Journal of Statistical Physics, Vol. 3, No. 3, 1971

Brownian Diffusion in a Nonuniform Gas

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Received January 12, 1971

An analysis is made of the effects on the diffusion of Brownian particles whose Knudsen number is large compared to unity, of nonuniformities in the host gas. As examples, in one type of nonuniformity of the host gas, the Chapman–Enskog velocity distribution function for the gas molecules is used; in the other, the host gas is a free-molecule Couette flow. In both cases, a new force on the Brownian particles appears. Two techniques are used (extending Kramers' method and utilizing the Chapman–Enskog method) to transform the new Fokker–Planck equation into generalized Smoluchowski and convective diffusion equations. In these equations, the diffusion coefficient appears as a second-order tensor. Thus, it is demonstrated that Brownian diffusion in a nonuniform gas is anisotropic.

KEY WORDS: Anisotropic Brownian motion; convective diffusion; stressphoresis; kinetic theory; stochastic processes; nonequilibrium transport phenomena.

1. INTRODUCTION

In most practical applications of the convective diffusion equation involving Brownian particles, the host fluid is not in equilibrium. Yet it is traditional to use Einstein's diffusion coefficient in this equation. However, Einstein's(1) and most subsequent derivations(2–6) of the diffusion coefficient are based on the assumption that the host fluid is in thermodynamic equilibrium. The purpose of this report is to describe our recent investigations(7–9) into the effects of nonuniformities in the host gas on Brownian diffusion.

A number of studies have been made on the mean motion, as opposed to the

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The work of Slinn was financially supported in part by Battelle Memorial Institute and in part by U.S. Atomic Energy Commission Contract AT(45-1)-1830. The work of Shen was supported in part by U.S. Air Force Office of Scientific Research Contract 49(638)-1346.

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diffusion, of Brownian particles (B particles) in a nonuniform gas. Such studies have illuminated, for example, the thermopheresis and diffusiophoresis phenomena. The recent review article by Waldmann and Schmitt(10) contains many references. An early reference which has been overlooked and which contains an indication of what we shall call stressphoresis (Section 3) is the paper by Bell and Schaaf.(11)

In addition, there have been a few analyses of Brownian diffusion in a nonequilibrium environment. Recently, Mazo(12) has extended the methods of Lebowitz and Resibois and their associates, and has analyzed the motion of a B particle of arbirtary size in a nonequilibrium environment. Although his method is more general than ours, his results are not so explicit. Further comments on his results will be made later in this paper. Zubarev and Bashkirov(13) have also recently studied Brownian motion in a nonuniform system but their major concern was with fluids in which there exists temperature gradient. It will be seen below that, although temperature gradients can significantly influence the mean motion of the particles, velocity gradients are more significant to the particles' diffusion.

The method which is used in this paper is a slight generalization(8) of Chandrasekhar's presentation(6) of Markov's method.(14) The use of Markov's method restricts our analysis to the case of B particles whose Knudsen number is large compared to unity. After describing the method in Section 2, it will be applied to the motion of a B-particle in a Chapman–Enskog host gas in Section 3 and in a free-molecule Couette flow in Section 4. The appropriate Fokker–Planck equation is discussed in Section 5, and in the following sections, the new convective-diffusion equation is derived. Throughout this report, interactions between B particles are ignored and, for simplicity, only spherical particles are considered.

2. MARKOV'S METHOD

Newton's second law will be used as the basis for our description of the motion of a B particle in a nonuniform gas. Thus, if the particle has mass M and velocity $\mathbf{V}$, then

$$\mathbf{F} = M\, d\mathbf{V}/dt \tag{1}$$

where $\mathbf{F}$ is the sum of the forces on the particle arising from impacts by the gas molecules. Rather than attempt to determine the statistical properties of $\mathbf{F}$, it is more convenient to seek the probability density function (pdf) of the total change in momentum,

$$\mathbf{P} = \mathbf{F}\,\Delta t = M\,\Delta\mathbf{V} \tag{2}$$

that the B particle incurs during Δt. If molecule j delivers momentum $\mathbf{p}_j$ to the particle during Δt, then

$$\mathbf{P} = \sum_{j=1}^{N} \mathbf{p}_j \tag{3}$$

where N is the (unknown) total number of molecules that collide with the particle during Δt.

Markov's method can be used to determine the pdf of $\mathbf{P}$ from the pdf's $\tau_j(\mathbf{q}_j)$ of the variables $\mathbf{q}_j$ upon which each $\mathbf{p}_j$ depends. For example, one of these variables upon which $\mathbf{p}_j$ depends is the velocity of the molecule $\boldsymbol{\xi}$. In this case, the pdf $\tau(\boldsymbol{\xi})$ is the velocity "distribution function." Unfortunately, Markov's method is restricted to the case for which the $\mathbf{p}_j$ are independent, random variables. Thus, it is necessary that the motion of the molecules in the neighborhood of the B particle be independent of one another. Consequently, it is required that the Knudsen number of the particle (the ratio of the mean free path for the gas molecules, λ, to the radius of the particle, a) satisfy $Kn \gg 1$. Similar restrictions permitted Uhlenbeck and Goudsmit to analyze the rotational Brownian movement of a mirror suspended on a fine wire in a rarefied gas (see Section 12 of Ref. 4).

Using Markov's result, the pdf for $\mathbf{P}$ is

$$W(\mathbf{P}) = [1/(2\pi)^3] \int d\boldsymbol{\rho}\, A_N(\boldsymbol{\rho}) \exp(-i\boldsymbol{\rho} \cdot \mathbf{P}) \tag{4}$$

where

$$A_N(\boldsymbol{\rho}) = \prod_{j=1}^{N} \int d\mathbf{q}_j\, \tau_j(\mathbf{q}_j) \exp(i\boldsymbol{\rho} \cdot \mathbf{p}_j) \tag{5}$$

For the case that the pdf's $\tau_j(\mathbf{q}_j)$ are the same for all j, then Eq. (5) becomes

$$A_N(\boldsymbol{\rho}) = \left[\int d\mathbf{q}\, \tau(\mathbf{q}) \exp(i\boldsymbol{\rho} \cdot \mathbf{p})\right]^N \tag{6}$$

Further, if N is large, then using

$$e = \lim_{h\to\infty}[1 + (1/h)]^h \qquad \text{and} \qquad \int d\mathbf{q}\, \tau(\mathbf{q}) = 1$$

Eq. (6) becomes

$$A_N(\boldsymbol{\rho}) = \exp[-C(\boldsymbol{\rho})] \tag{7}$$

where

$$C(\boldsymbol{\rho}) = N \int d\mathbf{q}\, \tau(\mathbf{q})[1 - \exp(i\boldsymbol{\rho} \cdot \mathbf{p})] \tag{8}$$

This result was indicated by Chandrasekhar$^{(6)}$ in his Eq. (54).

If the pdf's are sufficiently well behaved so that the central-limit theorem is applicable,$^{(15)}$ then Markov's method can be extend to an even more convenient result. Expanding $C(\boldsymbol{\rho})$ for small $\boldsymbol{\rho}$ and keeping only the first two terms of the expansion leads to

$$C(\boldsymbol{\rho}) = -i\boldsymbol{\rho} \cdot N\langle\mathbf{p}\rangle + \tfrac{1}{2}\boldsymbol{\rho} \cdot N\langle\mathbf{pp}\rangle \cdot \boldsymbol{\rho} \tag{9}$$

where

$$\langle\mathbf{p}\rangle = \int d\mathbf{q}\, \tau(\mathbf{q})\, \mathbf{p} \tag{10}$$

$$\langle\mathbf{pp}\rangle = \int d\mathbf{q}\, \tau(\mathbf{q})\, \mathbf{pp} \tag{11}$$

Substituting Eq. (9) into Eq. (7) and the result into Eq. (4) will lead to the prediction that **P** has a normal distribution with mean given by Eq. (10) and variance related to Eq. (11). The well-known restrictions for the central-limit theorem to be valid lead to the requirement that the number of events $\bar{M}$ (which can be estimated to $\bar{n}\bar{c}4\pi a^2\,\Delta t$, where $\bar{n}$ is the mean number density and $\bar{c}$ is the mean thermal speed of the molecules) must satisfy $\bar{M}^{1/2} \gg 1$. In the next two sections, Eqs. (10) and (11) will be evaluated for two specific flow fields.

3. CHAPMAN–ENSKOG HOST GAS

Since N is the number of molecules that hit the particle during Δt and since $\langle\mathbf{p}\rangle$ is the average momentum delivered by a single molecule, then $N\langle\mathbf{p}\rangle$ is the mean, total momentum which is delivered to the B particle during Δt. Similarly, $N\langle\mathbf{pp}\rangle$ is the average amount of the dyadic or second-order tensor, **pp**. Rather surprisingly, in spite of the considerable number of investigations into the mean motion of particles in a nonuniform gas (see Ref. 10), it appears that even the calculation of $N\langle\mathbf{p}\rangle$ has not been performed using the complete Chapman–Enskog velocity distribution function. In this section, both $N\langle\mathbf{p}\rangle$ and $N\langle\mathbf{pp}\rangle$ will be evaluated for the case of a B particle with large Knudsen number moving in a Chapman–Enskog host gas.

To simplify the calcualations, an external coordinate system (X', Y', Z') is chosen which, in the neighborhood of the particle, diagonalizes the viscous stress tensor $\boldsymbol{\tau}$. The Chapman–Enskog velocity distribution function is

$$f = f^{(0)}[1 - \phi] \tag{12}$$

where

$$f^{(0)} = (\gamma/\pi)^{3/2} \exp(-\gamma \mathbf{C} \cdot \mathbf{C}) \tag{13}$$

and

$$\phi = (\gamma/p)\{\mathbf{C} \cdot \boldsymbol{\tau} \cdot \mathbf{C} + 2[1 - (2/5)\gamma \mathbf{C} \cdot \mathbf{C}]\, \mathbf{q} \cdot \mathbf{C}\} \tag{14}$$

in which

$$\boldsymbol{\tau} = \tau_1 \hat{\mathbf{I}}\hat{\mathbf{I}} + \tau_2 \hat{\mathbf{J}}\hat{\mathbf{J}} + \tau_3 \hat{\mathbf{K}}\hat{\mathbf{K}} \tag{15}$$

τ_i are the principal stresses; **q** is the heat flux; **C** is the thermal velocity of the molecules; **p** is the pressure; $\gamma = m/2kT$, where m is the mass of a molecule; k is Boltzmann's constant; and T is the local temperature.

The Chapmann–Enskog distribution function will now be recast into a more convenient form. First, if with respect to the inertial frame (X', Y', Z'), the velocity of a molecule is $\boldsymbol{\xi}'$ and the local velocity of the fluid is $\mathbf{V}^{(f)}$, then

$$\mathbf{C} = \boldsymbol{\xi}' - \mathbf{V}^{(f)} \tag{16}$$

Further, if the velocity of the B particle with respect to (X', Y', Z) is **V**, then the velocity of a molecule with respect to the particle is

$$\boldsymbol{\xi} = \boldsymbol{\xi}' - \mathbf{V} = \mathbf{C} - (\mathbf{V} - \mathbf{V}^{(f)}) = \mathbf{C} - \mathbf{v} \tag{17}$$

where

$$\mathbf{v} = (\mathbf{V} - \mathbf{V}^{(f)}) = (u, v, w) \tag{18}$$

is the relative velocity between the particle and the fluid. We expect this velocity to be small compared with the thermal speed of the molecules; i.e.,

$$\mathbf{S} = \gamma^{1/2}\mathbf{V} \ll 1 \tag{19}$$

Finally, expanding Eq. (12) for $S \ll 1$ leads to

$$\begin{aligned} f = \pi^{-3/2} \exp(-\boldsymbol{\xi} \cdot \boldsymbol{\xi})[1 &- 2\boldsymbol{\xi} \cdot \mathbf{S} - 2\mathbf{q} \cdot \boldsymbol{\xi} - 2\mathbf{q} \cdot \mathbf{S} - \boldsymbol{\xi} \cdot \boldsymbol{\tau} \cdot \boldsymbol{\xi} - 2\boldsymbol{\xi} \cdot \boldsymbol{\tau} \cdot \mathbf{S} \\ &+ 2\boldsymbol{\xi} \cdot \mathbf{S}\boldsymbol{\xi} \cdot \boldsymbol{\tau} \cdot \boldsymbol{\xi} + (4/5)\boldsymbol{\xi} \cdot \boldsymbol{\xi}\mathbf{q} \cdot \boldsymbol{\xi} + (4/5)\boldsymbol{\xi} \cdot \boldsymbol{\xi}\, \mathbf{q} \cdot \mathbf{S} + (28/5)\boldsymbol{\xi} \cdot \mathbf{S}\mathbf{q} \cdot \boldsymbol{\xi} \\ &- (8/5)\boldsymbol{\xi} \cdot \mathbf{S}\mathbf{q} \cdot \boldsymbol{\xi}\boldsymbol{\xi} \cdot \boldsymbol{\xi} + O(S^2)] \end{aligned} \tag{20}$$

In Eq. (20), velocities are made dimensionless with $\gamma^{1/2}$ and the quantities $\boldsymbol{\tau}$ and $\gamma^{1/2}\mathbf{q}$ are made dimensionless with p, but we have retained the same symbols for the dimensionless quantities as were used when they possessed dimensions.

In this report, only the case of specular reflections of the gas molecules from a B particle's surface will be considered. Recently,(16) we have reported that even for the case of an equilibrium environment, there are some interesting consequences of diffuse reflections; for example, the diffusion coefficient can depend on the temperature of the particle. Similar phenomena occur in a nonequilibrium environment. However, unless the two analyses of uniform and nonuniform gases are presented together (as in Ref. 8), the case of diffuse reflections in the nonequilibrium case adds considerable complications.

To calculate $N\langle\mathbf{p}\rangle$ and $N\langle\mathbf{pp}\rangle$, it is convenient to introduce a coordinate system (x, y, z) with origin at an area element at (a, Θ, Φ) on the surface of the sphere. Here, (a, Θ, Φ) are the usual spherical coordinates of a point on the sphere with respect to the origin, at the center of the sphere, of a coordinate system (X, Y, Z). The basis vectors of (x, y, z) are chosen to be $(\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}) \rightarrow (e_\Theta, e_\Phi, e_R)$. Thus, $\hat{\mathbf{k}}$ is perpendicular to the area element.

For specular reflections of the molecules, the momentum delivered to the area element $\Delta A = a^2 \sin \Theta\, d\Theta\, d\Phi$ by a single molecule of the gas is (by definition)

$$\mathbf{p} = 2m\boldsymbol{\xi} \cdot \hat{\mathbf{k}}\, \hat{\mathbf{k}} \tag{21}$$

The number of molecules in the gas that will hit ΔA during Δt with velocity $\boldsymbol{\xi}$ to $\boldsymbol{\xi} + d\boldsymbol{\xi}$ is

$$\bar{n}f(\boldsymbol{\xi})\, d\boldsymbol{\xi}\, (-\boldsymbol{\xi} \cdot \hat{\mathbf{k}})\Delta A \Delta t \tag{22}$$

Therefore, the mean momentum delivered to the sphere during Δt is

$$-2m\bar{n}a^2\, \Delta t \int_0^{2\pi} d\Phi \int_0^{\pi} d\Theta \sin \Theta \int_{-\infty}^{+\infty} d\xi_x \int_{-\infty}^{+\infty} d\xi_y \int_{-\infty}^{0} d\xi_z\, \xi_z{}^2 f(\boldsymbol{\xi})\, \hat{\mathbf{k}} \qquad (23$$

Similarly, $N\langle \mathbf{pp} \rangle$ is given by

$$-4m^2\bar{n}a^2\,\Delta t\int_0^{2\pi} d\Phi \int_0^{\pi} d\theta \sin\theta \int_{-\infty}^{+\infty} d\xi_x \int_{-\infty}^{+\infty} d\xi_y \int_{-\infty}^{0} d\xi_z\,\xi_z{}^3 f(\boldsymbol{\xi})\,\hat{\mathbf{k}}\hat{\mathbf{k}} \tag{24}$$

Evaluating these integrals is tedious. The velocity distribution function is given by Eq. (20) and it is necessary to use, for example,

$$\hat{\mathbf{k}} = \hat{\mathbf{I}}\sin\Theta\cos\Phi + \hat{\mathbf{J}}\sin\Theta\sin\Phi + \hat{\mathbf{K}}\cos\Theta \tag{25}$$

The results are

$$N\langle \mathbf{p} \rangle = -M\beta\,\Delta t[\mathbf{v} - (1/5p)(\mathbf{q} + \boldsymbol{\tau}\cdot\mathbf{v})] \tag{26}$$

$$N\langle \mathbf{pp} \rangle = M^2\beta\,\Delta t(kT/M)[\mathsf{I} - \tfrac{3}{5}(\boldsymbol{\tau}/p)] \tag{27}$$

where dimensional quantities have again been used and

$$\beta = 4\pi a^2 m\bar{n}\bar{c}/3M \tag{28}$$

is Epstein's drag coefficient.$^{(17)}$ In Eq. (27), I is the identity (or metric) tensor,

$$\mathsf{I} = \hat{\mathbf{I}}\hat{\mathbf{I}} + \hat{\mathbf{J}}\hat{\mathbf{J}} + \hat{\mathbf{K}}\hat{\mathbf{K}} \tag{29}$$

and a term of order $\gamma\mathbf{q}\cdot\mathbf{v}/5p$ has been ignored since it is small compared to $\boldsymbol{\tau}/5p$ if $\gamma^{1/2}\mathbf{v}$ is small.

Equation (26) contains some interesting features. The first term on the right-hand side, the drag force, describes the force on the particle which attempts to nullify the relative velocity. The second term describes the thermophoresis effect: a specularly reflecting B particle with large Knudsen number will drift in the direction of the heat flux with drift velocity $\mathbf{q}/5p$. The third term is new and, in analogy to the second, might be called "stressphoresis." It has also been obtained, independently, by Mazo.$^{(12)}$ It can be seen that this force predicts, for example, that if the B particle is moving more slowly in a shear flow than the local fluid velocity, then the particle will drift across the streamlines, with drift velocity $\mathbf{v}\cdot\boldsymbol{\tau}/5p$ toward a point in the fluid where the relative velocity would be zero. There are some similarities between this force and the $\mathbf{v}\times B$ force of magnetodynamics; there is also the major difference that, in a chapman–Enskog gas, the stressphoresis effect is small.

In Section 5, Eqs. (26) and (27) will be used to obtain a Fokker–Planck equation. However, it might be interesting, now, to present the Langevin equation for the B particle. Substituting Eqs. (26) and (27) into Eq. (9) and evaluating Eqs. (8) and (4) leads to the result that the motion of the B particle can be described by

$$d\mathbf{V}/dt = -\beta\mathbf{V}\cdot[\mathsf{I} - (\boldsymbol{\tau}/5p)] + \mathbf{K} + \mathbf{A} \tag{30}$$

where

$$\mathbf{K} = \mathbf{f}^{(e)} + \beta(\mathbf{q}/5p) + \beta\mathbf{V}^{(f)}\cdot[\mathsf{I} - (\boldsymbol{\tau}/5p)] \tag{31}$$

in which $\mathbf{f}^{(e)}$ is any external force per unit mass acting on the particle and $\mathbf{A}$ is the stochastic acceleration with zero mean. If the principal axes are used, then the Ith component of the change in velocity

$$B_I(\Delta t) = \int_t^{t+\Delta t} A_I(s)\, ds \tag{32}$$

has a pdf given by

$$W(B_I) = \frac{\exp[-B_I^2/4(kT/M)\,\beta(\Delta t)(1 - 3\tau_I/5p)]}{[4\pi(kT/M)\,\beta(\Delta t)(1 - 3\tau_I/5p)]^{1/2}} \tag{33}$$

When the environment is in equilibrium, that is, when $\mathbf{q}$ and τ vanish, then Eqs. (30)–(33) reduce to the formalism developed by Chandrasekhar.(6) In particular, our derived result, Eq. (33), reduces to his postulated Eq. (144). Thereby, it can be shown(16) that we have derived the result that, at equilibrium, equipartition of energy is a consequence of the dynamics and randomness of the motion.(18)

4. FREE-MOLECULE COUETTE FLOW

From Eqs. (10) and (11), it is seen that all that is needed to evaluate the mean and variance of the stochastic force on a B particle whose Knudsen number is large compared to unity, is to know the velocity distribution function for the molecules. In the last section, the Chapman–Enskog velocity distribution function was used and it was found [see Eq. (33)] that the correction to the result for an equilibrium environment was of order τ/p. This ratio is necessarily small for the Chapman–Enskog expansion technique to be valid. Consequently, it is of interest to study the motion of a B particle in a flow in which τ/p could be large and for which the velocity distribution function is known. Perhaps the simplest such flow is the free-molecule Couette flow.

To describe the velocity distribution for the free-molecule Couette flow, consider an inertial coordinate system (X', Y', Z') in which two infinite plates lie parallel to the $X'Y'$ plane. The distance L along the Z' axis, between the plates, satisfies $\lambda \gg L \gg a$. The upper plate moves in the positive Y' direction with uniform speed U; the lower plate is stationary. With respect to this inertial frame, the velocity distribution function for the gas molecules is

$$f = f_b h(\xi'_{Z'}) + f_a[1 - h(\xi'_{Z'})] \tag{34}$$

where the molecules from "below" have the density function

$$f_b = (\gamma/\pi)^{3/2} \exp(-\gamma \boldsymbol{\xi}' \cdot \boldsymbol{\xi}') \tag{35}$$

and those from "above" have

$$f_a = (\gamma/\pi)^{3/2} \exp[-\gamma(\boldsymbol{\xi}' - U\mathbf{j})^2] \tag{36}$$

Here, $\gamma = m/2kT$, where T is the common temperature of the plates. The h functions are Heaviside step functions and $\boldsymbol{\xi}'$ is the velocity of a molecule with respect to (X', Y', Z').

As in the previous section, we choose a second coordinate system (X, Y, Z) with origin at the center of the sphere. If a molecule's velocity with respect to the B particle is $\boldsymbol{\xi}$, then

$$\boldsymbol{\xi}' = \boldsymbol{\xi} + \mathbf{V} \tag{37}$$

where $\mathbf{V}$ is the velocity of the particle with respect to (X, Y, Z').

There are two aspects of this analysis which limit the usefulness of the results. First, what might be called a shadow effect has been ignored. That is, when the particle approaches within a few radii of one of the plates, it seems that there would be fewer molecules hitting the particle on its "near-plate" side, because of the "shadow" that the particle casts. By ignoring this effect, we restrict the analysis to the motion in the region beyong a few particle radii from the wall. Of more important consequence, though, is that we were unable to evaluate some integrals, such as

$$\int_0^a \operatorname{erf}(\lambda\xi) \exp(-\xi^2)\, d\xi$$

This forced us to abandon the attempt to obtain a result which was valid for all τ/p. Instead, the analysis is adequate only to terms linear in τ/p.

Substituting Eq. (37) into (35) and (36) and expanding the Heaviside functions for small (dimensionless) V according to

$$h(\xi_Z + V_Z) = h(\xi_Z) + V_Z\, \delta(\xi_Z) + O(V_Z{}^2) \tag{38}$$

where δ is the Dirac delta function, and performing the many integrals as in Eqs. (23) and (24), leads to

$$N\langle \mathbf{p} \rangle = -M\beta\, \Delta t \left[\mathbf{V} - \frac{U}{2}\hat{\mathbf{J}} + \frac{9}{8}\frac{15}{128}\pi \mathbf{V} \cdot \frac{\boldsymbol{\tau}}{p}\right] \tag{39}$$

$$N\langle \mathbf{pp} \rangle = M^2\beta\, \Delta t \frac{kT}{M}\left[1 - \frac{15}{128}\frac{\boldsymbol{\tau}}{p}\right] \tag{40}$$

Here, the viscous stress tensor has been identified as[19]

$$\boldsymbol{\tau} = \tfrac{1}{2}\rho U \bar{c} (\hat{\mathbf{J}}\hat{\mathbf{K}} + \hat{\mathbf{K}}\hat{\mathbf{J}}) \tag{41}$$

In Eq. (39), terms with U^2 and U^3 could be displayed but since they contribute only to the mean force and not to the variance, they have been omitted. Eqs. (39) and (40) differ from Eqs. (26) and (27) only by numerical factors. In the sequel, the Chapman–Enskog case will be developed and the Couette flow results just stated.

5. FOKKER–PLANCK EQUATION

If we assume that the Brownian motion of a particle in a slightly nonuniform gas is Markovian, then a Fokker–Planck equation can be used to describe the particle's evolution in position $\mathbf{R}$ and velocity $\mathbf{V}$ phase space. To obtain this equation, let

$\Psi(\mathbf{R}, \mathbf{V}; \Delta\mathbf{R}, \Delta\mathbf{V})\, \Delta\mathbf{R}\, \Delta\mathbf{V}$ be the transition probability that, during Δt, the position of the particle changes by $\Delta\mathbf{R}$ and its velocity by $\Delta\mathbf{V}$. Since its position is certain to change by $\mathbf{V}\, \Delta t$, then, from Eqs. (26) and (27),

$$\Psi = \delta(\Delta\mathbf{R} - \mathbf{V}\, \Delta t) \prod_{I=1}^{3} \frac{\exp(-\,|\,\Delta V_I - \langle \Delta V_I \rangle|^2 / 2\langle \Delta V_I^2 \rangle)}{(2\pi \langle \Delta V_I^2 \rangle)^{1/2}} \tag{42}$$

where

$$\langle \Delta V_I \rangle / \Delta t = f_I^{(e)} + (\beta/5p)\, q_I - \beta[1 - (\tau_I/5p)][V_I - V_I^{(f)}] \tag{43}$$

$$\langle \Delta V_I^2 \rangle / \Delta t = (2kT/M)\, \beta[1 - (3\tau_I/5p)] \tag{44}$$

in which, again, I labels the components of the appropriate tensors along the principal axes.

Further, to obtain the Fokker–Planck equation, let $W(\mathbf{R}, \mathbf{V}, t; \mathbf{R}_0, \mathbf{V}_0, t_0) d\mathbf{R}\, d\mathbf{V}$ be the probability that the B particle is in the volume element of phase space $d\mathbf{R} d\mathbf{V}$ about $\mathbf{R}, \mathbf{V}$ at time t, if it were known to be at $\mathbf{R}_0, \mathbf{V}_0$ at time t_0. If the motion of the particle in phase space is Markovian, then the pdf W satisfies the Chapman–Kolmogorov equation

$$\begin{aligned} W(\mathbf{R}, \mathbf{V}, t + \Delta t) = \int d(\Delta\mathbf{R}) \int d(\Delta\mathbf{V})\; & W(\mathbf{R} - \Delta\mathbf{R}, \mathbf{V} - \Delta\mathbf{V}, t) \\ & \cdot \Psi(\mathbf{R} - \Delta\mathbf{R}, \mathbf{V} - \Delta\mathbf{V}; \Delta\mathbf{R}, \Delta\mathbf{V}) \end{aligned} \tag{45}$$

As in Chandrasekhar's article,(6) expanding all quantities in Taylor series about the values that they assume at $\mathbf{R}, \mathbf{V}, t$ and utilizing Eq. (42), the resultant Fokker–Planck equation is

$$\partial W/\partial t + \mathbf{V} \cdot \nabla_R W + \mathbf{K} \cdot \nabla_V W = -(\nabla_V \cdot \mathbf{K}) W + \nabla_V \cdot (\boldsymbol{\beta} \cdot \mathbf{V} W) + \nabla_V \cdot (\mathsf{D}_V \cdot \nabla_V W) \tag{46}$$

where

$$\mathbf{K} = \mathbf{f}^{(e)} + \beta \mathbf{q}/5p + \boldsymbol{\beta} \cdot \mathbf{V}^{(f)} \tag{47}$$

$$\boldsymbol{\beta} = \beta[\mathsf{I} - \boldsymbol{\tau}/5p] \tag{48}$$

$$\mathsf{D}_V = (kT/M)\beta[\mathsf{I} - 3\boldsymbol{\tau}/5p] \tag{49}$$

is the diffusion coefficient in velocity space.

Chandrasekhar(20) has kindly provided us with the useful observation that this method of obtaining the Fokker–Planck equation, whereby $C(\boldsymbol{\rho})$ was approximated by its first two terms [cf. Eq. (9)], is all that is required. That is, higher-order moments of the distribution could have been calculated but they would not appear in Eq. (46). Mazo's(12) Eq. (22) is similar to Eq. (46) and includes the dependence of the friction constant $\boldsymbol{\beta}$ on the gradient of the fluid velocity. Presumably, his formalism could be developed so that the explicit dependence of $\boldsymbol{\beta}$ on $\mathbf{V}^{(f)}$ could be calculated for specific flow fields such as in Eq. (48).

Consider now the simple case that during the time interval of interest, the B particle remains within a sufficiently small region so that $\nabla_R W$ may be ignored and the coordinate $\mathbf{R}$ appears only as a parameter. In addition suppose that $\mathbf{f}^{(e)}$ is a constant and that $\mathbf{V}^{(f)}$ and $\mathbf{q}$ are independent of time. Then, Eq. (46) becomes

$$\partial W/\partial t + (\mathbf{K} - \boldsymbol{\beta} \cdot \mathbf{V}) \cdot \nabla_V W = 3\beta W + \nabla_V \cdot (\mathsf{D}_V \cdot \nabla_V W) \tag{50}$$

To solve this equation, subject to the initial condition

$$W(\mathbf{V}, t \to 0) = \delta(\mathbf{V} - \mathbf{V}_0) \tag{51}$$

the coordinate system in velocity space is rotated to diagonalize D_V. A simple extension of Chandrasekhar's Lemma II [his equations (236)–(268)] yields the solution

$$\begin{aligned} W(\mathbf{V}, t) = \prod_{I=1}^{3} &\left\{2\pi \frac{kT}{M}\left(1 - \frac{2\tau_I}{5p}\right)(1 - e^{-2\beta_I t})\right\}^{-1/2} \\ &\times \exp\left\{\frac{-[V_I - (V_0)_I e^{-\beta_I t} - (K_I/\beta_I)(1 - e^{-\beta_I t})]^2}{2(kT/M)[1 - (2\tau_I/5p)](1 - e^{-2\beta_I t})}\right\} \end{aligned} \tag{52}$$

where

$$\beta_I = \beta(1 - \tau_I/5p) \tag{53}$$

An interesting prediction from Eq. (52) is that, for $t \gg \beta^{-1}$ and to terms of first order in gradients, the B particle will drift with a mean velocity given by

$$\langle \mathbf{V} \rangle = \frac{1}{\beta}\mathbf{f}^{(e)} + \mathbf{V}^{(f)} + \frac{1}{5p}\mathbf{q} + \frac{1}{\beta}\mathbf{f}^{(e)} \cdot \frac{\mathsf{T}}{5p} \tag{54}$$

It is hoped that the prediction of this new drift velocity, the last term in Eq. (54), would be tested experimentally.

6. KRAMERS' METHOD

From Eq. (52), it is seen that after a time interval of order β^{-1}, the velocity distribution function for the B particle approaches a constant, skewed Maxwellian, locally. If the details of this relaxation are not of interest, that is, if the smallest time interval of interest is very much larger than β^{-1}, then under certain conditions, a simpler description of the motion of the B particle can be obtained by eliminating the velocity distribution function from consideration. Thereby, an equation, the Smoluchowski–Kramers equation, is obtained which describes the particle's motion only in configuration space. Let $w(\mathbf{R}, t; \mathbf{R}_0, t_0)\, d\mathbf{R}$ be the probability that the B particle is located in $d\mathbf{R}$ about $\mathbf{R}$ at time t if it were known to be at $\mathbf{R}_0$ at time t_0. Thus,

$$w(\mathbf{R}, t; \mathbf{R}_0, t_0) = \int d\mathbf{V}_0 \int d\mathbf{V}\, W(\mathbf{R}, \mathbf{V}, t; \mathbf{R}_0, \mathbf{V}_0, t_0) f(\mathbf{V}_0) \tag{55}$$

where $f(\mathbf{V}_0)$ describes the distribution of initial velocities that the particle might possess. What is sought is an equation for $w(\mathbf{R}, t)$.

The resultant equation, obtained intuitively by Smoluchowski, can be derived in at least two ways. In our original investigation,(8) we appropriately extended Kramers' method(21) to the case of a nonuniform gas. Thus, it is found (as in Chandrasekhar's section II-5 for the case of constant β, D, and K) to be convenient to recast the Fokker–Planck equation (46) into the equivalent form

$$\frac{\partial W}{\partial t} = \beta_I \left(\frac{\partial}{\partial u} - \frac{1}{\beta_I}\frac{\partial}{\partial r}\right)\left[Wu + \beta_I D_I \frac{\partial W}{\partial u} + D_I \frac{\partial W}{\partial r} + \frac{W}{\beta_I}\frac{\partial}{\partial r}(\beta_I D_I) - \frac{KW}{\beta_I}\right]$$
$$+ \frac{\partial}{\partial r}\left[D_I \frac{\partial W}{\partial r} + \frac{W}{\beta_I}\frac{\partial}{\partial r}(\beta_I D_I) - \frac{KW}{\beta_I}\right] \tag{56}$$

where, for simplicity, only one-dimensional (r, u) motion of the B particle along one of the principal axes is considered. In Eq. (56),

$$K = f^{(e)} + \beta(q/5p) + \beta_I u^{(f)} \tag{57}$$

is assumed to be independent of u and

$$D_I = D_v/\beta_I^2 = D[1 - (\tau_I/5p)] \tag{58}$$

where D is Einstein's diffusion coefficient and $u^{(f)}$ is the fluid velocity.

During the time of order β^{-1} that the velocity distribution function for the B particle relaxes to its steady value, locally, the mean motion of the particle is governed by

$$du/dt = -\beta_I u + K \tag{59}$$

Again, if the local values of β_I and K suffice for the time interval and displacement of interest, then the trajectory of this mean motion is given by

$$r + u\beta_I^{-1} - Kt\beta_I^{-1} = \text{const} \equiv \zeta \tag{60}$$

Now, if Eq. (56) is integrated over all u, along the trajectory $\zeta = \text{const}$, then as in Chandrasekhar's article, one can obtain that

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial r}\left[D_I \frac{\partial w}{\partial r} + \frac{w}{\beta_I}\frac{\partial}{\partial r}(\beta_I D_I) - \frac{Kw}{\beta_I}\right] \tag{61}$$

In an arbitrary coordinate system, Eq. (61) is the generalized Smoluchowski–Kramers equation

$$\frac{\partial w}{\partial t} = \nabla \cdot [\mathsf{D} \cdot \nabla w - w\mathbf{v}_d] \tag{62}$$

where

$$\mathbf{v}_d = \mathbf{V}^{(\mathrm{f})} + \frac{\mathbf{q}}{5p} + \frac{\mathbf{f}^{(\mathrm{e})}}{\beta} \cdot \left(\mathsf{I} + \frac{\mathsf{T}}{5p}\right) + D\left(\frac{2}{5p}\nabla \cdot \mathsf{T} - \frac{\nabla T}{T}\right) \tag{63}$$

and in which the diffusion coefficient appears as the second-order tensor

$$\mathsf{D} = D[\mathsf{I} - (\boldsymbol{\tau}/5p)] \tag{64}$$

7. THE CHAPMAN-ENSKOG METHOD

We are grateful to Mazo(22) for calling to our attention an alternative derivation of the Smoluchowski–Kramers equation from the Fokker–Planck equation. The essence of the method is described by Lebowitz *et al.*,(23) but the thorough treatment by Resibois(24) is recommended for reference, especially because of his more careful treatment of the collisional invariants. In this method, a Champan–Enskog type of perturbation solution to the Fokker–Planck equation is sought.

For convenience, we return to the principal axes notation and write the Fokker–Planck equation in the form

$$\frac{\partial W}{\partial t} + u_i \frac{\partial W}{\partial r_i} = \beta_I \frac{\partial}{\partial u_i}\left[\left(c_i W + \frac{kT_I{}^*}{M}\frac{\partial W}{\partial u_i}\right)\right] \tag{65}$$

where

$$c_i = u_i - (K_i/\beta_I) = u_i - \bar{u}_i \tag{66}$$

$$kT_I{}^*/M = (kT/M)[1 - (2\tau_I/5p)] \tag{67}$$

and capital-letter indices are not to be summed. It is easy to see(25) that our collisional operator [the RHS of Eq. (65)] conserves "numbers of particles." Thus, integration Eq. (65) over all velocities, we obtain

$$\partial w/\partial t = -(\partial/\partial r_i)\left[\int u_i W\, d\mathbf{u}\right] \tag{68}$$

which already has the appearance of a diffusion equation. It is necessary now to obtain W so that the RHS of Eq. (68) can be evaluated.

To this end, following Resibois, we seek a solution to Eq. (65) in the form

$$W = W^{(0)} + \beta^{-1}W^{(1)} + O(\beta^{-2}) \tag{69}$$

Substituting Eq. (69) into (65), and equating coefficients which have the same power of β^{-1}, it is found that $W^{(0)}$ is given by Eq. (52) with $t \to \infty$; that is, the skewed Maxwellian. Further, the equation for $W^{(1)}$ is

$$\frac{\partial W^{(0)}}{\partial t} + u_i \frac{\partial W^{(0)}}{\partial r_i} = \left(1 - \frac{\tau_I}{5p}\right)\frac{\partial}{\partial u_i}\left[c_i W^{(1)} + \frac{kT_I{}^*}{M}\frac{\partial W^{(1)}}{\partial u_i}\right] \tag{70}$$

Fortunately, it is not necessary to solve Eq. (70) since, from Eq. (68),

$$\partial w/\partial t = -(\partial/\partial r_i)\left[\int u_i\{W^{(0)} + \beta^{-1}W^{(1)} + O(\beta^{-2})\right] d\mathbf{u} \tag{71}$$

Thus, to $O(\beta^{-1})$, we need determine only

$$\int u_i W^{(1)}\, d\mathbf{u} \tag{72}$$

The first integral in Eq. (71) is simply $\bar{u}_i$.

Expression (72) can be obtained directly from Eq. (70). First, however, we make the fundamental, Chapman–Enskog-type assumption that for time intervals large compared to β^{-1}, then the time dependence of $W^{(0)}$ is implicit in the time dependence of w (customarily, the density) and in the temperature T, etc. Thus, we assume that

$$\frac{\partial W^{(0)}}{\partial t} = \frac{\partial W^{(0)}}{\partial w}\frac{\partial w}{\partial t} + \frac{\partial W^{(0)}}{\partial T}\frac{\partial T}{\partial t} + \frac{\partial W^{(0)}}{\partial v_i^{(\mathrm{f})}}\frac{\partial v_i^{(\mathrm{f})}}{\partial t} + \frac{\partial W^{(0)}}{\partial f_i^{(\mathrm{e})}}\frac{\partial f_i^{(\mathrm{e})}}{\partial t} + \cdots \tag{73}$$

in which some terms (e.g., $\partial p/\partial t$, $\partial q_i/\partial t$) have been ignored since they lead to quantities which are of second order in gradients of fluid properties. Substituting Eq. (73) into (70), multiplying through by u_j, and integrating over $\mathbf{u}$ leads to

$$\begin{aligned}\int u_j W^{(1)}\, d\mathbf{u} = -\left(1 + \frac{\tau_j}{5p}\right)\Big[\bar{u}_j \frac{\partial w}{\partial t} + w\frac{\partial T}{\partial t}\frac{\partial \bar{u}_j}{\partial T} \\ + w\frac{\partial v_k^{(\mathrm{f})}}{\partial t}\frac{\partial u_j}{\partial v_k^{(\mathrm{f})}} + \frac{\partial}{\partial r_i}\int u_i u_j W^{(0)}\, d\mathbf{u}\Big]\end{aligned} \tag{74}$$

Evaluating the terms in Eq. (74) and substituting the results into Eq. (71) yields

$$\begin{aligned}\frac{\partial w}{\partial t} = \nabla \cdot [\mathsf{D} \cdot \nabla w - w\mathbf{u}] + \frac{\partial}{\partial r_j}\Big\{\frac{w}{\beta}\left(1 + \frac{\tau_J}{5p}\right)\delta_{ij}\frac{\partial}{\partial r_i}\frac{kT_I{}^*}{M} \\ + \frac{w}{\beta}\left[\bar{u}_i\frac{\partial \bar{u}_j}{\partial r_i} + \frac{\partial v_j^{(\mathrm{f})}}{\partial t} + \frac{1}{\beta}\frac{\partial f_j^{(\mathrm{e})}}{\partial t}\right]\Big\}\end{aligned} \tag{75}$$

At first glance it appears, that additional terms appear in this expression over those which were obtained in Eq. (62) via Kramers' method. However, the last three terms in Eq. (75) correspond to changes that occur during a time interval $O(\beta^{-1})$. These were specifically excluded in Kramers' method and, in fact, should be ignored here since if these properties change significantly during β^{-1}, then the Chapman–Enskog procedure is invalid. Thus, it is seen that the two methods yield essentially the same result.

8. THE CONVECTIVE-DIFFUSION EQUATION

If there is a number density N of noninteracting B particles in the fluid and if the initial location of these particles is not known with certainty, then it is convenient to recast Eq. (62) or (75) into a convective-diffusion equation. Since

$$N(\mathbf{R}, t) = \int d\mathbf{R}_0\, w(\mathbf{R}, t; \mathbf{R}_0, t_0)\, N(\mathbf{R}_0, t) \tag{76}$$

then operating on Eq. (62) with the operator in Eq. (76), and utilizing Eq. (62), yields(26)

$$\partial N/\partial t = \nabla \cdot [\mathsf{D} \cdot \nabla N - N\mathbf{v}_d] \tag{77}$$

where $\mathbf{v}_d$ and D are given by Eqs. (63) and (64), respectively.

For practical purposes, Eq. (77) is the main result of this analysis. It describes the influence on Brownian diffusion of nonuniformities in the host gas. The tensorial character of the diffusion coefficient implies that in a flow in which there exist viscous stresses, B particles do not diffuse spherically symmetrically about the mean position dicated by $\mathbf{v}_d$. Surfaces of constant density, instead of spherical, are ellipsoidal. The principal axes of these ellipsoids coincide with the principal axes that diagonalize the viscous stress tensor.

Actually, this result might have been expected on the basis of Curie's theorem.(27) That is, if Brownian diffusion is dependent on nonuniformities in the host gas, then to first order in gradients, the only measure of the nonuniformities which is an even-order tensor is the viscous stress. The major result of this analysis has been to predict the "proportionality constant" between the diffusion coefficient and the stress tensor. In summary, for a particle with large Knudsen number, the results are

$$\mathsf{D} = D[\mathsf{I} - (\sigma\mathsf{\tau}/p)] \tag{78}$$

where $\sigma = 1/5$ for a Chapman–Enskog host gas and $\sigma = 195\pi/512$ for a free-molecule Couette flow. Although these corrections are small in most applications, the parameter $\mathsf{\tau}/p$ can be large in low-density gas motion.

ACKNOWLEDGMENTS

This paper is the better for the assistance of R. M. Mazo, the corrections to an earlier draft by J. M. Burgers, and the comments from S. Chandrasekhar.

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