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Modified Fokker-Planck equation for the motion of Brownian particles in a nonuniform gas

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The Brownian-motion Fokker-Planck equation describing the velocity-distribution function of a collection of Brownian particles suspended in a rarefied carrier gas in equilibrium is generalized to the case of a nonuniform suspending gas. The gas-particle collision integral appearing in the Boltzmann equation is expanded in powers of the ratio of masses between gas molecules and particles, and the gas-distribution function is taken as the first approximation to the Chapman-Enskog expression. Also, the characteristic width of the particle-distribution function is assumed to be of the order of its value in equilibrium. The modified collision term obtained involves a new force proportional to the local temperature gradient, and closely related to the Chapman-Enskog thermal-diffusion effect. The contributions from the nonhomogeneity of the gas-velocity field is small, but introduces new "shear forces" proportional to the fluid-particle relative velocity and the local gas traceless symmetrized velocity-gradient tensor. The new equation can be used to describe the nonequilibrium dynamics of gas mixtures with disparity of masses when the heavy species is dilute and the light is not too far from equilibrium.

I. INTRODUCTION

The Fokker-Planck kinetic equation describing the distribution function $f_p(\vec{u}_p,\vec{x},t)$ of a collection of Brownian particles suspended in a rarefied gas at equilibrium is

$$\frac{\partial f_p}{\partial t}+\vec{\nabla}\cdot(f_p\vec{u}_p)=\tau^{-1}\vec{\nabla}_{u_p}\cdot\left[\vec{u}_pf_p+\frac{kT}{m}\vec{\nabla}_{u_p}f_p\right], \tag{1}$$

where $f_p(\vec{u}_p)$ is the density of Brownian particles in the phase space of its variables, $\vec{u}_p$ the velocity, t the time, and $\vec{x}$ the position vector; τ is the particle relaxation time, k the Boltzmann constant, m_p the particle mass, T the temperature of the gas, and $\vec{\nabla}_{u_p}$ the gradient operator in $\vec{u}_p$ space. Equation (1) has been known for many years as an important result of the theory of stochastic processes[1,2] where it is derived using several *ad hoc* assumptions. More interestingly, Eq. (1) has also been obtained for point particles by Green, and by Wang Chang and Uhlenbeck[3] starting from the Boltzmann equation, and for particles of arbitrary size by Mercer and Keyes[4] starting from the repeated ring equation.[5] Those authors expanded the collision integral in negative powers of the ratio m_p/m between the masses m_p and m of the heavy component (the particle) and the light one (the gas), assuming also a very small mass fraction of particles in the mixture so that particle-particle collisions could be ignored. They further assumed that $\vec{u}_p$ does not depart too much from the equipartition value, and assigned an equilibrium-Maxwellian distribution to the light gas.

The Fokker-Planck equation (1) has been used in a number of fields,[1,3,6,7] though not often emphasizing practical applications. More recently, however, the engineers' interest in the gas dynamics of mixtures with disparate masses has been revitalized by the industrial development of aerodynamic schemes for the separation of uranium isotopes.[8–10] There, if properly modified, the Fokker-Planck equation can provide a powerful analytical tool to study the nonequilibrium phenomena affecting the heavy species. The generalizations needed are numerous. Here, however, we will only relax the condition that the light gas be in equilibrium, allowing for the presence of slight velocity and temperature gradients. Because Eq. (1) is only valid in an isothermal motionless gas, the proposed generalization is essential to permit the study of heavy molecule dynamics within flowing gases where nonuniformities occur necessarily. We will first perform a mass expansion of the Boltzmann collision integral using the first-order Chapman-Enskog expression for the light-gas velocity-distribution function instead of the equilibrium-Maxwellian distribution employed by previous authors.[3,11] The new distribution contains terms proportional to the sources of nonuniformities (the light-gas temperature and velocity gradients), which modify the standard Fokker-Planck equation. It will be seen that the corrections due to velocity gradients in the light gas are small. However, they introduce a slight anisotropy in the diffusivity tensor as well as net shear forces proportional to the difference between particle and light-gas mean velocity and to the velocity-gradient tensor. Even more interesting is the effect of temperature gradients. These give rise to a new term in the Fokker-Planck equation, equivalent to the Chapman-Enskog *thermal-diffusion*[12] effect in near equilibrium conditions. The importance of the new term becomes increasingly dominant over that of Brownian diffusion as the ratio m_p/m is increased, and it has to be taken into account whenever temperature gradients are present. Finally, we conclude that, aside from the smaller velocity-gradient effects, the generalized Fokker-Planck equation governing the motion of Brownian particles or heavy molecules in a light nonuniform gas is

$$\frac{\partial f_p}{\partial t}+\vec{\nabla}\cdot(\vec{u}_p f_p) = \tau^{-1}\vec{\nabla}_{u_p}\cdot\left[(\vec{u}_p - D\alpha_T\vec{\nabla}\ln T-\vec{V})f_p + \frac{kT}{m_p}\vec{\nabla}_{u_p}f_p\right],$$

where D and α_T are the Chapman-Enskog diffusion coefficient and thermal-diffusion factor, respectively, and $\vec{V}=\vec{V}(\vec{x},t)$ is the light-gas velocity field.

II. MASS EXPANSION OF THE BOLTZMANN COLLISION OPERATOR FOR HEAVY PARTICLES

The change in the heavy-particle-distribution function due to collisions with the light gas is

$$\left[\frac{\delta f_p}{\delta t}\right]_{\rm coll} \equiv J_p=\int d^3u\, g\, d\Omega\, \sigma(g,\theta)[f_p(\vec{u}_p')f(\vec{u}\,')-f_p(\vec{u}_p)f(\vec{u})]\ , \tag{2}$$

where the subscript p refers to the particles or heavy molecules, and the primes denote postcollision values of the velocities. Magnitudes with no p subindex refer to the light carrier gas. We have used the definitions

$$\vec{g}\equiv\vec{u}_p-\vec{u} \tag{3}$$

for the relative (precollision) velocity,

$$\vec{V}\equiv M_p\vec{u}_p+M\vec{u} \tag{4}$$

for the center-of-mass velocity, and

$$M_p\equiv\frac{m_p}{m+m_p},\quad M=\frac{m}{m+m_p}\ , \tag{5}$$

while m_p and m are the masses of heavy and light particles, and $\vec{u}_p$ and $\vec{u}$ their respective velocities prior to collision. $\sigma(g,\theta)$ is the differential scattering cross section for collisions, and it is taken as independent of the azimuthal angle (Fig. 1) corresponding to molecules interacting with radially symmetric force fields.

Equations (3) and (4) can be inverted to give

$$\vec{u}_p=\vec{V}+M\vec{g}\ , \tag{6}$$

$$\vec{u}=\vec{V}-M_p\vec{g}\ , \tag{7}$$

and analogously for the postcollision values

$$\vec{u}_p'=\vec{V}+M\vec{g}\,'\ , \tag{8}$$

$$\vec{u}\,'=\vec{V}-M_p\vec{g}\,'\ , \tag{9}$$

where the center-of-mass velocity remains un-

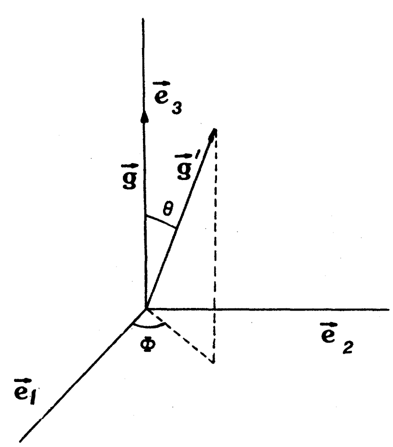

FIG. 1. Reference system.

changed due to momentum conservation, and $\vec{g}\,'$, the postcollision relative velocity, is obtained from $\vec{g}$ by a pure rotation due to the energy-conservation requirement, i.e.,

$$g' = |\vec{g}\,'| = g = |\vec{g}| \ . \tag{10}$$

Further defining

$$\Delta\vec{g} \equiv \vec{g}\,' - \vec{g} \ , \tag{11}$$

$$\vec{\eta} \equiv \vec{u} - \vec{g}\,' + \vec{g} = \vec{u}_p - \vec{g}\,' \ , \tag{12}$$

the postcollision velocities become

$$\vec{u}_p' = \vec{u}_p + M\Delta\vec{g} \ , \tag{13}$$

$$\vec{u}\,' = \vec{\eta} + M\Delta\vec{g} = \vec{u} - M_p\Delta\vec{g} \ . \tag{14}$$

The introduction of $\vec{\eta}$ will prove convenient subsequently. $\vec{\eta}$ corresponds to $\vec{u}\,'$ in the limit when the heavy-molecule velocity is unchanged during the collision (i.e., $m \to 0$, or $m_p/m \to \infty$). In what follows we exploit the smallness of M for disparate mass mixtures to simplify the form of J_p. For that purpose we shift from $\vec{u}$ to $\vec{g}$ as integration variable in (2):

$$J_p = \int d^3g\, g\sigma(\theta,g)d\Omega[f_p(\vec{u}_p + M\Delta\vec{g})f(\vec{u}\,') - f_p(\vec{u}_p)f(\vec{u})] \ . \tag{15}$$

As discussed in Sec. I, mass expansions have been used previously to reduce collision integrals to differential operators. A particularly clear derivation of the electron Fokker-Planck equation has been given by Bernstein[11]—an account which serves to motivate our approach here.

The derivation of Brownian-motion Fokker-Planck equations depends essentially on the smallness of the relative change of the particle velocity-distribution function f_p within a typical collision time. Accordingly, the change in $\vec{u}_p$ per collision has to be small compared to the width of $f_p(\vec{u}_p)$, which can in principle take arbitrary values. However, except for situations very far from equilibrium,[13] this characteristic width is of the order of the equipartition velocity $(kT/m_p)^{1/2}$. Also, from (13), the change in $\vec{u}_P$ per collision is $M\Delta\vec{g}$, of the order of $M(kT/m)^{1/2}$ for a light gas close to equilibrium. Thus, the relative change in $\vec{u}_P$ per collision is a small number of the order of $M^{1/2}$, and we can expand $f_p(\vec{u}_p + M\Delta\vec{g})$ in a Taylor series. We shall keep two terms in the expansion in order to make it valid to first order in M:

$$f_p(\vec{u}_p + M\Delta\vec{g}) = f_p(\vec{u}_p) + M\Delta\vec{g}\cdot\frac{\partial f_p(\vec{u}_p)}{\partial\vec{u}_p} + \frac{M^2}{2}\Delta\vec{g}\Delta\vec{g}:\frac{\partial^2 f_p(\vec{u}_p)}{\partial\vec{u}_p\partial\vec{u}_p} + \cdots \ . \tag{16}$$

We wish to emphasize that our approach differs slightly from existing theories of heavy-particle motion by the choice of expansion parameter. Our expansion is carried out using the small parameter M rather than m/m_p. In the limit $m/m_p \to 0$, both expansions yield the same asymptotic result. The expansion in M, however, takes partial account of the finite mass of the heavy particle (which would otherwise be obtained by more laborious summations of the full perturbation series). For practical applications this may extend the range of the theory at the expense of being unsystematic in the small parameter m/m_p. For purposes of comparison with the usual Fokker-Planck equation friction coefficient and the thermophoretic drag force, it is only necessary to replace M by m/m_p.

Substituting (16) in (15), and taking f_p and its derivatives out of the integral (they are independent on $\vec{g}$ and Ω), we obtain

$$J_p = f_p(\vec{u}_p)\int d^3g\, g\sigma\, d\Omega[f(\vec{u}\,') - f(\vec{u})] + M\frac{\partial f_p}{\partial\vec{u}_p}\cdot\int d^3g\, g\Delta\vec{g}\sigma\, d\Omega\, f(\vec{u}\,') + \tfrac{1}{2}M^2\frac{\partial^2 f_p}{\partial\vec{u}_p\partial\vec{u}_p}:\int d^3g\, g\Delta\vec{g}\Delta\vec{g}\sigma\, d\Omega\, f(\vec{u}\,') + \cdots \ . \tag{17}$$

With this little effort, the dependence of J_P on f_p has become rather simple. However, the coefficients (integrals) multiplying f_p and its derivatives in (17) are still functions of $\vec{u}_p$ and the mass ratio through $\vec{u}\,'$. Further reduction can be achieved by using the variable $\vec{\eta}$ in place of $\vec{u}\,'$ via a new mass expansion:

$$f(\vec{u}\,') = f(\vec{\eta} + M\Delta\vec{g}) = f(\vec{\eta}) + M\Delta g\cdot\frac{\partial f}{\partial\vec{\eta}} + \frac{M^2}{2}\Delta\vec{g}\Delta\vec{g}:\frac{\partial^2 f}{\partial\vec{\eta}\partial\vec{\eta}} \ . \tag{18}$$

Now, it might seem that the M^2 term in (18) is superfluous in a first-order theory because both $\vec{\eta}$ and $\Delta\vec{g}$ are of the order of $(kT/m)^{1/2}$. However, since

$\vec{\eta}=\vec{u}_p-\vec{g}\,'$, the $\partial/\partial\vec{\eta}$ operators acting on $f(\vec{\eta})$ within the intergrals can be converted into $\partial/\partial\vec{u}_p$ operators acting on the integrals themselves to show that the M^2 term in (18) is of first order. One can further check that the resulting expression for J_p does not conserve mass unless the M^2 term is retained. Then, regrouping terms, (17) becomes

$$J_p=af_p+\frac{\partial}{\partial\vec{u}_p}\cdot\left[\vec{b}f_p+\frac{1}{2}\frac{\partial}{\partial\vec{u}_p}\cdot(\overleftrightarrow{\Pi}f_p)\right] \tag{19}$$

in terms of only a, $\vec{b}$, and $\overleftrightarrow{\Pi}$ defined as

$$a\equiv\int d^3g\,\sigma g\,d\Omega[f(\vec{u}_p-\vec{g}\,')-f(\vec{u}_p-\vec{g})]\,, \tag{20}$$

$$\vec{b}\equiv\int d^3g\,d\Omega\,\sigma gM\Delta\vec{g}f(\vec{u}_p-\vec{g}\,')\,, \tag{21}$$

$$\overleftrightarrow{\Pi}\equiv\int d^3g\,d\Omega\,\sigma gM^2\Delta\vec{g}\Delta\vec{g}f(\vec{u}_p-\vec{g}\,')\,. \tag{22}$$

To show that a is zero and to simplify the angular integration of (21) and (22) we change from the variable $\vec{g}$ to $\vec{g}\,'$ via a rotation, keeping the solid angle variable unchanged. The Jacobian of the transformation is unity, and it preserves the value of g. For instance,

$$\int d^3g\,\sigma g\,d\Omega\,f(\vec{u}_p-\vec{g}\,')=\int d^3g'\sigma g'f(\vec{u}_p-\vec{g}\,')d\Omega\,,$$

and upon dropping the primes it becomes $\int d^3g\,gf(\vec{u}_p-\vec{g})\sigma\,d\Omega$, making

$$a=0\,. \tag{23}$$

Analogously,

$$\vec{b}=\int d^3g(\vec{g}-\vec{g}\,')Mg\sigma\,d\Omega\,f(\vec{u}_p-\vec{g})\,, \tag{24}$$

$$\overleftrightarrow{\Pi}=\int d^3g(\vec{g}-\vec{g}\,')(\vec{g}-\vec{g}\,')M^2g\sigma\,d\Omega\,f(\vec{u}_p-\vec{g})\,. \tag{25}$$

III. INTEGRATION OVER THE SOLID ANGLE $d\Omega$

The $d\Omega$ integration can be carried out in (24) and (25) because $f(\vec{\eta})$ is independent of Ω and $\sigma=\sigma(\theta,g)$. The only ϕ dependence is in $\vec{g}\,'$, which for $\vec{g}=(0,0,g)$ is (see Fig. 1)

$$\vec{g}\,'=g(\sin\theta\cos\phi,\sin\theta\sin\phi,\cos\theta)\,. \tag{26}$$

Then

$$\int_0^{2\pi}d\phi(\vec{g}-\vec{g}\,')=2\pi g(1-\cos\theta)\vec{e}_3=2\pi\vec{g}(1-\cos\theta)\,, \tag{27}$$

since odd terms in $\sin\phi$ or $\cos\phi$ integrate to zero. Analogously,

$$\int_0^{2\pi}d\phi(\vec{g}-\vec{g}\,')(\vec{g}-\vec{g}\,')=2\pi g^2[\tfrac{1}{2}\sin^2\theta(\vec{e}_1\vec{e}_1+\vec{e}_2\vec{e}_2)+(1-\cos\theta)^2\vec{e}_3\vec{e}_3]\,.$$

Again $g^2\vec{e}_3\vec{e}_3=\vec{g}\vec{g}$ while $\vec{e}_1\vec{e}_1+\vec{e}_2\vec{e}_2+\vec{e}_3\vec{e}_3=\overleftrightarrow{I}$, and $(1-\cos\theta)^2=2(1-\cos\theta)-\sin^2\theta$, so that,

$$\int_0^{2\pi}d\phi(\vec{g}-\vec{g}\,')(\vec{g}-\vec{g}\,')=2\pi[\tfrac{1}{2}\sin^2\theta(g^2\overleftrightarrow{I}-3\vec{g}\vec{g})+2\vec{g}\vec{g}(1-\cos\theta)]\,. \tag{28}$$

Defining

$$Q_1(g)\equiv2\pi\int_0^{\pi}\sigma(\theta,g)(1-\cos\theta)\sin\theta\,d\theta\,, \tag{29}$$

$$Q_2(g)\equiv2\pi\int_0^{\pi}\sigma(\theta,g)\tfrac{1}{2}\sin^2\theta\sin\theta\,d\theta\,, \tag{30}$$

we obtain

$$\vec{b}=M\int d^3g\,g\vec{g}Q_1f(\vec{\eta})\,, \tag{31}$$

$$\overleftrightarrow{\Pi}=M^2\int d^3g\,g[(g^2\overleftrightarrow{I}-3\vec{g}\vec{g})Q_2+2\vec{g}\vec{g}Q_1]f(\vec{\eta})\,. \tag{32}$$

This result is of a rather general value, being constrained only by the condition $m_p/m\gg1$. But to proceed further one has to specify the light-gas distribution function.

IV. LIGHT-GAS VELOCITY-DISTRIBUTION FUNCTION

In previous works, $f(\vec{u})$ has been taken to be a Maxwellian distribution. Here we shall consider the more general case of a slightly nonequilibrated gas, where f is given by the first-order Chapman-Enskog expansion for a nonuniform gas. The complete first-order expression contains functions which are solutions to integral equations occurring in the Chapman-Enskog theory. In the ensuing calculation, we will approximate these functions by the first term in their Sonine polynomial expansions. Accordingly, the first approximation is (Ref. 14, p. 280)

$$f(\vec{u})=n\left[\frac{m}{2\pi kT}\right]^{3/2}e^{-c^2}[1-\vec{\epsilon}\cdot\vec{c}(c^2-\tfrac{5}{2})-\overleftrightarrow{K}:\vec{c}\,\vec{c}\,]\,, \tag{33}$$

where n is the light-gas number density,

$$\vec{c} \equiv \vec{u}/(2kT/m)^{1/2} , \quad (34)$$

$\vec{\epsilon}$ is the nondimensional temperature gradient

$$\vec{\epsilon} \equiv \frac{3\mu}{p}\left[\frac{2kT}{m}\right]^{1/2} \vec{\nabla} \ln T , \quad (35)$$

$\overleftrightarrow{K}$ is the nondimensional, symmetrized, and traceless velocity-gradient tensor

$$K_{ij} \equiv \frac{\mu}{p}\left[\frac{\partial V_i}{\partial x_j}+\frac{\partial V_j}{\partial x_i}-\tfrac{2}{3}\delta_{ij}\vec{\nabla}\cdot\vec{V}\right] , \quad (36)$$

where $\vec{V}=(V_1,V_2,V_3)$ is the light-gas velocity field, and μ and p its viscosity coefficient and pressure, respectively. For simplicity we have used a reference frame in which $\vec{V}=\vec{0}$. The purpose of including the terms in $\vec{\epsilon}$ (proportional to $\vec{\nabla}\ln T$) and $\overleftrightarrow{K}$ (proportional to the deceleration tensor $\vec{\nabla}\vec{V}$) is to study the effects of nonuniformity on the governing equation for the light gas, particularly of thermal diffusion which has been absent from previous works. Once f is treated as known in (31) and (32), the coefficients $\vec{b}$ and $\overleftrightarrow{\Pi}$ can be calculated. They depend on $\vec{u}_p$ in a complicated form, and for that reason one might be tempted to expand again $f(\vec{u}_p-\vec{g})$ in the integrands of (31) and (32). However, this would not be a mass expansion because not only the standard deviation of $\vec{u}_p$ but also its mean value relative to the gas would have to be small compared with $(2kT/m)^{1/2}$. There are a number of problems in which such requirement is not met. Of particular interest among those is the expansion of a binary mixture of gases with disparate masses into a vacuum. There, the relative velocity between the light and heavy components does become comparable with $(2kT/m)^{1/2}$ and the full expression (31) for $\vec{b}$ has to be used. The recognition of this fact considerably widens the spectrum of possible Fokker-Planck equations. Nonetheless, such a general case will be left untreated here where we shall concentrate on the milder situation, where the mean value of $\vec{u}_p$ relative to the gas $\langle\vec{u}_p\rangle$, is small compared to the characteristic value of g, $(kT/m)^{1/2}$. Then, $f(\vec{u}_p-\vec{g})$ can be expanded about $-\vec{g}$, and the terms of order greater than first can be neglected being quadratic in the small parameter $\langle u_p\rangle/(2kT/m)^{1/2}$, the relative Mach number. In what follows, for simplicity, we treat this group as if it were of order $M^{1/2}$. Then, $\vec{b}$ and $\overleftrightarrow{\Pi}$ can be expressed in terms of the standard Chapman-Enskog coefficients of diffusion and thermal diffusion, as done below.

V. LIMIT OF SMALL MEAN RELATIVE MACH NUMBER $\langle u_p\rangle/(2kT/m)^{1/2}$

Treating $\vec{u}_p$ as a quantity of order $M^{1/2}$, J_p will remain the same to first order in M if we take for $\vec{b}$ and $\overleftrightarrow{\Pi}$,

$$\vec{b}=\vec{b}_1+\vec{u}_p\cdot\overleftrightarrow{B}+\cdots , \quad (37)$$

$$\overleftrightarrow{\Pi}=M^2\int d^3g\, g[(g^2\overleftrightarrow{I}-3\vec{g}\vec{g})Q_2 +2\vec{g}\vec{g}Q_1]f(-\vec{g})+\cdots , \quad (38)$$

where $\vec{b}_1$, $\overleftrightarrow{B}$, and $\overleftrightarrow{\Pi}$ are now $\vec{u}_p$ independent:

$$\vec{b}_1=M\int d^3g\, g\vec{g}Q_1 f(-\vec{g}) , \quad (39)$$

$$\overleftrightarrow{B}=M\int d^3g\, g\vec{g}Q_1\frac{\partial f(-\vec{g})}{\partial\vec{g}} . \quad (40)$$

Substituting now Eq. (33) for $f(\vec{g})$ in (39), by symmetry, the Maxwellian portion of f and the $\overleftrightarrow{K}$ term give no contribution. Thus,

$$\vec{b}_1=\frac{Mn}{\pi^{3/2}}\left[\frac{2kT}{m}\right]^2 \vec{\epsilon}\cdot\int d^3c\, \vec{c}\,\vec{c}\,(c^2-\tfrac{5}{2})cQ_1e^{-c^2} , \quad (41)$$

again, by symmetry, only the diagonal terms of the tensor $\vec{c}\,\vec{c}$ in (41) give a nonzero contribution to the above integral which is proportional to $\overleftrightarrow{I}$. Therefore,

$$\vec{b}_1=\frac{Mn}{3\pi^{1/2}}\frac{8kT}{m}\vec{\epsilon}S_b , \quad (42)$$

with

$$S_b\equiv\int_0^\infty dc\, c^5(c^2-\tfrac{5}{2})e^{-c^2}Q_1(c) . \quad (43)$$

Analogously, only the first and third components of f contribute to $\overleftrightarrow{B}$. Ignoring the latter for the moment, Eq. (40) yields[15]

$$\overleftrightarrow{B}=\frac{Mn}{\pi^{3/2}}\left[\frac{2kT}{m}\right]^{1/2}\int d^3c\, c\vec{c}(2\vec{c}e^{-c^2})Q_1(c) .$$

But again the integral is proportional to $\overleftrightarrow{I}$, reducing to

$$\overleftrightarrow{B}=\frac{8Mn}{\pi^{1/2}}\left[\frac{2kT}{m}\right]^{1/2}\overleftrightarrow{I}S_B , \quad (44)$$

with

$$S_B\equiv\int_0^\infty dc\, c^5e^{-c^2}Q_1(c) . \quad (45)$$

Finally, also ignoring $\overleftrightarrow{K}$, only the Maxwellian portion of f contributes to $\overleftrightarrow{\Pi}$, thus

$$\overleftrightarrow{\Pi}=M^2\frac{n}{\pi^{3/2}}\left[\frac{2kT}{m}\right]^{3/2}\times\int d^3c\, c e^{-c^2}[(c^2\overleftrightarrow{I}-3\vec{c}\,\vec{c}\,)Q_2+\vec{c}\,\vec{c}\,Q_1]\ .$$

Again the integral is proportional to $\overleftrightarrow{I}$, and because the tensor multiplying Q_2 has zero trace and does not contribute, $\overleftrightarrow{\Pi}$ reduces to

$$\overleftrightarrow{\Pi}=\frac{8nM^2}{3\pi^{1/2}}\left[\frac{2kT}{m}\right]^{3/2}\overleftrightarrow{I}S_B\ . \tag{46}$$

$\overleftrightarrow{B}$ and $\overleftrightarrow{\Pi}$ are related to the usual particle relaxation time τ (the inverse of the friction coefficient)

$$\tau^{-1}\equiv\frac{8Mn}{3\sqrt{\pi}}\left[\frac{2kT}{m}\right]^{1/2}S_B \tag{47}$$

by

$$\overleftrightarrow{B}=\tau^{-1}\overleftrightarrow{I}\ , \tag{48}$$

$$\overleftrightarrow{\Pi}=\tau^{-1}\overleftrightarrow{I}M\frac{2kT}{m}\simeq\tau^{-1}\overleftrightarrow{I}\frac{2kT}{m_p}\ . \tag{49}$$

Analogously, $\vec{b}_1$ can be related to the thermal-diffusion coefficient. Taking the limit of negligible heavy-species mole fraction and very small mass ratio $m/m_p\to 0$, the Chapman-Enskog thermal-diffusion coefficient becomes (Ref. 14, Sec. 14.7)

$$\alpha_T=-\frac{3}{2}\frac{S_b}{S_B}S_c\ , \tag{50}$$

where S_c is the Schmidt number or ratio between the kinematic viscosity of the carrier gas and the diffusivity of the mixture D,

$$S_c\equiv\frac{\mu}{mnD}\ , \tag{51}$$

and D is related to τ via

$$D=\frac{kT\tau}{m_p}\ . \tag{52}$$

Indeed, from (50), (47), and (35),

$$\vec{b}_1\tau=-D\alpha_T\vec{\nabla}\ln T\ , \tag{53}$$

and substituting (53), (50), (49), (48), and (37) into (19) we finally obtain

$$J_p=\frac{1}{\tau}\frac{\partial}{\partial\vec{u}_p}\cdot\left[f_p(\vec{u}_p-D\alpha_T\vec{\nabla}\ln T)+\frac{kT}{m_p}\frac{\partial f_p}{\partial\vec{u}_p}\right]\ . \tag{54}$$

This generalizes the usual Fokker-Planck Brownian-motion collision operator to include the effect of temperature gradients in the carrier gas. Interestingly enough, the only new effect is a "thermal acceleration" equal to $\tau^{-1}D\alpha_T\vec{\nabla}\ln T$. The second-order term remains unchanged.

VI. DISCUSSION: THERMAL DIFFUSION VERSUS THERMOPHORESIS

Equation (54) reveals that the direct consequence of including the distortion in the light-gas distribution function due to temperature gradients is the appearance of a thermal-diffusion term in the Fokker-Planck equation. This term is equivalent to a net thermal force on the particle equal to

$$F_T=\frac{m_p}{\tau}D\alpha_T\vec{\nabla}\ln T\ , \tag{55}$$

which leads to a particle-drift velocity equal to $D\alpha_T\vec{\nabla}\ln T$, identical with the Chapman-Enskog thermal-diffusion velocity for a dilute and very heavy species diffusing in a light gas. Such a result is not surprising on the perspective of the work of Waldmann[16] on thermophoresis, and the paper of Mason and Chapman[17] on the close connection between thermophoresis and thermal diffusion. Thermophoresis is the drift of Brownian particles down temperature gradients. It is a phenomenon closely related to thermal diffusion, except that it affects the particles in a two-phase flow (a dusty gas) rather than the components of a binary mixture of gases. Also, the coefficient α_T is of order unity for ordinary gas mixtures, but reaches values of 10^7 or higher for microscopic particles suspended in a gas.[18] A theoretical explanation of this phenomenon (for particles smaller than the suspending gas mean-free path) was given by Waldmann[16] by making a momentum balance on a spherical particle fixed somewhere within a gas. At every point on the surface of the particle the gas molecules impinge and rebound at a certain rate, exerting some stress, whose integral over the particle surface yields a net force. If the gas-distribution function and the laws of reflection at the wall are specified, such a momentum balance can be carried out straightforwardly and the result is a vanishing force when the chosen gas-velocity-distribution function f is Maxwellian. However, Waldmann found that the force has the expected order of values when the Chapman-Enskog expression [Eq. (33)] is used for f. He thus unequivocally showed the direct link between thermophoresis and the departure from the equilibrium Maxwellian, which temperature gradients impose upon the gas-velocity distribution. The next important step towards the clarification of the nature of thermophoresis was taken by Mason and Chapman,[17] who showed that Waldmann's thermophoresis and thermal diffusion were the same thing provided that the law of reflection of the gas molecules on the particle surface were of an elastic nature (like the interactions of the kinetic theory of monoatomic gases). Then, the integrals from Waldmann's momentum balance and those appearing in the Chapman-Enskog (CE) thermal-diffusion coefficient are identical,[19] and directly related to our coefficient $\vec{b}_1$ [Eq. (39)]. Our result (53) is thus another confirmation of what Waldmann and Mason and Chapman had already demonstrated by different means. However, our analysis also shows that the second-order term in (54) is unaffected by the presence of temperature gradients. In spite of the existence of a privileged direction $\vec{n}_T = \vec{\nabla}\ln T / |\vec{\nabla}\ln T|$, the diffusivity tensor is still isotropic. As seen in Sec. V, this results from the antisymmetry of the thermal perturbation to $f(\vec{u})$, and still holds true for inelastic gas-particle interactions provided the reflection laws are orientation independent (this is always true for spherical particles). Accordingly, even if the kinetic-theory formalism does not encompass the inelastic interaction occurring most often at the particle surface, Eq. (54) still holds for Brownian particles, provided the coefficient α_T is calculated properly (or measured).

VII. EFFECT OF NONUNIFORMITIES IN THE LIGHT-GAS VELOCITY FIELD

The $\overleftrightarrow{K}$ term (proportional to the light-gas velocity-gradient tensor) in Eq. (26) contributes to the tensors $\overleftrightarrow{\Pi}$ and $\overleftrightarrow{B}$ by the amounts $\Delta\overleftrightarrow{\Pi}$ and $\Delta\overleftrightarrow{B}$ given by

$$\Delta\overleftrightarrow{B} = Mn\left[\frac{m}{2\pi kT}\right]^{3/2}\left[\frac{2kT}{m}\right]^2 \times \int d^3c\, c\vec{c}\,Q_1(c)\frac{\partial}{\partial\vec{c}}(\vec{c}\,\vec{c}\,e^{-c^2}):\overleftrightarrow{K}\ , \quad (56)$$

$$\Delta\overleftrightarrow{\Pi} = -M^2 n\left[\frac{m}{2\pi kT}\right]^{3/2}\left[\frac{2kT}{m}\right]^3 \times \int d^3c\, ce^{-c^2}[(c^2\overleftrightarrow{I} - 3\vec{c}\,\vec{c})Q_2 + 2\vec{c}\,\vec{c}\,Q_1]\vec{c}\,\vec{c}:\overleftrightarrow{K}\ . \quad (57)$$

$\Delta\overleftrightarrow{B}$ will be evaluated using tensoral notation with (Einstein's notation) implicit summation with respect to repeated subindices

$$\left[a_i b_i \equiv \sum_{i=1}^{3} a_i b_i\right].$$

Since

$$\frac{\partial}{\partial c_i}(c_j c_k e^{-c^2}) = (\delta_{ij}c_k + \delta_{ik}c_i - 2c_i c_j c_k)e^{-c^2}\ , \quad (58)$$

evaluation of $\Delta\overleftrightarrow{B}$ requires the calculation of functions of the form

$$P_{ijkl} \equiv \int d^3c\, F(c)c_i c_j c_k c_l\ . \quad (59)$$

By its symmetry respect to all indices, using spherical coordinates in (59), one may relate P to the tensor Λ,

$$\Lambda_{ijkl} \equiv \delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{kj}\ , \quad (60)$$

as follows:

$$P_{ijkl} = \frac{4\pi}{15}\Lambda_{ijkl}\int_0^\infty c^6 F(c)dc\ . \quad (61)$$

One may also note that, because $\overleftrightarrow{K}$ is symmetric and has zero trace,

$$\Lambda_{ijkl}K_{kl} = 2K_{ij}\ . \quad (62)$$

With those results we find

$$\Delta\overleftrightarrow{B} = \frac{4\pi}{15}\overleftrightarrow{K}\tau^{-1}\frac{\alpha_T}{S_c} \quad (63)$$

and

$$\Delta\overleftrightarrow{\Pi} = -\overleftrightarrow{\Pi}\cdot\overleftrightarrow{K}\frac{S_\pi}{5S_B} \quad (64)$$

with

$$S_\pi \equiv \int_0^\infty c^7 e^{-c^2}dc\,(2Q_1 - 3Q_2)\ . \quad (65)$$

But both S_π and α_T/S_c are numbers of order unity, while $\overleftrightarrow{K}$ is a very small number formed with the macroscopic fluid deceleration time $(\sim\vec{\nabla}\vec{V})^{-1}$ and the very small light-gas relaxation time μ/p. The tensor $\overleftrightarrow{K}$ is therefore of the order of the light-gas Knudsen number, and the corrections $\Delta\overleftrightarrow{\Pi}$ and $\Delta\overleftrightarrow{B}$ are small.[23] The only generalization to Eq. (54) accounting for the fact that the light-gas velocity field is not zero is a local translation by an amount $\vec{V}(\vec{x},t)$ of the velocity $\vec{u}_p$ appearing in the collision operator with no consideration for the gradients of $\vec{V}$. The final form of the Fokker-Planck equation in a nonuniform gas is therefore

$$\frac{\partial f_p}{\partial t}+\vec{\nabla}\cdot(\vec{u}_p f_p)+\vec{\nabla}_{u_p}\cdot(\vec{a}f_p) =\frac{1}{\tau}\vec{\nabla}_{u_p}\cdot\left[f_p(\vec{u}_p-\vec{V}-D\alpha_T\vec{\nabla}\ln T)+\frac{kT}{m_p}\vec{\nabla}_{u_p}f_p\right], \quad (66)$$

where $\vec{a}$ is the acceleration due to external body forces on the Brownian particles.

VIII. FINAL NOTE ON RELATED WORKS

After submitting this paper for publication we have found several related works[26] which reach conclusions similar to ours, although starting from the theory of stochastic processes rather than from the Boltzmann equation. Those references are reviewed by Brock,[27] whose paper also contains a valuable section on thermophoresis.

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(Ref. 20). We are in debt to R. Israel for pointing out the coincidence between the Chapman-Enskog α_T and Waldmann's thermophoretic coefficient before we were aware of Ref. 17 (see Ref. 21). Waldmann himself discussed such similarity in his more recent work with Schmitt (Ref. 22).

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