbf{U}) + \nabla\cdot(n\mathbf{U}\mathbf{U} + \underline{\mathbf{P}}/m) = [J(1+\phi),\mathbf{c}], \tag{25}$$

$$\partial_t(ne) + \nabla\cdot(ne\mathbf{U} + \mathbf{Q}/m) + \underline{\mathbf{P}}:\nabla\mathbf{U}/m = [J(1+\phi),c^2/2], \tag{26}$$

where $e \equiv 3kT/2m$ is the light gas internal energy. Equations (24)–(26) differ from those arising in the CE theory for a pure gas in their right-hand sides, which accounts for the interchange of momentum and energy between the two species. Proceeding as in the CE theory of a pure gas, we eliminate time derivatives appearing in the expression for Df_0 by means of the conservation equations (24) and (26), in which $\underline{\mathbf{P}}$ and $\mathbf{Q}$ are taken to be $nkT\underline{\mathbf{I}}$ and zero, respectively (Euler level). In terms of the dimensionless variable

$$\boldsymbol{\xi} \equiv \mathbf{c}/(2kT/m)^{1/2}, \tag{27}$$

the result is

$$Df_0 = \mathrm{Grad} + D_u + D_T, \tag{28}$$

with

$$\mathrm{Grad} \equiv f_0[2\boldsymbol{\xi}\boldsymbol{\xi}:\nabla^{\circ}\mathbf{U} + \mathbf{c}\cdot\nabla \ln T(\xi^2 - \tfrac{5}{2})], \tag{29}$$

$$D_u \equiv (2f_0/n)\boldsymbol{\xi}\cdot[\boldsymbol{\xi},J(1+\phi)], \tag{30}$$

$$D_T \equiv (f_0/n)(2\xi^2/3 - 1)[\xi^2,J(1+\phi)], \tag{31}$$

while $\nabla^{\circ}\mathbf{U}$ denotes the symmetrized traceless velocity gradient tensor.

Regrouping terms in ϕ on the left-hand side, we obtain the nonhomogeneous integral equation for ϕ:

$$(K + J_1)\phi = \mathrm{Grad} + D_u^0 + D_T^0 - J(1), \tag{32}$$

where D_u^0 and D_T^0 are given by the definitions (30)–(31) for the particular case when $\phi = 0$, and the new operator J_1 is

$$J_1(\phi) = J_0(\phi) - (2f_0/n)\boldsymbol{\xi}\cdot[\boldsymbol{\xi},J_0\phi]. \tag{33}$$

Obviously, in a first-order theory in the parameters Kn, M, and $\mathbf{v}$, J may be substituted by J_0 when acting upon ϕ, but not when operating on the Maxwellian distribution function $[J(1)]$. The expression for $J(1)$ is given in Appendix B. The equation that results finally for ϕ is

$$(K + J_1)\phi = \mathrm{Grad} + 2\mathbf{v}\cdot\boldsymbol{\xi}(\nu_1 - \nu_0)f_0, \tag{34}$$

where the driving forces are Grad (identical to the one in the CE theory for a pure gas) and the velocity slip $\mathbf{v}$ [Eq. (17)]. An additional driving force proportional to a tensor associated with temperature differences has been neglected because it leads to higher order effects in the parameter M, see Appendix B. (However, it must be retained in the calculation of the energy transfer $[J(1+\phi), c^2/2]$ because in this case it becomes the lowest order significant term, see Appendix E.) The terms ν_0 and ν_1 are collision frequencies (defined in Appendix B), ν_0 being a constant, while ν_1 depends on the velocity variable $\boldsymbol{\xi}$.

C. Solution of the homogeneous equation $(J_1 + K)\phi = 0$

Let us first find the solutions ϕ_α to the homogeneous equation

$$(K + J_1)\phi_\alpha = 0, \tag{35}$$

which play the role of the collisional invariants 1, $\boldsymbol{\xi}$, ξ^2, the

only solutions to the homogeneous equation $K\phi = 0$. Using Eq. (33), Eq. (35) may be written as

$$(K + J_0)\phi_\alpha = (2f_0/n)\boldsymbol{\xi}\cdot\mathbf{a}, \tag{36}$$

where

$$\mathbf{a} \equiv [\phi_\alpha, J_0\boldsymbol{\xi}]. \tag{37}$$

Equation (36) may be solved as if $\mathbf{a}$ were an arbitrary constant, checking *a posteriori* whether the solution ϕ_α is such that the constraint (37) is satisfied. But then, the constraint (37) is satisfied automatically for any value of $\mathbf{a}$,

$$[\phi_\alpha, J_0\boldsymbol{\xi}] = [\phi_\alpha, (J_0 + K)\boldsymbol{\xi}]$$

$$= [\boldsymbol{\xi}, (J_0 + K)\phi_\alpha] = [\boldsymbol{\xi}, (2f_0/n)\boldsymbol{\xi}\cdot\mathbf{a}] = \mathbf{a}, \tag{38}$$

where we have used the facts that $[\boldsymbol{\xi}, (2f_0/n)\boldsymbol{\xi}] = \underline{\mathbf{I}}, K\boldsymbol{\xi} = 0$, and that $K + J_0$ is a symmetric operator. Accordingly, the general solution to the homogeneous Eq. (35) is given by a linear combination of the solution to $(K + J_0)\phi = 0$ plus an arbitrary multiple of the new function $\boldsymbol{\phi}_\alpha$ such that

$$(K + J_0)\boldsymbol{\phi}_\alpha = 2f_0\boldsymbol{\xi} \equiv \boldsymbol{\psi}_\alpha, \tag{39}$$

with no constraints now. Obviously, the isotropy of the operator $K + J_0$ allows for solutions to (39) of the form $\boldsymbol{\phi}_\alpha = \alpha^*(\xi)\boldsymbol{\xi}$, so that

$$(K + J_0)\alpha^*(\xi)\boldsymbol{\xi} = 2f_0\boldsymbol{\xi}. \tag{40}$$

To find the solutions to the new homogeneous problem

$$(K + J_0)\phi_H = 0, \tag{41}$$

we form the inner product of ϕ_H and Eq. (41) to obtain

$$[\phi_H, K\phi_H] + [\phi_H, J_0\phi_H] = 0. \tag{42}$$

But because both K and J_0 are nonpositive, Eq. (42) implies that both $K\phi_H$ and $J_0\phi_H$ must vanish. Accordingly, the function ϕ_H must belong to the set of collisional invariants $\{1, \boldsymbol{\xi}, \xi^2\}$ for which $K\phi_H = 0$. Of these functions, only 1 and ξ^2 vanish also upon the action of the operator J_0, so that the general solutions to Eqs. (41) and (35) are, respectively,

$$\phi_H = C_1 + C_3\xi^2 \tag{43}$$

and

$$\phi_\alpha = C_1 + \mathbf{C}_2\alpha^*(\xi)\cdot\boldsymbol{\xi} + C_3\xi^2. \tag{44}$$

The collisional invariant $\boldsymbol{\xi}$ from the CE theory is substituted here by the new function $\alpha^*(\xi)\boldsymbol{\xi}$ that results from solving the integral Eq. (40). That Eq. (40) has a unique solution (except for a linear combination of 1 and ξ^2) is ensured by the fact that its right-hand side is orthogonal to the two solutions 1 and ξ^2 of the homogeneous Eq. (41). We thus have three, and only three, eigenfunctions associated with the zero eigenvalue of the operator $K + J_1$. They will permit imposing the condition that the function ϕ in (18) does not contribute to n, $\mathbf{U}$, or T. This requirement is essential if the number density n, mean velocity $\mathbf{U}$, and temperature T of the light gas are to coincide with the quantities n, $\mathbf{U}$, and T appearing in the lowest order solution f_0 and in the hydrodynamical equations [(24)–(26)].

On the other hand, since the operator $K + J_1$ is singular ($\lambda = 0$ belongs to its spectrum), Eq. (32) has solutions provided its right-hand side satisfies some compatibility relations. That this is so is verified in Appendix C.

D. Variational approach for the optimal determination of the transport coefficients

It follows from our previous analysis of the homogeneous equation $(K + J_1)\phi_\alpha = 0$ that finding the solution ϕ to the integral equation

$$(K + J_1)\phi = f_0[2\boldsymbol{\xi}\boldsymbol{\xi}:\boldsymbol{\nabla}^\circ\mathbf{U} + \mathbf{c}\cdot\boldsymbol{\nabla}\ln T(\xi^2 - \tfrac{5}{2})] + 2\mathbf{v}\cdot\boldsymbol{\xi}(\nu_1 - \nu_0)f_0 \tag{45}$$

is equivalent to solving the new problem involving a self-adjoint operator,

$$(K + J_0)\phi_0 = f_0[2\boldsymbol{\xi}\boldsymbol{\xi}:\boldsymbol{\nabla}^\circ\mathbf{U} + \mathbf{c}\cdot\boldsymbol{\nabla}\ln T(\xi^2 - \tfrac{5}{2})] + 2\mathbf{v}\cdot\boldsymbol{\xi}(\nu_1 - \nu_0)f_0, \tag{46}$$

where ϕ is related to ϕ_0 through

$$\phi = \phi_0 + C_1 + \mathbf{C}_2\cdot\boldsymbol{\xi}\alpha^*(\xi) + C_3\xi^2, \tag{47}$$

and where the coefficients C_i are determined from the conditions that ϕ does not contribute to the hydrodynamic quantities n,$\mathbf{U}$, and T. We may use linear superposition to decompose the problem into the following ones:

$$\phi_0 \equiv \phi_{0a} + \phi_{0T} + \phi_{0b}, \tag{48a}$$

with

$$(K + J_0)\phi_{0a} = \psi_a \equiv f_0 2\boldsymbol{\xi}\boldsymbol{\xi}:\boldsymbol{\nabla}^\circ\mathbf{U}, \tag{48b}$$

$$(K + J_0)\phi_{0b} = \psi_b \equiv 2f_0\mathbf{v}\cdot\boldsymbol{\xi}\nu_1, \tag{48c}$$

$$(K + J_0)\phi_{0T} = \psi_T = f_0\mathbf{c}\cdot\boldsymbol{\nabla}\ln T(\xi^2 - \tfrac{5}{2}), \tag{48d}$$

where in Eq. (48c) we have put ν_1 instead of $(\nu_1 - \nu_0)$ as in Eq. (34). But because ν_0 is a constant the difference is proportional to $f_0\boldsymbol{\xi}$ and thus to the right-hand side of Eq. (40). Accordingly, the resulting solution ϕ_{0b} changes only in a trivial multiple of the function $\alpha^*(\xi)\boldsymbol{\xi}$. Both Eqs. (48) and Eq. (40) may be written as

$$(K + J_0)\phi_{0i} = \psi_i,$$

whose solution ϕ_{0i} coincides with the function χ_i that extremalizes the functional

$$\Lambda_i\{\chi_i\} \equiv [\chi_i, (K + J_0)\chi_i - 2\psi_i]. \tag{49}$$

Furthermore, the extremal value Λ_i^* of Λ_i is

$$\Lambda_i^* = -[\phi_{0i}, \psi_i], \tag{50}$$

which is related to the transport coefficients that we wish to obtain. Our treatment will follow that of Bernstein[16] in exploiting the fact that errors of order ϵ in the evaluation of ϕ_{0i} lead to errors of order ϵ^2 in the resulting value for Λ_i (and thus for the evaluation of the transport coefficients). Indeed, if $\chi = \phi + \epsilon$, then

$$\Lambda(\chi) = -[\phi, \psi] + [(\mathrm{K} + \mathrm{J}_0)\epsilon, \epsilon].$$

Furthermore, because $[(K + J_0)\epsilon, \epsilon]$ is nonpositive, Λ^* is an absolute maximum.

1. Pressure tensor and viscosity coefficient

The nonequilibrium contribution to the pressure tensor of the light gas is

$$\underline{\mathbf{P}}' = [m\mathbf{c}\mathbf{c}, f_0\phi] \equiv -2\mu\boldsymbol{\nabla}^\circ\mathbf{U}. \tag{51}$$

But because the terms ϕ_T and ϕ_b do not contribute to the

inner product, and because, by parity considerations, ϕ_{0a} contains no contributions of $\alpha^*\xi$, we may write

$$\mu = -(kT/2)[\phi_{0a},\psi_a]/(\nabla^s U:\nabla^s U), \tag{52}$$

where the inner product $[\phi_{0a},\psi_a]$ may be determined optimally from Eqs. (49) and (50),

$$-[\phi_{0a},\psi_a] = \mathrm{Max}[\chi,(K+J_0)\chi - 2\psi_a]. \tag{53}$$

2. Heat conductivity

The heat flux for the light gas is

$$\mathbf{Q} = [mcc^2/2, f_0\phi], \tag{54}$$

which has no contribution from ϕ_{0a}. Realizing also that $[\mathbf{c}, f_0\phi] = 0$, we may write

$$\mathbf{Q}\cdot\nabla \ln T = kT[\phi_T + \phi_b, \psi_T], \tag{55}$$

where ϕ_T and ϕ_b are related to ϕ_{0T} and ϕ_{0b} through Eq. (47). The flux has therefore two additive components, proportional to ϕ_T and ϕ_b, respectively. We therefore introduce the two transport coefficients λ and η,

$$\mathbf{Q} \equiv -\lambda\nabla T + \eta(\mathbf{U} - \mathbf{U}_p), \tag{56}$$

so that

$$\lambda = -k[\psi_T,\phi_T]/(\nabla \ln T)^2, \tag{57}$$

$$\eta = kT[\psi_T,\phi_b]/[(\mathbf{U} - \mathbf{U}_p)\cdot\nabla \ln T]. \tag{58}$$

The optimal determination of these coefficients is complicated by the fact that ϕ_T and ϕ_b contain contributions of $\alpha^*\xi$,

$$\phi_T = \phi_{0T} + \lambda_T \nabla \ln T\cdot\alpha^*\xi, \tag{59a}$$

$$\phi_b = \phi_{0b} + \lambda_b \mathbf{v}\cdot\alpha^*\xi, \tag{59b}$$

so that, for instance,

$$[\phi_T,\psi_T] = [\phi_{0T} + \lambda_T\alpha^*\xi\cdot\nabla \ln T,\psi_T] = [\phi_{0T},\psi_T] + \lambda_T[\alpha^*\xi\cdot\nabla \ln T,\psi_T]. \tag{60}$$

The unknown coefficient λ_T may be obtained optimally from the condition that the mean velocity of $f_0\phi_T$ vanishes,

$$[\phi_{0T} + \lambda_T\alpha^*\xi\cdot\nabla \ln T, f_0\xi] = 0, \tag{61}$$

by realizing that $f_0\xi$ is related to the driving force ψ_α [Eq. (40)], so that

$$\lambda_T[\phi_\alpha\cdot\nabla \ln T,\psi_\alpha] = -[\phi_{0T},\psi_\alpha]. \tag{62}$$

Accordingly

$$[\phi_T,\psi_T] = [\phi_{0T},\psi_T] - [\phi_\alpha\cdot\nabla \ln T,\psi_T] \times [\phi_{0T},\psi_\alpha]/[\phi_\alpha\cdot\nabla \ln T,\psi_\alpha], \tag{63}$$

and if each one of the four inner products appearing in Eq. (63) is found optimally, the resulting thermal conductivity coefficient will be also. The determination of the diagonal terms $[\phi_{0T},\psi_T]$ and $[\phi_\alpha,\psi_\alpha]$ is straightforward based on Eqs. (49) and (50),

$$-[\phi_{0T},\psi_T] = \mathrm{Max}[\chi_T,(K+J_0)\chi_T - 2\psi_T], \tag{64}$$

$$-[\phi_\alpha,\psi_\alpha] = \mathrm{Max}[\chi_\alpha,(K+J_0)\chi_\alpha - 2\psi_\alpha]. \tag{65}$$

The two off-diagonal terms $[\phi_\alpha,\psi_T]$ and $[\phi_{0T},\psi_\alpha]$ are equal to each other as a result of the symmetry of the operator $(K+J_0)$. They may also be related to diagonal terms through the identity

$$[\phi_{0T} + \phi_\alpha\cdot\nabla \ln T,\psi_T + \psi_\alpha\cdot\nabla \ln T] = [\phi_{0T},\psi_T] + 2[\phi_{0T},\psi_\alpha\cdot\nabla \ln T] + [\phi_\alpha\cdot\nabla \ln T,\psi_\alpha\cdot\nabla \ln T], \tag{66}$$

so that

$$\begin{aligned} -2[\phi_{0T},\psi_\alpha\cdot\nabla \ln T] &= \mathrm{Max}[\chi_{\alpha T},(K+J_0)\chi_{\alpha T} - 2\psi_T - 2\psi_\alpha\cdot\nabla \ln T] \\ &\quad - \mathrm{Max}[\chi_T,(K+J_0)\chi_T - 2\psi_T] \\ &\quad - \mathrm{Max}[\chi_\alpha\cdot\nabla \ln T,(K+J_0)\chi_\alpha\cdot\nabla \ln T \\ &\quad - 2\psi_\alpha\cdot\nabla \ln T]. \end{aligned} \tag{67}$$

It may be shown that, within a given space of functions, the function $\chi^*_{\alpha T}$ that maximizes the first term in the right-hand side of Eq. (67) is the sum $\chi^*_\alpha\cdot\nabla \ln T + \chi^*_T$ of the functions that makes extremal Eqs. (64) and (65) so that $[\phi_{0T},\psi_\alpha]$ is given optimally by either $[\chi^*_T,\psi_\alpha]$ or $[\chi^*_\alpha,\psi_T]$. Accordingly, for optimal results, one must take

$$[\phi_T,\psi_T] = [\chi^*_T - \phi_\alpha[\chi^*_T,\psi_\alpha]:\underline{\mathbf{I}}/[\phi_\alpha,\psi_\alpha]:\underline{\mathbf{I}},\psi_T], \tag{68}$$

where the term proportional to ϕ_α added on to χ^*_T is such as to make its mean velocity null, exactly as if our guess for χ^*_T were the exact solution ϕ_{0T}.

To calculate η one could use the optimal trial function χ^*_T. Alternatively, ϕ_{0b} can be obtained analytically by noticing that

$$\psi_b = 2\mathbf{v}\cdot\xi f_0\nu_1 = -2J_0(\xi\cdot\mathbf{v}) = -2(K+J_0)\xi\cdot\mathbf{v}, \tag{69}$$

from which Eq. (48c) can be integrated exactly to give

$$\phi_{0b} = -2\mathbf{v}\cdot\xi \tag{70}$$

and, from (59)

$$\phi_b = \mathbf{v}\cdot\xi(\lambda_b\alpha^* - 2). \tag{71}$$

Similarly to λ_T, λ_b is such that $f_0\phi_b$ has null mean velocity

$$[\phi_{0b} + \lambda_b\phi_\alpha\cdot\mathbf{v},\psi_\alpha] = 0, \tag{72}$$

from which

$$\lambda_b = (3n)/[\xi\alpha^*,\psi_\alpha]:\underline{\mathbf{I}}. \tag{73}$$

Thus Eq. (58) gives

$$\eta = kT\frac{[\psi_T,\phi_b]}{(\mathbf{U} - \mathbf{U}_p)\cdot\nabla \ln T} = \frac{m}{2}n\left(\frac{2kT}{m}\right)^{1/2}\frac{[(\xi^2 - 5/2)\mathbf{c}f_0,\xi\alpha^*]:\underline{\mathbf{I}}}{[\xi\alpha^*,2f_0\xi]:\underline{\mathbf{I}}}, \tag{74}$$

since $[(\xi^2 - 5/2)\mathbf{c}f_0,\xi] = 0$.

3. Transfer of momentum between species

An important term entering into the hydrodynamical equations is the right-hand side of Eq. (25) accounting for the interspecies transfer of momentum

$$\mathbf{M} \equiv m[J(1+\phi),\mathbf{c}]. \tag{75}$$

From Appendix B, in first approximation,

$$J(1) = -\psi_b = -2\mathbf{v}\cdot\xi f_0\nu_1, \tag{76}$$

and using the symmetry of K and J_0 together with the properties $K\mathbf{c}=0$ and $[\psi_T,\mathbf{c}]=0$, we may rewrite (75) as

$$\mathbf{M}=\mathbf{M}_v+\mathbf{M}_T, \tag{77}$$

with

$$\mathbf{M}_T=m\lambda_T[\psi_\alpha,\mathbf{c}]\cdot\nabla\ln T=(2kT/m)^{1/2}nm\lambda_T\nabla\ln T \tag{78}$$

and

$$\mathbf{M}_v=m\lambda_b[\psi_\alpha,\mathbf{c}]\cdot\mathbf{v}=(2kT/m)^{1/2}mn\lambda_b\mathbf{v}. \tag{79}$$

The coefficient λ_b is given by Eq. (73) while, from Eq. (62), λ_T can be related to η through [Eq. (74)]

$$\eta=-nm(2kT/m)^{1/2}\lambda_T.$$

To unify, we define a thermal diffusion ratio k_T as

$$k_T\equiv\eta/n_0kT_0=-nm(2kT/m)^{1/2}\lambda_T/n_0kT_0, \tag{80}$$

where n_0 and T_0 are the mixture number density and temperature ($n_0=n+n_p, n_0T_0=nT+n_pT_p$), so that the heat flux and $\mathbf{M}_T$ become

$$\mathbf{Q}=-\lambda\nabla T+n_0kT_0k_T(\mathbf{U}-\mathbf{U}_p), \tag{56'}$$

$$\mathbf{M}_T=-n_0kT_0k_T\nabla\ln T. \tag{78'}$$

The variational techniques described in this section are used in Appendix D to calculate the light gas transport coefficients for arbitrary spherically symmetric molecular interaction potentials.

IV. FOKKER–PLANCK COLLISION OPERATOR

The cross-collision integral appearing in the heavy species Boltzmann equation, which accounts for the changes in the distribution function f_p caused by light–heavy species collisions, can be written as

$$J_{21}=\int d^3u\,d\Omega\,g\sigma(g,\theta)\left[f_p(\mathbf{u}_p')f(\mathbf{u}')-f_p(\mathbf{u}_p)f(\mathbf{u})\right], \tag{81}$$

where the differential cross section is the same as in Eq. (1). Similarly to the cross-collision integral J_{12}, Eq. (81) may be expanded in the mass ratio M to yield the so-called Fokker–Planck collision operator [see Eqs. (16)–(18) of Ref. 15] valid to first order in M,

$$J_{21}=\nabla_{u_p}\cdot\left[\mathbf{b}f_p+\tfrac{1}{2}\nabla_{u_p}\cdot\underline{\Pi}f_p\right]+\cdots, \tag{82}$$

where the vector $\mathbf{b}$ and the tensor $\underline{\Pi}$ are defined as

$$\mathbf{b}=M_1\int d^3g\,\mathbf{gg}Q_1f(\mathbf{u}_p-\mathbf{g}), \tag{83}$$

$$\underline{\Pi}=M_1{}^2\int d^3g\,g\left(\frac{1}{2}(g^2\mathbf{I}-3\mathbf{gg})Q_2+2\mathbf{gg}Q_1\right)f(\mathbf{u}_p-\mathbf{g}). \tag{84}$$

Here M_1 is defined in Eq. (2a), and the functions Q_1 and Q_2 are defined in Eq. (B1) of Appendix B.

Using now the expression found previously for f, the coefficients $\mathbf{b}$ and $\underline{\Pi}$ may be obtained including all nonequilibrium effects to first order in M and Kn. The present treatment generalizes previous work[15] in that it incorporates the kinetic effects of the heavy gas in f, including those resulting from differences in the mean velocities and temperatures between the species. The new terms resulting from the analysis that follows are of the order n_p/n, so that the conclusions of Ref. 15 are still valid in the limit $n_p\ll n$. With a complete specification of f, $\mathbf{b}$ and $\underline{\Pi}$ may be obtained for arbitrary values of $\mathbf{u}_p-\mathbf{U}$. But because f has been determined only to first order in $\mathbf{U}_p-\mathbf{U}$, we may consistently compute these coefficients to first order in $\mathbf{U}_p-\mathbf{U}$, Kn, and M only, to obtain

$$\mathbf{b}=M\int d^3g\,\mathbf{gg}Q_1f(-\mathbf{g})+(\mathbf{u}_p-\mathbf{U})M\cdot\int d^3g\,\mathbf{gg}Q_1\nabla_gf_0(-\mathbf{g})+\cdots, \tag{85}$$

$$\underline{\Pi}=M^2\int d^3g\,g\left(\frac{1}{2}(g^2\mathbf{I}-3\mathbf{gg})Q_2-2\mathbf{gg}Q_1\right)\times f_0(-\mathbf{g})+\cdots. \tag{86}$$

Let us write (85) as

$$\mathbf{b}=\mathbf{b}_1+(\mathbf{u}_p-\mathbf{U})\cdot\mathbf{B}+\cdots. \tag{85'}$$

The tensor $\mathbf{B}$ is equal to $\tau^{-1}\underline{\mathbf{I}}$, where τ is given by Eq. (B5) and $\underline{\mathbf{I}}$ is the unit tensor. Similarly,

$$\underline{\Pi}=(2kT/m_p\tau)\underline{\mathbf{I}} \tag{86'}$$

[notice that the first term in (86) is zero].

To evaluate $\mathbf{b}_1$, we notice that

$$n_p\mathbf{b}_1=-M[n_p\mathbf{u}\mathbf{u}Q_1,f(\mathbf{u})]. \tag{87}$$

Since $n_puQ_1\equiv\nu_1$ (Appendix B) and $J_0\mathbf{u}=-\mathbf{u}f_0\nu_1$, Eq. (87) becomes

$$n_p\mathbf{b}_1=M[J_0\mathbf{u},(1+\phi)]=M[\mathbf{u},J_0\phi], \tag{88}$$

where use has been made of the symmetry of J_0 and of the fact that $J_0(1)=0$. Comparing Eq. (88) with Eq. (75), we can relate $\mathbf{b}_1$ with the momentum transfer between species $\mathbf{M}$,

$$\rho_p\mathbf{b}_1=\mathbf{M}-m[J(1),\mathbf{u}], \tag{89}$$

which after using the relation (Appendix B)

$$m[J(1),\mathbf{u}]=-(\rho_p/\tau)(2kT/m)^{1/2}\mathbf{v},$$

can be written as

$$\rho_p\mathbf{b}_1=\mathbf{M}+(\rho_p/\tau)(\mathbf{U}-\mathbf{U}_p). \tag{90}$$

Thus from Eq. (85a),

$$\rho_p\mathbf{b}=\mathbf{M}+(\rho_p/\tau)(\mathbf{u}_p-\mathbf{U}_p), \tag{91}$$

and substituting this expression and Eq. (86a) into Eq. (82), we are led to the modified Fokker–Planck collision operator

$$J_{21}=\nabla_{u_p}\cdot\{[\mathbf{M}/\rho_p+\tau^{-1}(\mathbf{u}_p-\mathbf{U}_p)]f_p+(kT/m_p\tau)\nabla_{u_p}f_p\}. \tag{92}$$

V. HEAVY GAS DISTRIBUTION FUNCTION WHEN $n_p/n\geqslant O(1)$

As mentioned in the Introduction, a Knudsen number expansion for the heavy species distribution function, similar to that of Sec. III for the light gas, is only possible in the case in which the heavy gas is not very dilute. This is readily seen from the relative order of magnitude of the collision terms in the Boltzmann equation for the heavy species distri-

bution function with respect to the free-streaming operator: the self-collision term is of order $p_p\omega^{-1}/\mu_p$, and the cross-collision term (Fokker–Planck operator) is of order $(\omega\tau)^{-1}$. Now, $p_p\omega^{-1}/\mu_p$ can be written as

$$(T_p/T)(n_p/n)(\mu/\mu_p)\mathrm{Kn}^{-1}\sim(n_p/n)\mathrm{Kn}^{-1},$$

where $\mathrm{Kn}=\omega\mu/p$ is the light gas Knudsen number. On the other hand, using relation (B6) between τ and the diffusion coefficient D, in addition to the definition of the Schmidt number $\mathrm{Sc}\equiv\mu/m(n+n_p)D$, $(\omega\tau)^{-1}$ can be written as

$$(\omega\tau)^{-1}=(T_0/T)\mathrm{Sc}\,M\,\mathrm{Kn}^{-1}\sim M\,\mathrm{Kn}^{-1}.$$

Accordingly, because Sc is almost temperature independent and of order unity ($\mathrm{Sc}\simeq 2.3$ for He–Xe mixtures), the Boltzmann equation for the heavy species and the order of magnitude of its terms can be written symbolically as

$$\begin{aligned} &D_p f_p = J_{21}(f,f_p)+J_{22}(f_p),\\ &\mathrm{Kn}, \quad M, \quad n_p/n. \end{aligned} \tag{93}$$

If n_p/n is of order unity or larger, we can expand f_p in powers of Kn (provided, of course, that $\mathrm{Kn}\ll 1$)

$$f_p = f_{p0}(1+\phi_p+\cdots), \tag{94}$$

and solve Eq. (93) by the Chapman–Enskog procedure. A peculiarity is that now the zeroth-order equation for f_{p0} *is*

$$J_{22}(f_{p0})=0,$$

which yields a Maxwellian distribution for f_{p0} with mean velocity and temperature independent from those of the light gas

$$f_{p0}=n_p(m_p/2\pi kT_p)^{3/2}\exp[-(m_p/2kT)|\mathbf{u}_p-\mathbf{U}_p|^2]. \tag{95}$$

However, if $n_p/n=O(M)$, this expansion is not valid except in the case when $\mathrm{Kn}\ll M$ for which the Chapman–Enskog theory for binary mixtures can be applied. Therefore, in the limit $\mathrm{Kn}\sim M\sim(n_p/n)\ll 1$, the complete kinetic equation (93) has to be solved. A simplification arises in the limit of extreme dilution of the heavy species ($n_p/n\ll M$) in which Eq. (93) is reduced to a Fokker–Planck equation by neglecting the self-collision term.

In the remainder of this section we will restrict ourselves to the case $n_p/n\gtrsim O(1)$ and will derive and solve the integral equation for the first-order correction ϕ_p. The corresponding results are obviously far more restricted than those in the previous sections. The principal difference with respect to the light gas is that now the cross-collision and the free-streaming terms are of the same order of magnitude (when Kn and M are comparable) and the linearized equation for ϕ_p must be written as

$$K_p\phi_p = D_p f_{p0} - F(1), \tag{96}$$

where $K_p\phi_p\equiv J_{22}(f_{p0}\phi_p)$ and $F(1)$ is the Fokker–Planck operator applied to $f_p=f_{p0}$. From Eqs. (92), (95), (77), (78a), and (79),

$$\begin{aligned} F(1)=2f_{p0}\{&\boldsymbol{\xi}_p\cdot[n_0kT_0k_T(m_p/2kT_p)^{1/2}\\ &\times\nabla\ln T-M_T\rho\lambda_b\mathbf{v}]/\rho_p\\ &+\tau^{-1}(1-T/T_p)(\tfrac{3}{2}-\xi_p^2)\}, \end{aligned} \tag{97}$$

where $M_T=(T_pm/Tm_p)^{-1/2}$ and

$$\boldsymbol{\xi}_p=(\mathbf{u}_p-\mathbf{U}_p)/(2kT_p/m_p)^{1/2}.$$

On the other hand, similar to the case of the light gas, $D_p f_{p0}$ can be written as

$$D_p f_{p0}=\mathrm{Grad}_p+D_{pu}+D_{pT}, \tag{98}$$

with

$$\mathrm{Grad}_p=f_{p0}\{(\xi_p^2-5/2)\mathbf{c}_p\cdot\nabla\ln T_p+2\boldsymbol{\xi}_p\boldsymbol{\xi}_p:\nabla\mathbf{U}_p\}, \tag{99}$$

$$D_{pu}=(2/n_p)\boldsymbol{\xi}_p\cdot[\boldsymbol{\xi}_p,F(1)], \tag{100}$$

$$D_{pT}=(\tfrac{2}{3}n_p)(\xi_p^2-\tfrac{3}{2})[\xi_p^2,F(1)]. \tag{101}$$

Using Eq. (97) to evaluate Eqs. (100) and (101), and substituting into Eq. (96), we have

$$K_p\phi_p=\mathrm{Grad}_p, \tag{102}$$

where the terms associated with $F(1)$ cancel exactly. Therefore, as expected, in first approximation the heavy gas behaves as a pure gas.

The hydrodynamic two-fluid equations for this case $n_p/n\gtrsim O(1)$ are given in Appendix E.

It is worth pointing out that, in the limit $\mathrm{Kn}\ll 1$, $n_p/n\gtrsim O(1)$, the problem may be treated with greater generality for arbitrary values of the parameter M by expansion of the original Boltzmann equations in the two Knudsen numbers Kn and Kn_p. The corresponding analysis is presented in Ref. 17.

VI. CONCLUSIONS AND COMPARISON WITH PREVIOUS WORKS

In the present work we have made a rigorous expansion of the cross-collision Boltzmann operators in the small parameters M and $\mathbf{v}$ [Eqs. (2b) and (17)] retaining terms up to first order in both of them, to obtain new simplified operators (Lorentz–Bernstein and Fokker–Planck). Then, the Chapman–Enskog method has been used to solve the Boltzmann equation for the light gas when its Knudsen number is small. Provided the temperatures of the two gases are of the same order, the method yields a correct description of the light gas distribution function for arbitrary interaction potentials even when the heavy gas is dilute and far from equilibrium. From it, all the coefficients entering in the expression of the Fokker–Planck operator are calculated to first order in the Knudsen number. No such description of either the light gas distribution function or the Fokker–Planck operator had been given previously.

A two-fluid hydrodynamic description of the behavior of the heavy gas is only possible when $n_p/n\gtrsim O(1)$, and is given here for arbitrary potentials of interaction. Previous literature on two-fluid hydrodynamic descriptions of disparate-mass mixtures[8–11] followed early ideas of Grad.[7] For instance, Goldman and Sirovich[9] developed a general two-fluid Chapman–Enskog theory for the case of Maxwell molecules, while Goebel, Harris, and Johnson[10] made use of Grad's 13 moments approximation also for Maxwell molecules. The more recent work of Tiem[11] is also based on Grad's[18] expansion of the distribution function in Hermite polynomials, but allowing for arbitrary interaction potentials. From this expansion and using the hard sphere model

to estimate orders of magnitude, Tiem derives a scaling of the collision terms. He makes the hypothesis of similar molecular diameters for light and heavy species, which would imply that the viscosity of the pure heavy gas is $(m_p/m)^{1/2}$ times larger than that of the light gas. However, because the experimental data for noble gases indicate that the viscosity is mass independent,[1] the validity of this scaling is limited to some hypothetical gases that might not be easily found in nature. Incidentally, the arbitrary assumption $\mu/\mu_p = O(M^{1/2})$ was first suggested in the pioneering work of Grad[7] and has prejudiced much of the literature in this field. A direct consequence of such scaling is that the light gas stress tensor does not appear in Tiem's hydrodynamic equations, a result that is not correct even for the case $n_p/n = O(1)$ assumed in his derivation. Furthermore, Tiem's expansion is restricted to $M^{1/2} = O(\mathrm{Kn})$, while we expand independently in Kn and M, to first order in both.

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APPENDIX A: SYMMETRY OF THE OPERATOR J_0

The following derivation is from Professor I. B. Bernstein of Yale University (unpublished). From Eqs. (15a) and (20c),

$$J_0(\psi) = \int d\Omega\, v f_0(\mathbf{u})[\psi(\mathbf{k}) - \psi(\mathbf{u})],$$

with

$$\mathbf{k} = \underline{\Omega}\mathbf{u} \quad \text{and} \quad v = n_p u\sigma(u,\theta).$$

Then,

$$[\phi, J_0\psi] = n_p \int d^3u\, d\Omega\, u\sigma(u,\theta)\phi(\mathbf{u}) f_0(\mathbf{u})[\psi(\mathbf{k}) - \psi(\mathbf{u})],$$

and after changing the variable of integration from $\mathbf{u}$ to $\mathbf{k}$

$$[\phi, J_0\psi] = n_p \int d^3k\, d\Omega\, u\sigma(u,\theta)\phi(\mathbf{k}) f_0(\mathbf{u})[\psi(\mathbf{u}) - \psi(\mathbf{k})].$$

[Notice that the Jacobian of the transformation is unity, that $u = k$ and that $f_0(\mathbf{u}) = f_0(\mathbf{k})$ in the reference frame in which $\mathbf{U} = 0$.] Adding these two expressions and dividing by 2, we obtain

$$[\phi, J_0\psi] = -\frac{n_p}{2} \int d^3u\, d\Omega\, u\sigma(u,\theta) f_0(u) \times [\phi(\mathbf{k}) - \phi(\mathbf{u})][\psi(\mathbf{k}) - \psi(\mathbf{u})],$$

from which it follows that J_0 is a symmetric and nonpositive operator. Moreover, from its definition, $J_0\psi = 0$ for any function $\psi(\mathbf{u})$ invariant under rotation.

APPENDIX B: EXPRESSION FOR $J(1)$

Using $f = f_0$ [Eq. (19)] in Eqs. (15), we obtain

$$N_0 = 0, \quad \mathbf{L}_0 = \frac{m}{kT} f_0 n_p \int d\Omega\, \sigma u(\mathbf{u} - \mathbf{k}) = \frac{mn_p}{kT} f_0 Q_1 \mathbf{cc},$$

$$\underline{\mathbf{Y}}_0 = \left(\frac{m}{kT}\right)^2 f_0 n_p \int d\Omega\, \sigma u(\mathbf{uu} - \mathbf{kk}) = \frac{3}{2}\left(\frac{m}{kT}\right)^2 n_p f_0 c\left(\mathbf{cc} - \frac{c^2}{3}\underline{\mathbf{I}}\right) Q_2, \quad \mathbf{R}_0 = f_0 n_p c\mathbf{c} Q_1,$$

where $\mathbf{u} = \mathbf{c}$ in our reference frame in which $\mathbf{U} = 0$ and the Q_i's are functions of c defined by

$$Q_i(c) = 2\pi \int_0^\pi d\theta (1 - \cos^i\theta)\sigma(c,\theta)\sin\theta. \tag{B1}$$

Thus, up to first order in M, we can write

$$J(1) = -2f_0\nu_1 \mathbf{v}\cdot\boldsymbol{\xi} + M\left(\frac{1}{\xi}\frac{d(f_0\nu_1)}{d\xi} + \frac{3\nu_2 f_0}{2}\right)\underline{\boldsymbol{\Sigma}}^\circ : \boldsymbol{\xi}\boldsymbol{\xi} + M\left(f_0\nu_1 + \frac{1}{3}\xi\frac{d(f_0\nu_1)}{d\xi}\right)\mathrm{Tr}(\underline{\boldsymbol{\Sigma}}), \tag{B2}$$

where $\nu_1 = n_p c Q_1$, $\nu_2 = n_p c Q_2$, and the tensor $\underline{\boldsymbol{\Sigma}}$ is defined by

$$\underline{\boldsymbol{\Sigma}} = \underline{\mathbf{I}} - \underline{\mathbf{T}}_p/T - 2\mathbf{vv}/M, \tag{B3}$$

and $\underline{\mathbf{I}}$ is the unit tensor. Here $\mathrm{Tr}(\underline{\boldsymbol{\Sigma}})$ denotes the trace of $\underline{\boldsymbol{\Sigma}}$ and

$$\underline{\boldsymbol{\Sigma}}^\circ = \underline{\boldsymbol{\Sigma}} - \mathrm{Tr}(\underline{\boldsymbol{\Sigma}})\underline{\mathbf{I}}/3.$$

Only the first term of $J(1)$ will be retained since our aim is to develop a first order theory in the mass ratio M [except in the evaluation of the energy transfer between species since the first term in $J(1)$ does not contribute and the next significant term has to be retained]. From Eq. (B2), we can calculate the contribution of $J(1)$ to D_u and D_T:

$$D_u^0 = (2f_0/n)\boldsymbol{\xi}\cdot[\boldsymbol{\xi}, J(1)] = -2\nu_0 f_0 \mathbf{v}\cdot\boldsymbol{\xi},$$
$$D_T^0 = (f_0/n)(2\xi^2/3 - 1)[\xi^2, J(1)] = Mf_0\nu_0(2\xi^2/3 - 1)\mathrm{Tr}(\underline{\boldsymbol{\Sigma}}), \tag{B4}$$

where $\nu_0 = n_p/nM\tau$, with τ given by

$$\tau = \tfrac{3}{16}(1/nM\Omega_{12}^{(1,1)}), \tag{B5}$$

which is a measure of the energy relaxation time between species, and is related to the first approximation of the diffusion coefficient D given by the Chapman–Enskog theory for binary mixtures[2]:

$$D = (kT_0/m_p)[n/(n + n_p)]\tau. \tag{B6}$$

APPENDIX C: COMPATIBILITY RELATIONS FOR EQ. (32)

Let us write Eq. (32) as

$$(K + J_1)\phi = \psi. \tag{C1}$$

Since $K + J_1$ is a singular operator, according to Fredholm's theorem for linear integral equations,[19] Eq. (C1) has nontrivial solutions if, and only if,

$$[\psi, \Upsilon_i] = 0,$$

where the Υ_i functions are the nontrivial solutions of the transposed homogeneous equation

$$(K+J_1)^T\Upsilon_i = 0. \tag{C2}$$

Multiplying Eq. (C2) by a generic function ϕ and forming the inner product, we can write

$$[\phi,(K+J_1)^T\Upsilon_i] = [\Upsilon_i,(K+J_1)\phi] = 0,$$

or, from Eq. (33),

$$[\Upsilon_i,(K+J_0)\phi] - (2/n)[\Upsilon_i,\xi f_0]\cdot[\xi,J_0\phi] = 0. \tag{C3}$$

Since K and J_0 are self-adjoint operators, (C3) may be written as

$$[\phi,\{(K+J_0)\Upsilon_i - (2/n)[\Upsilon_i,\xi f_0]\cdot J_0\xi\}] = 0.$$

This equation is valid for any ϕ and thus Υ_i satisfies the relation

$$(K+J_0)\Upsilon_i - (2/n)[\Upsilon_i,\xi f_0]\cdot J_0\xi = 0$$

or, since $K\xi = 0$,

$$(K+J_0)\{\Upsilon_i - (2/n)[\Upsilon_i,\xi f_0]\cdot\xi\} = 0.$$

Any solution of this equation is a linear combination of the functions 1, ξ, and ξ^2 (that ξ is a solution is readily seen from the equality $[\xi,\xi f_0] = n\underline{I}/2$) because the only functions that vanish upon the action of $(K+J_0)$ are 1 and ξ^2 [see discussion following Eq. (42)].

Thus, the compatibility relations that have to be satisfied are

$$[\psi,1] = [\psi,\xi] = [\psi,\xi^2] = 0, \tag{C4}$$

where from Eqs. (28) and (23),

$$\psi = f_0\{2\xi\xi:\nabla^\circ U + c\cdot\nabla \ln T(\xi^2 - \tfrac{5}{2}) + 2v\cdot\xi(\nu_1 - \nu_0)\}.$$

By parity considerations, the first and the third of Eqs. (C4) are straightforwardly satisfied (notice that $\xi^\circ\xi$ is traceless). Also, for the same reason

$$[2\xi\xi:\nabla^\circ U,\xi] = 0.$$

The two remaining relations are satisfied since

$$\int_0^\infty d\xi\, e^{-\xi^2}\xi^4\left(\xi^2 - \frac{5}{2}\right) = 0$$

and

$$\int_0^\infty d\xi\, \nu_1\xi^4 \exp(-\xi^2) = \nu_0\int_0^\infty d\xi\, \xi^4 \exp(-\xi^2).$$

Moreover, it is easy to show that the neglected terms in $J(1)$ related to the tensor $\underline{\Sigma}$ [see Eq. (B2)] also verify the compatibility relations (C4) when they are included in ψ.

APPENDIX D: TRANSPORT COEFFICIENTS FOR THE LIGHT GAS

In this appendix, we use the variational methods described in Sec. III D to calculate the functions χ_a, χ_T, and χ_α that maximize the inner products $[\chi_a,\psi_a]$, $[\chi_T,\psi_T]$, and $[\chi_\alpha,\psi_\alpha]$, for a specific set of trial functions (expansions in Sonine polynomials). Then, these functions are used to obtain expressions for the light gas transport coefficients.

Expanding the functions χ_i in the orthogonal set of Sonine polynomials,[20]

$$\chi_a = \sum_{k=0}^{\infty} a_k S_{5/2}^{(k)}(\xi^2)\xi\xi:\nabla^\circ U, \tag{D1}$$

$$\chi_\tau = \sum_{k=0}^{\infty} t_k S_{3/2}^{(k)}(\xi^2)c\cdot\nabla \ln T, \tag{D2}$$

$$\chi_\alpha = \sum_{k=0}^{\infty} \alpha_k S_{3/2}^{(k)}(\xi^2)\xi, \tag{D3}$$

the equations for the coefficients a_i, t_i, and α_i that satisfy relations (53), (64), and (65), respectively, are given by

$$\sum_{ij} a_j \underline{A}_{ij} = n\delta_{i0}, \tag{D4}$$

$$\sum_{ij} t_j A_{ij} = -\frac{5n\delta_{i1}}{4}, \tag{D5}$$

$$\sum_{ij} \alpha_j A_{ij} = n\delta_{i0}. \tag{D6}$$

To obtain these equations, the orthogonality properties of the Sonine polynomials have been used. The matrices A_{ij} and $\underline{A}_{ij}$ are defined by

$$A_{jk}\underline{I} = [S_{3/2}^{(j)}\xi,(K+J_0)S_{3/2}^{(k)}\xi], \tag{D7}$$

$$\underline{A}_{jk}\underline{\Lambda} = [S_{5/2}^{(j)}\xi^\circ\xi,(K+J_0)S_{5/2}^{(k)}\xi^\circ\xi], \tag{D8}$$

where $\underline{I}$ is the unit second order tensor and the fourth order tensor $\underline{\Lambda}$ is defined by $\Lambda_{klnm} = \delta_{kl}\delta_{mn} + \delta_{kn}\delta_{lm} + \delta_{km}\delta_{nl}$. The portions associated with the operator K in Eqs. (D7) and (D8) are known from the Chapman–Enskog theory of a pure gas (see, e.g., Ref. 2, pp. 157–159 or Ref. 21, Sec. 7.2). The part of (D7) and (D8) corresponding to J_0 is easily evaluated using the definition of J_0 given by Eqs. (15a) and (20c), and the orthogonality properties of the Sonine polynomials.[20] In terms of the Ω integrals,[21] the first few terms of these matrices are

$$A = -\frac{8}{3}nn_p\Omega_{12}^{(1,1)} \times \begin{bmatrix} 1 & a & c \\ a & (n/n_p)a_1 + b & (n/n_p)b_1 + d \\ c & (n/n_p)b_1 + d & (n/n_p)c_1 + e \end{bmatrix},$$

$$\underline{A} = -\frac{8}{5}nn_p\Omega_{12}^{(2,2)} \begin{bmatrix} 1 + (n/n_p)\bar{a}_1 & \bar{a} + (n/n_p)\bar{b}_1 \\ \bar{a} + (n/n_p)\bar{b}_1 & \bar{b} + (n/n_p)\bar{c}_1 \end{bmatrix},$$

where

$$a = \frac{5}{2} - \frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}}, \quad b = \frac{25}{4} - 5\frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}} + \frac{\Omega_{12}^{(1,3)}}{\Omega_{12}^{(1,1)}},$$

$$c = \frac{35}{8} - \frac{7}{2}\frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}} + \frac{1}{2}\frac{\Omega_{12}^{(1,3)}}{\Omega_{12}^{(1,1)}},$$

$$d = \frac{175}{16} - \frac{105}{8}\frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}} + \frac{19}{4}\frac{\Omega_{12}^{(1,3)}}{\Omega_{12}^{(1,1)}} - \frac{1}{2}\frac{\Omega_{12}^{(1,4)}}{\Omega_{12}^{(1,1)}},$$

$$e = \frac{1225}{64} - \frac{245}{8}\frac{\Omega_{12}^{(1,2)}}{\Omega_{12}^{(1,1)}} + \frac{133}{8}\frac{\Omega_{12}^{(1,3)}}{\Omega_{12}^{(1,1)}} - \frac{7}{2}\frac{\Omega_{12}^{(1,4)}}{\Omega_{12}^{(1,1)}} + \frac{1}{4}\frac{\Omega_{12}^{(1,5)}}{\Omega_{12}^{(1,1)}},$$

$$a_1 = \frac{1}{2}\frac{\Omega_1^{(2,2)}}{\Omega_{12}^{(1,1)}},$$

$$b_1 = \frac{1}{2}\left(7\frac{\Omega_1^{(2,2)}}{\Omega_{12}^{(1,1)}} - 2\frac{\Omega_1^{(2,3)}}{\Omega_{12}^{(1,1)}}\right),$$

$$c_1=\frac{1}{2}\left(\frac{77}{4}\frac{\Omega_1^{(2,2)}}{\Omega_{12}^{(1,1)}}-7\frac{\Omega_1^{(2,3)}}{\Omega_{12}^{(1,2)}}+\frac{\Omega_1^{(2,4)}}{\Omega_{12}^{(1,1)}}\right),$$

$$\bar{a}=\frac{7}{2}-\frac{\Omega_{12}^{(2,3)}}{\Omega_{12}^{(2,2)}},\quad \bar{b}=\frac{49}{4}-7\frac{\Omega_{12}^{(2,3)}}{\Omega_{12}^{(2,2)}}+\frac{\Omega_{12}^{(2,4)}}{\Omega_{12}^{(2,2)}},$$

$$\bar{a}_1=\frac{1}{2}-\frac{\Omega_1^{(2,2)}}{\Omega_{12}^{(2,2)}},\quad \bar{b}_1=\frac{1}{8}\left(7\frac{\Omega_1^{(2,2)}}{\Omega_{12}^{(2,2)}}-2\frac{\Omega_1^{(2,3)}}{\Omega_{12}^{(2,2)}}\right),$$

$$\bar{c}_1=\frac{1}{8}\left(\frac{301}{12}\frac{\Omega_1^{(2,2)}}{\Omega_{12}^{(2,2)}}-7\frac{\Omega_1^{(2,3)}}{\Omega_{12}^{(2,2)}}+\frac{\Omega_1^{(2,4)}}{\Omega_{12}^{(2,2)}}\right).$$

Notice that from the nature of the right-hand sides of Eqs. (D4) and (D5), one more term is needed in the matrix A than in the matrix $\underline{A}$ to obtain the same degree of approximation.

Once the coefficients a_j, t_j, and α_j are known, the viscosity, thermal conductivity, and coefficient η of the light gas can be calculated using equations (52), (57), and (74), respectively. The first approximation (resulting from taking one term in $\underline{A}_{ij}$ and two terms in A_{ij}) is given by

$$[\mu]_1=\frac{5nkT}{16n_p\Omega_{12}^{(2,2)}[(n/n_p)\bar{a}_1+1]},\tag{D9}$$

$$[\lambda]_1=\frac{75nk^2T}{64mn_p\Omega_{12}^{(1,1)}[(n/n_p)a_1+b]},\tag{D10}$$

$$[\eta]_1=\frac{5nkTa}{2[(n/n_p)a_1+b]}.\tag{D11}$$

The second approximation is easily computed using the terms of the matrices A and $\underline{A}$ given above. It is observed that in the limit $n/n_p\to\infty$ (pure light gas), Eqs. (D9) and (D10) are the first approximations for the viscosity and thermal conductivity of a pure gas given by the Chapman–Enskog theory (Ref. 2, Eq. 9.7,3). In the opposite limit $n/n_p\to 0$, the above expressions agree with the viscosity and thermal conductivity in the Lorentz limit (Ref. 2, Sec. 10.5). The comparison between our results for μ and λ and the exact values in the Lorentz limit is made in Table I for molecules repelling each other with a negative power of their distance, using the first and second approximations of μ and λ. As an indication of the convergence of the successive approximations in the Sonine polynomial expansion, Fig. 2 represents the ratio $[\lambda]_2/[\lambda]_1$ between second and first approximations of λ as a function of the light gas molar fraction $n/(n_p+n)$. It is observed that the minimum ($[\lambda]_2/[\lambda]_1=1$) is reached at $n/n_p=1$.

From Eqs. (80) and (D11), the first approximation of the coefficient k_T may be written as

$$[k_T]_1=\frac{5nTa}{2n_0T_0[(n/n_p)a_1+b]},\tag{D12}$$

which is equal to the first approximation of the thermal diffusion ratio k_T of the Chapman–Enskog theory in the limit $M\to 0$ (Ref. 2, p.165).

Finally, from Eq. (73), the second approximation to the coefficient λ_b appearing in the transfer of momentum is given by

$$[\lambda_b]_2=-\frac{16}{3}n_p\Omega_{12}^{(1,1)}\left(1-\frac{a^2}{b+na_1/n_p}\right)$$

$$=-\frac{n_p}{nM\tau}\left(1-\frac{a^2}{b+na_1/n_p}\right),\tag{D13a}$$

where τ is defined in Eq. (B5). Notice that the second rather than the first approximation is obtained since we have retained two terms in A_{ij} in order to obtain the first approximations for λ and k_T while, from the right-hand side of Eq. (D6), only one term of A_{ij} is needed for the first approximation of λ_b, which is

$$[\lambda_b]_1=-n_p/nM\tau.\tag{D13b}$$

APPENDIX E: TWO-FLUID HYDRODYNAMIC EQUATIONS FOR $n_p/n\geqslant O(1)$

In this particular case we can complete the system of hydrodynamic equations for the two fluids:

$$\partial_t n+\nabla\cdot(n\mathbf{U})=0,\quad nm\partial_t\mathbf{U}+nm\mathbf{U}\cdot\nabla\mathbf{U}+\nabla\cdot\underline{\mathbf{P}}=\mathbf{M},$$

$$\tfrac{3}{2}nk\,\partial_t T+\tfrac{3}{2}nk\,\mathbf{U}\cdot\nabla T+\nabla\cdot\mathbf{Q}+\underline{\mathbf{P}}:\nabla\mathbf{U}=E,$$

TABLE I. Comparison between the first and second approximations $[\mu]_1$, $[\mu]_2$ and $[\lambda]_1$, $[\lambda]_2$ of viscosity and thermal conductivity in the limit $n/n_p\to 0$ and the corresponding values for the Lorentz gas μ_L and λ_L (Ref. 2, Sec. 10.5). The comparison is made using repulsive molecular potentials varying as $r^{-\delta}$ ($\delta=4$ corresponds to Maxwell molecules and $\delta=\infty$ to hard spheres). The ratios $[\mu]_i/\mu_L$ and $[\lambda]_i/\lambda_L$ are temperature independent. Notice that, from Fig. 2, it is in this limit $n=0$ when the convergence of the Sonine polynomial series is the slowest. Also notice that the convergence is slower for the thermal conductivity than for the viscosity.

δ	$[\mu]_1/\mu_L$	$[\mu]_2/\mu_L$	$[\lambda]_1/\lambda_L$	$[\lambda]_2/\lambda_L$
4	1	1	1	1
6	0.9909	0.9984	0.9663	0.9946
12	0.9639	0.9918	0.8625	0.9749
∞	0.9204	0.9779	0.7282	0.9383

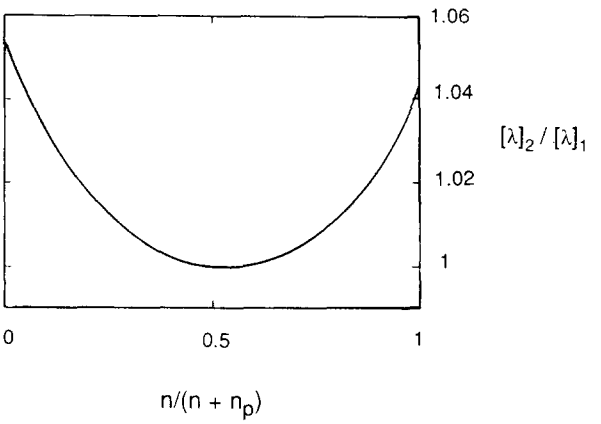

FIG. 2. Ratio $[\lambda]_2/[\lambda]_1$ between second and first approximations of the thermal conductivity as a function of the light gas molar fraction. A Lennard–Jones molecular potential with reduced temperature $T^*=10$ has been used to evaluate the Ω integrals.[22] This ratio is almost independent of T^*. Because of the faster convergence of the Sonine polynomial series for the viscosity (i.e., Table I), the equivalent ratio $[\mu]_2/[\mu]_1$ is smaller.

$$\partial_t n_p + \nabla\cdot(n_p \mathbf{U}_p) = 0,$$

$$n_p m_p\, \partial_t \mathbf{U}_p + n_p m_p \mathbf{U}_p\cdot\nabla\mathbf{U}_p + \nabla\cdot\underline{\mathbf{P}}_p = -\mathbf{M},$$

$$\tfrac{3}{2} n_p k\, \partial_t T_p + \tfrac{3}{2} n_p k\, \mathbf{U}_p\cdot\nabla T_p + \nabla\cdot\mathbf{Q}_p + \underline{\mathbf{P}}_p : \nabla\mathbf{U}_p = -E,$$

$$\underline{\mathbf{P}} = p\underline{\mathbf{I}} - 2\mu\nabla^{\circ}\mathbf{U}, \quad \mathbf{Q} = -\lambda\nabla T + n_0 k T_0 k_T(\mathbf{U} - \mathbf{U}_p),$$

$$\underline{\mathbf{P}}_p = p_p\underline{\mathbf{I}} - 2\mu_p\nabla^{\circ}\mathbf{U}_p, \quad \mathbf{Q}_p = -\lambda_p\nabla T_p.$$

The transport coefficients of the light species, which are not restricted with respect to the number density ratio, have been introduced in Sec. III A and evaluated in Appendix D by means of a Sonine polynomial expansion [Eqs. (D9), (D10), and (D12)]. The transport coefficients for the heavy gas are those of a pure gas (see, e.g., Ref. 2, Sec. 9.7). It must be noticed that, when both temperatures are the same, the mixture transport coefficients μ_0, λ_0, and k_{T0} defined as the sum of the respective transport coefficient for each species coincide with those given by the Chapman–Enskog theory[2] in the limits $M \ll 1$, $n_p/n \gg M$.

The momentum transfer $\mathbf{M}$ between species is given by either $m[\mathbf{c}J(1+\phi)]$ or $m_p[\mathbf{c}_p F(1)]$, which obviously coincide, and are given by Eqs. (77), (79), and (78') with λ_b and k_T calculated, at the first approximation of the Sonine polynomial expansion, in Eqs. (D12) and (D13a) of Appendix D.

The energy transfer term in the light gas energy equation can be written as

$$E = m[J(1+\phi), c^2/2] = m[J(1), c^2/2],$$

since $[J_0\phi, c^2/2] = 0$. From Appendix B, using the complete expression (B2) for $J(1)$, we have

$$\begin{aligned} E &= -mn_p(2kT/m)\mathrm{Tr}(\boldsymbol{\Sigma})/2\tau \\ &= -3kn_p(T - T_p)/\tau + m_p n_p (U - U_p)^2/\tau, \end{aligned} \tag{E1}$$

τ being given by Eq. (B5). The corresponding term in the heavy gas equation is

$$E_p \equiv m_p[F(1), c_p^2/2] = 3n_p k(T - T_p)/\tau.$$

The term proportional to $(U - U_p)^2$ in Eq. (E1) must be neglected in this first-order theory. In fact, the sum $E + E_p$ should be equal to $\mathbf{M}\cdot(\mathbf{U} - \mathbf{U}_p)$, but this is a higher order term that is taken to be zero in first approximation.

[1] The room temperature viscosities for the noble gases are in micropoises 194, 311, 221, 250, and 226 for He, Ne, Ar, Kr, and Xe, respectively.

[2] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge U. P., New York, 1970), Chap. 8.

[3] For the problem of light scattering in He–Xe mixtures see, for instance, E. A. Johnson, Phys. Rev. A **23**, 1146 (1983).

[4] On shock wave structure in mixtures see, for instance, F. S. Sherman, J. Fluid Mech. **8**, 465 (1960); G. A. Bird, *ibid.* **31**, 657 (1968); E. Goldman and L. Sirovich, *ibid.* **33**, 575 (1969); W. L. Harris and G. K. Bienkowski, Phys. Fluids **14**, 2652 (1971); R. Fernández-Feria and J. Fernández de la Mora, J. Fluid Mech. (in press).

[5] The acoustic problem has been discussed, among others, by R. J. Huck and E. A. Johnson, Phys. Rev. A **44**, 142 (1980); E. A. Johnson, Phys. Fluids **23**, 2558 (1980); M. Fuentes Losa and J. D. Foch, Phys. Rev. Lett. **29**, 209 (1972); E. B. Goldman, J. Acoust. Soc. Am. **44**, 708 (1968); J. Fernández de la Mora and A. Puri, J. Fluid Mech. **168**, 369 (1986); R. Fernández-Feria and J. Fernández de la Mora, in *Rarefied Gas Dynamics*, edited by V. Boffi and C. Cercignani (Teubner, Stuttgart, 1986), Vol. 1, pp. 25–34.

[6] J. Fernández de la Mora, J. Chem. Phys. **82**, 3453 (1985); J. Fernández de la Mora, J. Wilson, and B. L. Halpern, J. Fluid Mech. **149**, 217 (1984).

[7] H. Grad, in *Rarefied Gas Dynamics*, edited by M. Devienne (Pergamon, New York, 1960), pp. 127–128.

[8] B. B. Hamel, Phys. Fluids **9**, 12 (1966).

[9] E. Goldman and L. Sirovich, Phys. Fluids **10**, 1928 (1967).

[10] C. G. Goebel, S. M. Harris, and E. A. Johnson, Phys. Fluids **19**, 617 (1976).

[11] D. H. Tiem, J. Mec. Th. Appl. **3** (4), 601 (1984).

[12] For the original paper see H. A. Lorentz, Proc. Amst. Acad. **7**, 438, 585, 684 (1905).

[13] I. B. Bernstein, in *Advances in Plasma Physics*, edited by A. Simon and W. B. Thomson (Wiley, New York, 1969), Vol. 3, pp. 127–156.

[14] M. S. Green, J. Chem. Phys. **19**, 1036 (1951) treated the hard-sphere case. C. Wang Chang and G. E. Uhlenbeck studied the case where the light gas is in equilibrium in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1970), Vol. V, pp. 89–92. See also W. G. N. Slin and S. F. Shen, J. Stat. Phys. **3**, 291 (1971); O. A. Grechannyi, J. Eng. Phys. **26**, 777 (1975); and V. N. Sazonov, J. Tech. Phys. **49**, 1538 (1979).

[15] J. Fernández de la Mora and J. M. Mercer, Phys. Rev. A **26**, 2178 (1982).

[16] I. B. Bernstein, Phys. Fluids **12**, 64 (1969).

[17] J. Fernández de la Mora and R. Fernández-Feria, submitted to Phys. Fluids.

[18] H. Grad, Commun. Pure Appl. Math. **2**, 325 (1949).

[19] See, e.g., R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1962), Vol. 1, p. 116.

[20] For the definition and some properties of the Sonine polynomials see Ref. 2, p. 127, or, for more details, D. Burnet, Proc. London Math. Soc. **40**, 382 (1935).

[21] See, for instance, J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1977), Sec. 7.1.

[22] J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), Sec. 8.4.