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**BROWNIAN DIFFUSION
OF SUBMICRON PARTICLES IN AIR
UNDER NONEQUILIBRIUM CONDITIONS**

FEBRUARY 1969

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IN AIR UNDER NONEQUILIBRIUM CONDITIONS

By

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ABSTRACT

Brownian diffusion of particles with Knudsen number large compared to one is analyzed both in equilibrium and nonequilibrium environments. For air in equilibrium it is shown, using only Newton's laws and the central limit theorem that for specular reflection of the molecules, equipartition is a consequence of the motion. For diffuse reflections the diffusion coefficient is found to depend upon the temperature of the particle and on the number of molecules reflected diffusely. This illustrates a limitation of the fluctuation-dissipation theorem.

The motion of Brownian particles in air that is in thermal and translational nonequilibrium, is influenced by heat flux and viscous stress. A new force is described which is similar to that used to explain the thermophoresis effect but which depends upon the viscous stress. The solution is found to the new Fokker-Planck equation. In the generalized convective-diffusion equation, the diffusion coefficient appears as a second order tensor and contains the influence of the viscous stress tensor on diffusion.

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BROWNIAN DIFFUSION OF SUBMICRON PARTICLES IN AIR UNDER NONEQUILIBRIUM CONDITIONS

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I. INTRODUCTION

Brownian diffusion has been the subject of many investigations. Some interesting historical comments are included in references 1 and 2. Using the assumptions that both the particle and its fluid environment are in thermodynamic equilibrium, Einstein³ predicted that the diffusion coefficient, D , is related to the drag coefficient per unit mass, β , according to

$$D = kT/M\beta \quad , \quad (1)$$

where k is Boltzmann's constant, T is the temperature of the environment and M is the mass of the Brownian particle. Smoluchowski⁴ and Langevin⁵ removed the requirement that the particle be in equilibrium with its environment and thereby initiated the study of the dynamics of Brownian motion.

Langevin started from Newton's second law of dynamics and divided the total force on the particle into two parts: a continuous drag force, $-\beta\vec{V}$, where $\vec{V}$ is the velocity of particle, and a stochastic force, $M\vec{A}$. Thus Langevin wrote Newton's law in the form

$$d\vec{V}/dt = -\beta\vec{V} + \vec{A}(t) \quad . \quad (2)$$

Introducing the postulates that the stochastic acceleration is uncorrelated with the position of the particle and that it would result in the particle eventually attaining its

equipartition value of energy, $3kT/2$, Langevin was able to obtain Einstein's result (1).

Many investigators have searched for a more complete description of the stochastic acceleration. In his classic paper⁶, Chandrasekhar reviews and extends the earlier investigations. With reference to Ornstein and Uhlenbeck's pioneering work⁷, Chandrasekhar postulates a specific description for

$$\vec{B}(\Delta t) = \int_t^{t + \Delta t} \vec{A}(s) ds \quad . \quad (3)$$

In (3), Δt is taken to be, at once, long enough so that many molecules of the fluid environment collide with the particle and short enough so that the mean position and velocity of the Brownian particle do not change significantly during Δt . Chandrasekhar proposed that the distribution (or statistical density) function for $\vec{B}$ is

$$w(\vec{B}) = (4\pi kT\beta\Delta t/M)^{-3/2} \exp \left\{ -M |\vec{B}|^2 / 4kT\beta\Delta t \right\} \quad . \quad (4)$$

He explains that two considerations motivated his choice (4). The first was that, since Δt is taken to be large enough for many molecules to collide with the particle, it could be expected by the central limit theorem that $\vec{B}$ would have a normal distribution. The second consideration follows from his demonstration that the presence of β in the

variance of (4), insures that the particle will attain a Maxwellian velocity distribution for $t \gg \beta^{-1}$. This will be seen below.

There have been many investigations concerned with the theory of Brownian motion since Chandrasekhar's review article appeared. Of late, though, most authors have sought a theory that follows from the Liouville or Boltzmann equations. For example, Lebowitz and Rubin⁸ develop the Liouville equation into a pair of coupled equations describing the distribution functions for the fluid and for the particle. Prigogine expands the statistical distribution function for a Gibbsian ensemble in terms of the eigenfunctions of the Liouville operator. Montgomery¹⁰ proceeds from the coupled Boltzmann equations for two species of dilute gases.

The purpose of this work is to study the motion of a Brownian particle starting from the base presented by Chandrasekhar. Using Markoff's method, Section II, it will be shown in Section III how Chandrasekhar's formula (4) can be derived - at least for submicron particles in a dilute gas. In Section IV a complete theory that describes the motion of a submicron particle in equilibrium air is presented. It relies only on Newton's second law and the central limit theorem. The theory is extended to the case of a nonequilibrium environment in Section V. In the final

sections, the new Fokker-Planck, Smoluchowski and convective-diffusion equations are studied.

II. MARKOFF'S METHOD

Markoff's method⁶ is a generalization of what is known in the theory of probability as the method of characteristic functions.¹¹ Let $\vec{\phi}_j$ be N , independent, n -dimensional vectors, each depending on s generalized coordinates $\vec{q}_j = (q_1, q_2, \dots, q_s)$, whose density functions are known to be $\tau_j(q_j)$. Then Markoff's result is that if

$$\vec{\Phi} = \sum_{j=1}^N \vec{\phi}_j \quad (5)$$

then the distribution (or statistical density) function describing $\vec{\Phi}$ is

$$W(\vec{\Phi}) = \frac{1}{(2\pi)^n} \int d\vec{\rho} A_N(\vec{\rho}) \exp \left\{ -i\vec{\rho} \cdot \vec{\Phi} \right\} \quad (6)$$

where

$$A_N(\vec{\rho}) = \prod_{j=1}^N \int d\vec{q}_j \tau_j(\vec{q}_j) \exp \left\{ i\vec{\rho} \cdot \vec{\phi}_j \right\} \quad (7)$$

If $\vec{q}_j$ and $\tau_j(\vec{q}_j)$ are the same for all j , then (7) becomes

$$A_N(\vec{\rho}) = \left[\int d\vec{q} \tau(\vec{q}) \exp \left\{ i\vec{\rho} \cdot \vec{\phi} \right\} \right]^N \quad (8)$$

In addition, if N is large then, using the definition of the exponential

$$e = \lim_{h \rightarrow \infty} (1 + 1/h)^h$$

and using

$$\int d\vec{q} \tau(\vec{q}) = 1 \quad ,$$

(8) becomes

$$A_N(\vec{\rho}) = \exp \left\{ -C(\vec{\rho}) \right\} \quad (9)$$

where

$$C(\vec{\rho}) = N \int d\vec{q} \tau(\vec{q}) \left\{ 1 - \exp(i\vec{\rho} \cdot \vec{\phi}) \right\} \quad . \quad (10)$$

Finally, suppose that $\vec{\phi}$ is a one dimensional vector and that dominant contribution to the integral in (6) occurs near $\rho = 0$. Then expanding $C(\rho)$ in a power series in ρ and identifying the various moments of ϕ as

$$\lambda_n = N \int d\vec{q} \tau(\vec{q}) \phi^n \quad ,$$

there results the Edgeworth series:¹²

$$W(\phi) = \frac{D(0)}{\sigma} - \frac{\lambda_3 D^{(3)}}{3! \sigma^4} + \left[\frac{\lambda_4 D^{(4)}}{4! \sigma^5} + \frac{\lambda_3^2 D^{(6)}}{72 \sigma^7} \right] - O(N^{-2}) \quad (11)$$

where

$$D^{(n)}(x) = (2\pi)^{-1/2} d^n [\exp(-x^2/2)]/dx^n$$

and

$$x = (\phi - \lambda_1)/\sigma \quad .$$

If $N^{1/2} \gg 1$, the first term of the series (11) dominates and therefore $W(\phi)$ approaches a normal distribution. This is a restricted demonstration of the central limit theorem.¹³

Before turning to the Brownian motion problem, it may be useful to illustrate the use of Markoff's method by calculating the statistical density function which describes the number of molecules that, during Δt , strike one side of an area element, ΔA , immersed in a dilute gas in equilibrium. Let the total number of molecules that hit the plate during Δt be H . If h_j takes on the value 1, if molecule j hits the plate and 0, if it does not, then

$$H = \sum_{j=1}^N h_j ,$$

where N is the total number of molecules that could conceivably hit the plate during Δt . The velocity distribution function for the molecules of the gas will be taken to be Maxwellian. Since this admits the possibility that molecules have extremely large speeds, then it is consistent to assume that any molecule in the hemisphere of radius $R \rightarrow \infty$, above the plate, could hit ΔA during Δt . If $\bar{n}$ is the mean number density, then

$$N = \frac{1}{2} \left(\frac{4}{3} \pi R^3 \right) \bar{n} \gg 1 . \quad (12)$$

The coordinates $\vec{q}_j$ upon which each h_j depends are the molecule's speed, ξ , its initial location, $\vec{r} = (r, \theta, \omega)$

and direction of travel. Collisions between molecules need not be considered if the fluid is in equilibrium (by the theorem of detailed balance¹⁴) or even for a nonequilibrium fluid, if Δt is short enough.¹⁵ Molecule j will hit the plate during Δt if the molecule has speed $\xi \geq r/\Delta t$ and if it is travelling in the solid angle $\Delta\Omega = \Delta A \cos \theta / r^2$ subtended at r , by the plate; it will not, if either of these conditions is not satisfied. It is convenient to express this last sentence in the mathematically inexact form

$$h_j(\vec{q}_j) = h(\text{direction}) h(\text{speed}) \quad . \quad (13)$$

The distribution of the coordinates is as follows. The distribution function for the speeds is

$$\tau(\xi) = 4\pi(\gamma/\pi)^{3/2} \xi^2 \exp(-\gamma\xi^2) \quad (14)$$

where $\gamma = m/2kT$ and m is the mass of a molecule of the gas. The probability that molecule j is travelling toward the plate is taken to be

$$\tau(\Omega) d\Omega = (\Delta A \cos \theta / 4\pi r^2) d\Omega \quad . \quad (15)$$

The probability that it is initially in a volume element dV is taken as

$$\tau(r, \theta, \omega) dV = dV / (4\pi R^2 / 6) \quad . \quad (16)$$

These distributions are the same for all j .

Substituting (12) through (16) into (10), there results

$$C(\rho) = \bar{n}(\gamma/\pi)^{3/2} \int_0^{R \rightarrow \infty} dr \quad r^2 \int_0^{\pi/2} d\theta \sin \theta \int_0^{2\pi} d\omega \int_0^\infty d\xi \xi^2 \int_0^{4\pi} d\Omega \exp(-\gamma\xi^2) \left\{ 1 - \exp[i\rho h(\text{direction}) h(\text{speed})] \right\}. \quad (17a)$$

The effect of the h factors in (17a) is to limit the ranges of integration over Ω and ξ . Evaluating the integrals results in

$$C(\rho) = (1/4) \bar{n} \bar{c} \Delta A \Delta t [1 - e^{i\rho}] \quad (17b)$$

where $\bar{c} = (8kT/\pi m)^{1/2}$. Substituting (17b) into (6) leads to¹¹

$$W(H) = (\bar{M}^H e^{-\bar{M}}) / \bar{M}! \quad (18)$$

where $\bar{M} = (1/4) \bar{n} \bar{c} \Delta A \Delta t$. Equation (18) is the familiar result¹⁶ that the number of molecules that strike an area element during Δt has a Poisson distribution. If $\bar{M}^{1/2} \gg 1$, an adequate approximation to (18) is a normal distribution. This can be obtained either by expanding (18) or by expanding (17b) and thereby, obtaining a series equivalent to (11).

III. THE MOMENTUM DELIVERED TO A STATIONARY SPHERE

Consider a spherical Brownian particle immersed in a dilute gas which is in thermodynamic equilibrium. No approximation is involved if the total force on the particle is divided into two parts or, for that matter, any other number. Therefore Langevin's equation, equation (2), is exact. In this section though, the approximation is introduced that the stochastic force on a moving Brownian particle is the same as the stochastic force on a stationary particle. This assumption will be removed in the next section.

The method that will be used in this section to obtain the stochastic force on a stationary Brownian particle is, first, to calculate the momentum delivered during Δt to an area element ΔA of the sphere and then, to sum the contributions over the entire sphere. Consider the area element on the sphere

$$\Delta A = a^2 \sin \theta \, d\theta \, d\phi$$

where (a, θ, ϕ) are the usual spherical coordinates of a point on the surface of the sphere, with respect to the origin of the coordinate system (X, Y, Z) at the center of the sphere. Choose a second coordinate system (x, y, z) at the area element with basis vectors $(\hat{k}, \hat{i}, \hat{j}) = (\hat{e}_R, \hat{e}_\theta, \hat{e}_\phi)$. Thus $\hat{k}$ is perpendicular to the area element.

The momentum delivered during Δt by the molecules of the gas to the area element ΔA is

$$\vec{P} = \sum_{j=1}^N \vec{p}_j \quad ; \quad (19)$$

that is, the sum over all molecules that hit the area element during Δt , of the momentum delivered by each. In this section it will be assumed that the molecular collisions are specular so that

$$\vec{p}_j = 2m\xi \cos \theta (-\hat{k}) \quad (20)$$

where θ is the polar angle measured from the z-axis, of a point (r, θ, ω) within the gas.

Markoff's method can be applied to (19) to obtain $W(\vec{P})$. Either by introducing the factors $h(\text{speed}) h(\text{direction})$ as in the previous section or, equivalently, by integrating over only that domain in the space of coordinates $\xi, r, \theta, \omega, \Omega$ that contributes to momentum transfer to the area element, (10) becomes

$$C(\vec{\rho}) = \bar{n}(\gamma/\pi)^{3/2} \int_0^{R \rightarrow \infty} dr r^2 \int_0^{\pi/2} d\theta \sin \theta \int_0^{2\pi} d\omega \int_{r/\Delta t}^{\infty} d\xi \frac{\Delta A \cos \theta}{r^2} \xi^2 \exp(-\gamma \xi^2) [1 - \exp \left\{ i \vec{\rho} \cdot (-\hat{k}) 2m\xi \cos \theta \right\}] \quad . \quad (21)$$

Evaluating these integrals there results

$$C(\vec{\rho}) = \text{im}(\pi/\gamma)^{1/2} \bar{M} \rho_z w(-m \rho_z \gamma^{-1/2}) \quad (22)$$

where, again,

$$\bar{M} = \bar{n} \bar{c} \Delta A \Delta t/4 \quad (23)$$

and

$$w(z) = \exp(-z^2) \text{erfc}(-iz) \quad (24)$$

is the error function with complex argument.¹⁷

Substituting (22) into (5) and integrating over ρ_x and ρ_y leads to

$$W(\vec{P}) = \frac{1}{2\pi} \delta(P_x) \delta(P_y) \int d\rho_z \exp \left\{ -\text{im}(\pi/\gamma)^{1/2} \bar{M} \rho_z \right. \\ \left. \cdot w(-m \rho_z \gamma^{-1/2}) \right\} \exp(-i \rho_z P_z) \quad , \quad (25)$$

where the δ 's are Dirac delta functions. Thus (25) confirms the obvious fact that for a stationary area element, there is no momentum transfer to the area in its own plane.

Unfortunately we have not been able to perform the remaining integration in (25). Expanding $w(z)$ of (24) in the uniformly converging power series¹⁷

$$w(z) = \sum_{n=0}^{\infty} (iz)^n / \Gamma(n/2 + 1) \quad (26)$$

and keeping only the first two terms leads to

$$W(\vec{P}) = \delta(P_x)\delta(P_y)(2\pi\sigma^2)^{-1/2} \exp \left\{ - (P_z + \mu)^2/2\sigma^2 \right\} \quad (27a)$$

$$\text{where} \quad \mu = \bar{n}kT \Delta t \Delta A \quad (27b)$$

$$\text{and} \quad \sigma^2 = \pi \bar{M} (\bar{m}\bar{c})^2 \quad (27c)$$

Comparing this procedure to that used to obtain (11) it is clear that for (27) to be accurate, the number of events, which can be estimated to be $\bar{M}$, must satisfy $\bar{M}^{1/2} \gg 1$.

For Markoff's method to be applicable, the individual events must be statistically independent. To obtain (27), the area element could be chosen small enough so that the molecules in its neighborhood could be assumed to move independently of one another. However, to proceed to the calculation of the momentum transfer to the entire sphere, it must be assumed that the momentum delivered to each area element is independent of that delivered to any other area element. Equivalently, the motion of the molecules about the entire sphere must be independent of one another. This restricts the entire theory presented here, to the case of free-molecule flow. That is, the Knudsen number, K_N , the ratio of the mean free path of the molecules, λ , to the radius of the sphere, a , must satisfy $K_N = \lambda/a \gg 1$.

Let $\vec{M}$ be the total momentum delivered to the sphere during Δt . Then

$$\vec{M} = \sum_{j=1}^L \vec{P}_j \quad (28)$$

where $\vec{P}_j$ is the momentum delivered to area element j

$$\text{and} \quad L = 4\pi a^2 / \Delta A \quad . \quad (29)$$

Instead of attempting to find the distribution of $\vec{M}$, it is convenient to study a component of $\vec{M}$ along some arbitrary direction Z . Thus consider

$$M_Z = \sum_{j=1}^L P_j \cos \theta_j \quad . \quad (30)$$

The components of $\vec{M}$ in mutually orthogonal directions X , Y , will have distributions identical to that of M_Z .

From (27), each $m_j \equiv P_j \cos \theta_j$ is distributed according to

$$\tau(m_j) = (2\pi\sigma_j^2 \cos^2 \theta_j)^{-1/2} \exp \left\{ - (m_j - \mu_j \cos \theta_j)^2 / 2\sigma_j^2 \cos^2 \theta_j \right\} \quad (31a)$$

$$\text{where} \quad \sigma_j^2 = (\pi/4) \bar{n} \bar{c} \Delta t (\bar{m} \bar{c})^2 \Delta A_j \quad (31b)$$

$$\text{and} \quad \mu_j = \bar{n} k T \Delta t \Delta A_j \quad . \quad (31c)$$

In analogy to equations (5), (6) and (7), to calculate $W(M_Z)$ it is necessary to evaluate first

$$A_L(\rho) = \prod_{j=1}^L \int dm_j \tau(m_j) \exp(i\rho m_j) \quad . \quad (32)$$

Substituting (31) into (32) results in

$$A_L(\rho) = \exp \left\{ i\rho \sum_{j=1}^L \mu_j \cos \theta_j - (\rho^2/2) \sum_{j=1}^L \sigma_j^2 \cos^2 \theta_j \right\} \quad . \quad (33)$$

In the limit as L becomes large, the summations in (33) may be changed to integrals so that $A_L(\rho)$ becomes

$$A_L(\rho) = \exp \left\{ - \rho^2 \pi \bar{M} (\overline{mC})^2 4\pi a^2/6 \right\} \quad . \quad (34)$$

Consequently, using (6),

$$W(M_Z) = (2\pi\overline{\sigma}^2)^{-1/2} \exp \left\{ - M_Z^2/2\overline{\sigma}^2 \right\} \quad (35a)$$

where

$$\overline{\sigma}^2 = \pi \bar{n} \bar{C} (4\pi a^2) \Delta t (\overline{mC})^2/12 \quad . \quad (35b)$$

If the particle were free to move and if it were to receive momentum $\vec{M}$, then its change in velocity could be found from the momentum by dividing it by the mass of the particle, M . Therefore, from (35), the probability that during Δt the Brownian particle's velocity changes by $\vec{B}$ to $\vec{B} + d\vec{B}$ as a result of the random collisions by the molecules of the gas, is

$$W(\vec{B}) d\vec{B} = d\vec{B} \left(\frac{4\pi kT}{M} \frac{\Delta t}{\tau} \right)^{-3/2} \exp \left\{ - |\vec{B}|^2 / \frac{4kT}{M} \frac{\Delta t}{\tau} \right\} \quad (36a)$$

where

$$\tau = 3M / m\bar{n}\bar{c} \quad 4\pi a^2 \quad . \quad (36b)$$

The result (36) is to be compared to Chandrasekhar's postulate, (4). The only difference is that in (36), τ appears in place of $1/\beta$ in (4). Proceeding as in Chandrasekhar's review article, the velocity distribution function for a Brownian particle whose initial velocity is $\vec{V}_0$, is found to be

$$W(\vec{V}, t) = \frac{1}{\left[\frac{2\pi kT}{M} \frac{1}{\tau\beta} (1 - e^{-2\beta t}) \right]^{3/2}} \exp \left\{ \frac{-|\vec{V} - \vec{V}_0 e^{-\beta t}|^2}{\frac{2kT}{M} \frac{1}{\tau\beta} (1 - e^{-2\beta t})} \right\} . \quad (37)$$

Thus the particle will eventually attain a Maxwellian velocity distribution if

$$\tau\beta = 1 \quad . \quad (38)$$

Equation (38) is satisfied; Epstein's¹⁸ drag coefficient, β , for specular reflections of the molecules from a sphere in free-molecule flow is exactly the result (36b) for $1/\tau$.

That this formalism has predicted the drag coefficient from information that is available when the sphere is at rest (provided equation (38) is enforced), is not too surprising. The fluctuation-dissipation theorem^{19,20,21}

predicts that properties characteristic of equilibrium fluctuations are related, simply, to the first-order term of the dissipative response of a thermodynamic system. Einstein's relation (1) is considered as one example of the theorem. However there are two interesting features of the above results. First, the fluctuation-dissipation relation appears here in a "reverse-order" in the sense that usually the dissipative process is used to obtain information about the fluctuations. Thus in (1), information about β is used to obtain D . Here, τ has been calculated and can be used to determine β . The second observation is that there is no a priori reason to force $\tau\beta = 1$. However, here, both τ and β could be calculated and do in fact satisfy $\tau\beta = 1$. The reason for commenting on this will become apparent in the next section.

IV. BROWNIAN MOTION IN AN EQUILIBRIUM ENVIRONMENT

In this section the limitations of the previous section to specular reflections of the molecules and to a stationary Brownian particle, will be removed. However, the restriction to an equilibrium environment will be retained. Newton's second law describes the motion of a Brownian particle:

$$\vec{F} = M(d\vec{V}/dt) \quad (39)$$

where $\vec{F}$ is the sum of the forces applied to the particle from molecular encounters. In attempting to describe the total force statistically, it becomes apparent immediately that there is no need to utilize Langevin's division of the total force. Instead, a description can be sought for the distribution of the total change in momentum of the particle,

$$M \Delta \vec{V} = \sum_{j=1}^N \vec{F}_j \Delta t \quad , \quad (40)$$

that occurs during Δt arising from the N molecular encounters.

Consider a spherical particle moving with instantaneous velocity $\vec{V}$ in the Z direction. The coordinate systems are the same as that of the previous section and the environment is a dilute gas with $K_N \gg 1$. The momentum transferred to the particle during Δt is, say,

$$\vec{M} = \sum_{j=1}^N \vec{p}_j \quad ; \quad (41)$$

that is, the sum over all molecules that hit the entire particle during Δt , of the momentum delivered by each. Now, Markoff's method could be utilized to determine $W(\vec{M})$ but, recognizing the difficulty that appeared in the simpler calculation of the previous section, it seems advisable to invoke the central limit theorem here, from the outset. Consequently (10) is expanded for small $\vec{\rho}$ and yields, when only the first two terms of the expansion are retained:

$$C(\vec{\rho}) \doteq -i\vec{\rho} \cdot N \langle \vec{p} \rangle + (1/2) \vec{\rho} \cdot N \langle \vec{p}\vec{p} \rangle \cdot \vec{\rho} \quad (42a)$$

where

$$\langle \vec{p} \rangle = \int d\vec{q} \, \tau(\vec{q}) \, \vec{p} \quad (42b)$$

$$\langle \vec{p}\vec{p} \rangle = \int d\vec{q} \, \tau(\vec{q}) \, \vec{p}\vec{p} \quad (42c)$$

and in which it has been assumed that the distributions $\tau_j(\vec{q}_j)$ of the coordinates $\vec{q}_j$ are the same for all j .

Since N is the number of molecules that hit the particle during Δt and since $\langle \vec{p} \rangle$ is the average momentum delivered by each molecule, then $N\langle \vec{p} \rangle$ is the (total) mean momentum delivered to the particle during Δt . This is just the drag on the sphere multiplied by the time interval.

According to Epstein¹⁸ and others^{22,23} this is, for example, for a particle which is a perfect thermal conductor:

$$N \langle \vec{p} \rangle = M\beta^* \Delta t = M\beta \Delta t \left\{ (1 + f\pi/8) + O(S^2) \right\} \quad (43)$$

where f is the fraction of the total number of molecules, N , that is reflected diffusely and S is the molecular speed ratio

$$S = \sqrt{\gamma} V \quad (44)$$

which is close to the particle's Mach number. As Epstein has shown, the numerical factor $\pi/8$ in (43) changes slightly if different reflection models are used.

Similarly, $N \langle \vec{p}\vec{p} \rangle$ is the total of the dyadic, or second order tensor, $\vec{p}\vec{p}$ delivered to the sphere during Δt . To calculate this, consider an area element ΔA at (a, θ, ϕ) on the sphere. To an observer at the area element, the incident molecules are characterized by the distribution function

$$f_I(\vec{\xi}) = (\gamma/\pi)^{3/2} \exp \left\{ -\gamma \vec{\xi} \cdot \vec{\xi} \right\} [1 + 2\gamma \vec{\xi} \cdot \vec{V} + O(S^2)] \quad (45)$$

Therefore the incident molecules deliver to ΔA during Δt an amount of $\vec{p}\vec{p}$ given by

$$\Delta t a^2 m^2 n (\gamma/\pi)^{3/2} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_{(\xi_z < 0)} d\vec{\xi} (-\hat{k} \cdot \vec{\xi}) \exp (-\gamma \vec{\xi} \cdot \vec{\xi}) \vec{\xi} \vec{\xi} [1 + 2\gamma \vec{\xi} \cdot \vec{V} + O(S^2)] \quad (46)$$

Performing these integrals and expressing the result in the X,Y,Z coordinate system leads to

$$(1/24)\pi\bar{n}\bar{c} \Delta t 4\pi a^2 (\bar{m}\bar{c})^2 [(\hat{I}\hat{I} + \hat{J}\hat{J} + \hat{K}\hat{K}) + O(S^2)] \quad . \quad (47)$$

The reflected molecules also contribute to the total $N \langle \vec{p}\vec{p} \rangle$ delivered to the sphere. For diffuse reflection of the molecules, it is assumed that the molecules are entrained by the surface long enough so that they acquire a Maxwellian velocity distribution function characteristic of the temperature of the particle, T_p . Therefore, the number of reflected molecules per unit volume that have velocity between $\vec{\xi}$ to $\vec{\xi} + d\vec{\xi}$, namely, $n_R f_R d\vec{\xi}$ is:²³

$$\bar{n}(T/T_p)^{1/2} [1 + \pi^{1/2} S_\theta + O(S^2)] (\gamma_R/\pi)^{3/2} \exp(-\gamma_R \vec{\xi} \cdot \vec{\xi}) d\vec{\xi} \quad (48a)$$

where

$$S_\theta = S \cos \theta \quad (48b)$$

and

$$\gamma_R = m/(2kT_p) \quad . \quad (48c)$$

Using (48), the amount of $\vec{p}\vec{p}$ delivered to the sphere by the reflected molecules can be calculated from

$$\Delta t a^2 \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \int_{(\xi_z > 0)} d\vec{\xi} \hat{k} \cdot \vec{\xi} n_R f_R m^2 \vec{\xi} \vec{\xi} \quad . \quad (49)$$

Combining the result of (49) with (47) gives

$$N \langle \vec{p}\vec{p} \rangle = (4\pi/3) \bar{n}\bar{c} \Delta t a^2 mkT (\hat{I}\hat{I} + \hat{J}\hat{J} + \hat{K}\hat{K}) \\ [(2-f) + f(T_p/T)] \quad (50)$$

where f is the fraction of the total number of molecules, N , that is reflected diffusely.

Substituting (43) and (50) into (42) and the result into (6) yields, for the probability that during Δt the change in velocity of a Brownian particle is between $\vec{B}$ to $\vec{B} + d\vec{B}$,

$$w(\vec{B})d\vec{B} = \frac{d\vec{B}}{\left(\frac{4\pi kT}{M} \frac{\Delta t}{\tau^*}\right)^{3/2}} \exp \left\{ -\frac{|\vec{B} + \beta^* \vec{V} \Delta t|^2}{\frac{4kT}{M} \frac{\Delta t}{\tau^*}} \right\} \quad (51a)$$

Here

$$\beta^* = \beta [(1 + f\pi/8) + O(S^2)] \quad (51b)$$

and

$$(\tau^*)^{-1} = \beta \left[\left\{ 1 + f/2(T_p/T-1) \right\} + O(S^2) \right] \quad (51c)$$

In the subsequent analysis, asterisks on quantities will be used to indicate that the effects of diffuse reflections are included in the quantity. It is to be noticed in (51) that the mean of the distribution is independent of the temperature of the particle - whereas the variance depends on T_p . However if $T_p = T$, the variance becomes independent of the fraction of molecules reflected diffusely.

The limitations of the results (51) should be recorded. It is seen that the motion of the particle has

changed the variance by a term $O(S^2)$, from that obtained in the previous section. This correction can (and will) be ignored for particles with $(M/m) \gg 1$. To satisfy the central limit theorem,

$$\bar{M} \doteq (1/4) \bar{n} \bar{c} \Delta t 4\pi a^2 \gg 1 \quad . \quad (52)$$

In (52), Δt can not be chosen arbitrarily large because it has been assumed that during Δt , the mean velocity of the particle does not change significantly. Thus

$$\Delta t \ll \tau \doteq 3M/(4\pi a_m^2 \bar{n} \bar{c}) \quad . \quad (53)$$

Combining (52) and (53) it is seen that

$$(M/m)^{1/2} \gg 1 \quad . \quad (54)$$

In addition, again, $K_N \gg 1$.

Another interpretation of (51) is that it gives the transition probability, $\Psi(\vec{R}, \vec{V}; \vec{B}) d\vec{B}$, that a Brownian particle at position $\vec{R}$ with velocity $\vec{V}$ has its velocity changed by an amount between $\vec{B}$ to $\vec{B} + d\vec{B}$ during the time interval Δt . The change in position of the particle is certain to be $\vec{V} \Delta t$. Therefore the transition probability in $(\vec{R}, \vec{V})$ phase space is

$$\Psi(\vec{R}, \vec{V}, t; \Delta \vec{R}, \Delta \vec{V}) = \frac{\delta(\Delta \vec{R} - \vec{V} \Delta t)}{\left(\frac{4\pi kT}{M} \frac{\Delta t}{\tau^*}\right)^{3/2}} \exp \left\{ - \frac{|\Delta \vec{V} + \beta^* \vec{V} \Delta t|^2}{\frac{4kT}{M} \frac{\Delta t}{\tau^*}} \right\} \quad . \quad (55)$$

Let $W(\vec{R}, \vec{V}, t; \vec{R}_0, \vec{V}_0, t_0) d\vec{R} d\vec{V}$ be the probability that the Brownian particle is in the volume element of phase space $d\vec{R} d\vec{V}$ about $\vec{R}, \vec{V}$ at time t , if it were known to have velocity $\vec{V}_0$ at $\vec{R}_0$ at time t_0 . If the motion of the particle in phase space is Markoffian then W is described by the Chapman-Kolmogoroff equation²⁴

$$W(\vec{R}, \vec{V}, t + \Delta t) = \int d(\Delta\vec{R}) \int d(\Delta\vec{V}) W(\vec{R} - \Delta\vec{R}, \vec{V} - \Delta\vec{V}, t) \Psi(\vec{R} - \Delta\vec{R}, \vec{V} - \Delta\vec{V}; \Delta\vec{R}, \Delta\vec{V}) \quad (56)$$

Expanding all quantities in Taylor series about the values that they assume at $\vec{R}, \vec{V}, t$ and utilizing (55), the resultant Fokker-Planck equation⁶ is

$$\frac{\partial W}{\partial t} + \vec{V} \cdot \nabla_R W = \beta^* \nabla_V \cdot W \vec{V} + \frac{kT}{M_T^*} \nabla_V^2 W, \quad (57)$$

in which the subscripts R or V on ∇ indicate that the operations are to be performed in configuration or velocity space, respectively.

The solution to (57) in velocity space, subject to the initial condition

$$W(\vec{V}, t) \rightarrow \delta(\vec{V} - \vec{V}_0) \quad \text{as } t \rightarrow 0, \quad (58)$$

can be obtained by simply relabeling quantities in Chandrasekhar's solution (his equation 239). The result is

$$W(\vec{V}, t) = \left[\frac{2\pi kT}{M\tau^*\beta^*} (1 - e^{-2\beta^*t}) \right]^{-3/2} \exp \left\{ \frac{-|\vec{V} - \vec{V}_0 e^{-\beta^*t}|^2}{\frac{2kT}{M\tau^*\beta^*} (1 - e^{-2\beta^*t})} \right\} . \quad (59)$$

There are two important results here. First, (59) predicts that for $t \gg \beta^{-1}$ and for specular reflection of the molecules, $W(\vec{V}, t)$ becomes a Maxwellian velocity distribution function characteristic of the temperature of the gas, T . This is a prediction rather than a postulate of the theory. It follows, more or less directly, from Newton's second law and the requirements of the central limit theorem.

The second result in (59) is that, because of (51), it is only for specular reflections that the distribution function becomes Maxwellian characteristic of the temperature of the environment. In general, the velocity distribution function is Gaussian but it is characteristic of a temperature

$$T^* = \frac{T}{\tau^*\beta^*} = T \frac{\{1 + f/2(T_p/T-1)\}}{\{1 + f\pi/8\}} . \quad (60a)$$

That T^* should depend on T_p is reasonable. However, (60a) predicts that even if the particle's temperature has come to its equilibrium value, $T_p = T$, T^* still differs from T :

$$T^* = T/(1 + f\pi/8) ; T_p = T \quad . \quad (60b)$$

The solution to (57) in phase space can also be obtained from Chandrasekhar's solution (his equation 286). For $t \gg \beta^{-1}$, it becomes

$$W(\vec{R}, \vec{V}, t \gg \beta^{-1}) \rightarrow \frac{W(\vec{V})}{(4\pi D^* t)^{3/2}} \exp \left\{ -\frac{|\vec{R} - \vec{R}_0|^2}{4 D^* t} \right\} \quad . \quad (61)$$

In (61), a diffusion coefficient has been identified as

$$D^* = \frac{kT^*}{M\beta^*} = \frac{kT}{M\beta^*} \left[\frac{1 + f/2 (T_p/T - 1)}{(1 + f\pi/8)} \right] \quad . \quad (62)$$

As in (60a), the presence of T_p in (62) is reasonable but the extra factor of $(1 + f\pi/8)$ in (62) is unexpected.

If the above calculations are correct then either (59) and (61) correctly describe nature or some phenomenon has been overlooked. In the case of diffuse reflections, there is a stochastic torque on the particle which would cause it to rotate with some angular velocity $\vec{\omega}$. However, upon substituting into (45)

$$\vec{V} = \vec{V}_c + \vec{\omega} \times a \hat{k} \quad , \quad (63)$$

where $\vec{V}_c$ is the velocity of the center of mass of the particle, it is found that neither the mean nor the variance of the density function (51a) depends on $\vec{\omega}$. If there is no other phenomenon overlooked then it must be concluded that

the fluctuation-dissipation theorem has a practical limitation. That is, it is only if the external perturbation is, in some sense, an "analytic continuation" or a "mirror image" of the thermodynamic system (as is the case for specular reflections) that the details of the dissipative response can be obtained from the equilibrium state. In addition, although (59) is consistent with the equipartitioning of energy among the particle's degrees of freedom, it is as if the entropy of the system depends upon the fraction of molecules reflected diffusely. This concept is not inconsistent with the information-theory interpretation of entropy.

V. THE STOCHASTIC FORCE IN NONEQUILIBRIUM ENVIRONMENT

To extend the results of the previous section to the motion of a particle in a nonequilibrium environment, the Chapman-Enskog velocity distribution function is used to describe the molecules. Perhaps surprisingly, it appears that previously no one has calculated the complete, mean force on a free-molecule sphere in a nonequilibrium environment. Bell and Schaaf²⁵ have performed a similar calculation for a cylinder. Mason and Chapman²⁶ and others²⁷ have studied the mean force on a spherical particle under the influence of a temperature gradient.

To simplify the calculations, an external coordinate system (X,Y,Z) is chosen to (locally) diagonalize the viscous stress tensor, $\overset{\sim}{\tau}$. The Chapman-Enskog velocity distribution function²⁸ is

$$f = f^{(0)} [1 - \phi] \quad (64a)$$

$$\text{where} \quad f^{(0)} = (\gamma/\pi)^{3/2} \exp(-\gamma \vec{C} \cdot \vec{C}) \quad (64b)$$

$$\text{and} \quad \phi = (\gamma/p) [\vec{C} \cdot \overset{\sim}{\tau} \cdot \vec{C} + 2\{1 - (2/5)\gamma \vec{C} \cdot \vec{C}\} \vec{q} \cdot \vec{C}] \quad (64c)$$

$$\text{in which} \quad \overset{\sim}{\tau} = \tau_1 \hat{I}\hat{I} + \tau_2 \hat{J}\hat{J} + \tau_3 \hat{K}\hat{K} \quad , \quad (65)$$

where τ_I are the principal stresses

$\vec{q}$ is the heat flux and

$\vec{C}$ is the thermal velocity of a molecule.

If $\vec{\xi}'$ is the velocity of a molecule with respect to the fixed coordinate system (X,Y,Z), and if the local fluid velocity is $\vec{V}_f$, then

$$\vec{C} = \vec{\xi}' - \vec{V}_f \quad (66)$$

If the velocity of the particle with respect to (X,Y,Z) is $\vec{V}_p$ then the velocity of a molecule with respect to the particle is

$$\vec{\xi} = \vec{\xi}' - \vec{V}_p = \vec{C} + (\vec{V}_p - \vec{V}_f) = \vec{C} + \vec{v} \quad (67)$$

where $\vec{v} = \vec{V}_p - \vec{V}_f = (u,v,w) \quad (68)$

is the relative (or slip) velocity between the particle and fluid.

Nondimensionalizing velocities with respect to $\gamma^{1/2}$ (but retaining the same symbols for the nondimensional as for the dimensional quantities) and expanding (64) for small $\vec{S} = \gamma^{1/2} \vec{v}$, there results,

$$\begin{aligned} f = & \pi^{-3/2} \exp(-\vec{\xi} \cdot \vec{\xi}) [1 - 2\vec{\xi} \cdot \vec{S} - 2\vec{q} \cdot \vec{\xi} - 2\vec{q} \cdot \vec{S} \\ & - \vec{\xi} \cdot \vec{\tau} \cdot \vec{\xi} - 2\vec{\xi} \cdot \vec{\tau} \cdot \vec{S} + 2\vec{\xi} \cdot \vec{S} \vec{\xi} \cdot \vec{\tau} \cdot \vec{\xi} + (4/5)\vec{\xi} \cdot \vec{\xi} \vec{q} \cdot \vec{\xi} \\ & + (4/5) \vec{\xi} \cdot \vec{\xi} \vec{q} \cdot \vec{S} + (28/5) \vec{\xi} \cdot \vec{S} \vec{q} \cdot \vec{\xi} + O(S^2)] \quad (69) \end{aligned}$$

in which $\vec{\tau}$ and $\gamma^{1/2} \vec{q}$ have been nondimensionalized with the pressure.

It is relatively easy to see from (69) that detailed calculation need not be performed for both specular and diffuse reflections. To account for diffuse reflections in this linearized approximation (69), some terms (see equations 45 and 48) would be added to the right hand side of (69). Therefore the calculations here need be done only for specular reflections and then asterisks may be added to β and τ as in (51).

To calculate $N \langle \vec{p} \rangle$ and $N \langle \vec{p}\vec{p} \rangle$ to be used in (42), it is necessary to express $\vec{\xi}$ in the coordinate system (x, y, z) at the area element at (a, θ, ϕ) ; for example:

$$\xi_X = \xi_Z \sin \theta \cos \phi + \xi_X \cos \theta \cos \phi - \xi_Y \sin \phi \quad (70)$$

Evaluating the many integrals in the expression

$$\frac{4m^2 \bar{n}}{\gamma^{3/2}} \frac{\Delta t}{\pi^{3/2}} a^2 \int_0^\pi d\theta \sin \theta \cos^2 \theta \int_0^{2\pi} d\phi \int_{(\xi_Z > 0)} d\vec{\xi} (-\xi_Z^3) f \quad (71)$$

and in a similar expression for $N \langle \vec{p}\vec{p} \rangle$, leads to

$$N \langle p_i \rangle = \beta \Delta t \left[v_i - \frac{1}{5p} \left\{ q_i + \sum_j \tau_{ij} v_j \right\} \right] \quad (72)$$

and

$$N \langle p_I p_I \rangle = (8/3) \pi a^2 \bar{n} \bar{c} \Delta t m k T \left[1 - \frac{3}{5} \left\{ \frac{\tau_I}{p} + \frac{4}{5} H_I S_I + \frac{2}{5} \vec{H} \cdot \vec{S} \right\} \right] \quad (73)$$

Here, dimensional quantities have been returned to and

$$\vec{H} = (\gamma^{1/2}/5p)\vec{q} \quad . \quad (74)$$

Since $|\vec{q}|/5p = O(\tau_I/p)$ is small for the Chapman-Enskog distribution function to be valid, then, for $S \ll 1$,

$$H_I S_I = o(\tau_I/p) \quad (75)$$

and will be ignored.

As Chandrasekhar has shown, the Langevin equation can be used to describe the motion of a Brownian particle. Substituting (72) and (73) into (42) yields the Langevin equation for a Brownian particle in a nonequilibrium environment:

$$\frac{dV_i}{dt} = -\beta^* (V_i - \frac{1}{5p} \sum_j \tau_{ij} V_j) + k_i(\vec{R}, \vec{V}, t) + A_i(t) \quad (76)$$

where

$$k_i = f_i^{(e)}(\vec{R}, \vec{V}, t) + \beta^* [(V_f)_i + \frac{1}{5p} \left\{ q_i - \sum_j \tau_{ij} (V_f)_j \right\}] \quad (77)$$

in which $\vec{f}^{(e)}$ is any external force per unit mass acting on the particle and $\vec{A}$ is the stochastic acceleration. If the principal axes are used, then

$$B_I(\Delta t) = \int_t^{t+\Delta t} A_I(s) ds \quad (78)$$

is distributed according to

$$w(B_I) = \left[4\pi \frac{kT}{M} \frac{\Delta t}{\tau^*} \left(1 - \frac{3\tau_I}{5p} \right) \right]^{-1/2} \exp \left\{ \frac{-B_I^2}{\frac{4kT}{M} \frac{\Delta t}{\tau^*} \left(1 - \frac{3\tau_I}{5p} \right)} \right\} . \quad (79)$$

When the environment is in equilibrium, that is, when $\vec{q}$ and $\hat{\tau}$ vanish, then equations (76) through (79) reduce to the equations used by Chandrasekhar.

VI. THE APPROPRIATE FOKKER-PLANCK EQUATION

If (72) and (73) are interpreted as defining the mean and variance of the transition probability in velocity space, then as in Section IV a Fokker-Planck equation can be obtained. The Chapman-Kolmogoroff equation leads to

$$\begin{aligned} \frac{\partial W}{\partial t} + \vec{V} \cdot \nabla_R W = & - \sum_i \frac{\partial}{\partial V_i} (W \langle \Delta V_i \rangle) \\ & + \frac{1}{2} \sum_i \frac{\partial^2}{\partial V_i^2} (W \langle \Delta V_i^2 \rangle) \end{aligned} \quad (80)$$

where, from (72) and (73),

$$\langle \Delta V_I \rangle = f_I^{(e)} + \frac{\beta^*}{5p} q_I - \beta^* \left(1 - \frac{\tau_I}{5p} \right) [V_I - (V_f)_I] \quad (81)$$

and

$$\langle \Delta V_I^2 \rangle = \frac{2kT}{M\tau^*} \left(1 - \frac{3\tau_I}{5p} \right) \quad (82)$$

In (81) an external force per unit mass, $f_I^{(e)}$ has been added and in both (81) and (82), terms $O(\Delta t)$ have been ignored.

Substituting (81) and (82) into (80) and invoking the fundamental theorem of tensor analysis, there results the appropriate Fokker-Planck equation, valid in all coordinate systems:

$$\frac{\partial W}{\partial t} + \vec{V} \cdot \nabla_R W + \vec{k} \cdot \nabla_V W = -(\nabla_V \cdot \vec{k})W + \nabla_V \cdot (\tilde{\beta} \cdot \vec{V} W) + \nabla_V \cdot (\tilde{D}_V \cdot \nabla_V W) \quad (83a)$$

where

$$\vec{k} = \vec{f}^{(e)} + \frac{\beta^*}{5p} \vec{q} + \tilde{\beta} \cdot \vec{V}_f \quad (83b)$$

$$\tilde{\beta} = \beta^* \left(\tilde{I} - \frac{1}{5p} \tilde{\tau} \right) \quad (83c)$$

$\tilde{I}$ is the identity or metric tensor

and a diffusion coefficient in velocity space has been identified as the second order tensor:

$$\tilde{D}_V = \frac{kT}{M\tau^*} \left(\tilde{I} - \frac{3}{5p} \tilde{\tau} \right) \quad (83d)$$

Equation (83) is the fundamental result of this analysis. It contains all the information of the preceding theory. Since, in general, it cannot be solved for arbitrary $\vec{V}_f$ and $\vec{q}$, the subsequent discussion will evolve from simplifications and approximations of (83). Professor Chandrasekhar has kindly provided us with the useful observation that our method of obtaining (83), whereby $C(\vec{\rho})$ was approximated by its first two terms (see equation 42), is all that is required for the Fokker-Planck equation. That is, higher order moments of the distribution could have been calculated but they would not appear in (83).

A major simplification of (83) is to ignore the $\vec{R}$ dependence of $W(\vec{R}, \vec{V}, t)$. Suppose, in addition, that the external force per unit mass $\vec{f}^{(e)}$ is a constant and that $\vec{V}_f$ and $\vec{q}$ are independent of time. Then (83) becomes

$$\frac{\partial W}{\partial t} + \left\{ \vec{k} - \tilde{\beta} \cdot \vec{V} \right\} \cdot \nabla_V W = 3\beta^* W + \nabla_V \cdot (\tilde{D}_V \cdot \nabla_V W) \quad (84)$$

To solve (84), it is convenient to change from the Cartesian coordinate system (V_1, V_2, V_3) in velocity space to the natural coordinate system defined by the "undiffused trajectory":

$$\frac{dV_i}{dt} = k_i - \beta_i^j V_j \quad (85)$$

where

$$\beta_j^i = \beta^*(\delta_j^i - \frac{1}{5p} \tau_j^i) \quad (86)$$

In (85) and (86), and throughout this section, the summation convention will be used. Indices that are capitalized are not to be summed. The purpose of using both subscripts as well as superscripts is only to assist in accounting for indices.

Since $\tilde{\tau}$ is a symmetric, second order tensor, it can be diagonalized by a simple rotation of the coordinate system. The new coordinate system is, of course, the coordinate system used in the derivation of (72) and (73). For definiteness, suppose τ_j^i is diagonalized (locally) by the matrix of transformation c_j^i . Thus, rotate V_i to U_i according to

$$V_i = c_i^j U_j \quad (87)$$

Let γ_j^i be the inverse of c_j^i ; that is,

$$\gamma_j^i c_k^j = \delta_k^i \quad (88)$$

Since τ_j^i is symmetric, $\gamma_j^i = c_i^j$.

Substituting (87) into (85) and multiplying through by γ_ℓ^i leads to the equation for the undiffused trajectory

$$\frac{dU}{dt}^\ell = \lambda_L U_\ell + K_\ell \quad (89)$$

where λ_L are the (real) eigenvalues of β_j^i ,

$$\gamma_\ell^i \beta_i^j c_j^k = \lambda_L \delta_\ell^k, \quad (90)$$

namely

$$\lambda_L = \beta^*(1 - \tau_L/5p) \quad (91)$$

and

$$K_\ell = \gamma_\ell^i k_i \quad (92)$$

are the components of $\vec{k}$ along the principal axes. The solution to (89) is

$$U_\ell = (U_\ell)_0 \exp(-\lambda_L t) + (K_\ell/\lambda_L) [1 - \exp(-\lambda_L t)] \quad (93)$$

Thus, to simplify (84), introduce the new independent variables ρ_ℓ and t where

$$\rho_\ell = [U_\ell - K_\ell/\lambda_L] \exp(\lambda_L t) \quad (94)$$

Substituting (94) into (84) leads to

$$\frac{\partial W}{\partial t} = 3\beta^* W + \frac{kT}{M\tau^*} \left(1 - \frac{3\tau_L}{5p}\right) e^{2\lambda_L t} \frac{\partial^2 W}{\partial \rho_\ell^2} \quad (95)$$

Suppose the initial velocity of the particle is known to be $\vec{U}_0$, then a simple extension of Chandrasekhar's Lemma II (his equations 236-238) leads to the solution

$$W(\vec{U}, t) = \prod_{L=1}^3 \left\{ \frac{2\pi kT}{M\tau^* \beta^*} \left(1 - \frac{2\tau_L}{5p}\right) \left(1 - e^{-2\lambda_L t}\right) \right\}^{-1/2} \exp \left\{ \frac{-[U_L - (U_L)_0 e^{-\lambda_L t} - (K_L/\lambda_L) (1 - e^{-\lambda_L t})]^2}{\frac{2kT}{M\tau^* \beta^*} \left(1 - \frac{2\tau_L}{5p}\right) \left(1 - e^{-2\lambda_L t}\right)} \right\} \quad (96)$$

Equation (96) predicts (to terms of first order in gradients) that for $t \gg \beta^{-1}$, the particle will drift with a mean velocity given by

$$\langle \vec{V} \rangle = \frac{1}{\beta^*} \vec{f}(e) + \vec{V}_f + \frac{1}{5p} \vec{q} + \frac{1}{\beta^*} \vec{f}(e) \cdot \frac{\vec{\tau}}{5p} \quad (97)$$

The first two terms on the right-hand side of (97) are familiar. The third term explains the thermophoresis effect^{26,27}. This is the Brownian motion counterpart of thermal diffusion^{28,29}. The last term is new and might in analogy, be called the stressphoresis effect. It is hoped that an experimentalist could devise a method to observe this new drift velocity.

VII. THE CONVECTIVE-DIFFUSION EQUATION

In equation (96) it is seen that after a time interval $O(\beta^{-1})$, the velocity distribution function for the Brownian particle approaches a constant, skewed Maxwellian, locally. If the details of this relaxation of the velocity distribution function 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 particle can be obtained by eliminating the velocity distribution function from consideration. Thereby an equation is obtained which describes the particle's motion only in configuration space. Let $w(\vec{R}, t; \vec{R}_0, t_0) d\vec{R}$ be the probability that the Brownian particle is located in $d\vec{R}$ about $\vec{R}$ at time t if it were known to be at $\vec{R}_0$ at time t_0 . Thus

$$w(\vec{R}, t; \vec{R}_0, t_0) = \int d\vec{V}_0 \int d\vec{V} w(\vec{R}, \vec{V}, t; \vec{R}_0, \vec{V}_0, t_0) f(\vec{V}_0) \quad , \quad (98)$$

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

To obtain the resultant Smoluchowski-Kramers equation, consider one-dimensional (r, u) motion of the particle along one of the principal axes. Kramers' method^{31,6} can be generalized to include the effects of a nonequilibrium

environment by recasting the generalized Fokker-Planck equation (83) into the identity

$$\begin{aligned} \frac{\partial W}{\partial t} = & \beta_I \left(\frac{\partial}{\partial u} - \frac{1}{\beta_I} \frac{\partial}{\partial r} \right) \left[Wu + \beta_I D_I \frac{\partial W}{\partial u} + D_I \frac{\partial W}{\partial r} \right. \\ & + \frac{W}{\beta_I} \frac{\partial}{\partial r} (\beta_I D_I) - \frac{KW}{\beta_I} \left. \right] + \frac{\partial}{\partial r} \left[D_I \frac{\partial W}{\partial r} \right. \\ & + \frac{W}{\beta_I} \frac{\partial}{\partial r} (\beta_I D_I) - \frac{KW}{\beta_I} \left. \right] . \end{aligned} \quad (99)$$

In (99),

$$K = f^{(e)} + \beta^* q / (5p) + \beta_I u_f \quad (100)$$

is assumed to be independent of u and β_I and D_I are defined by:

$$\beta_I = \beta^* [1 - \tau_I / (5p)] \quad (101)$$

$$D_I = D_V / \beta_I^2 \div D^* [1 - \tau_I / (5p)] . \quad (102)$$

The identity (99) removes the restriction to an isothermal environment which is discussed by Chandrasekhar⁶.

During the time $O(\beta^{-1})$ that the velocity distribution function relaxes to its steady value, locally, the mean motion of the particle is governed by

$$\frac{du}{dt} = -\beta_I u + K . \quad (103)$$

If β_I and K do not vary significantly during the time interval $O(\beta^{-1})$ and over the distance $O(K\beta^{-2})$, then the trajectory of this mean motion is given by

$$r + u/\beta_I - Kt/\beta_I = \text{constant} \quad . \quad (104)$$

In the new independent variables

$$\xi = r + u/\beta_I - Kt/\beta_I, \quad \eta = u, \quad \zeta = t \quad , \quad (105)$$

where $\xi = \text{constant}$ is the mean trajectory of the Brownian particle, the identity (99) becomes

$$\begin{aligned} \left[\frac{\partial}{\partial \zeta} - \frac{K}{\beta_I} \frac{\partial}{\partial \xi} \right] W = & \beta_I \frac{\partial}{\partial \eta} \left[Wu + \beta_I D_I \frac{\partial W}{\partial u} + D_I \frac{\partial W}{\partial r} \right. \\ & + \frac{W}{\beta_I} \frac{\partial}{\partial r} (\beta_I D_I) - \frac{KW}{\beta_I} \left. \right] \\ & + \frac{\partial}{\partial \xi} \left[D_I \frac{\partial W}{\partial \xi} + \frac{W}{\beta_I} \frac{\partial}{\partial \xi} (\beta_I D_I) \right. \\ & \left. - \frac{KW}{\beta_I} \right] \quad . \quad (106) \end{aligned}$$

Now, to eliminate the velocity distribution function from the analysis, equation (106) is integrated over all velocities u (or η) from $-\infty$ to $+\infty$ along the trajectory (104); that is, keeping ξ constant. Obviously, from (105), if ξ is to remain constant then r and/or t must vary. However, since β^{-1} is typically extremely small ($\approx 10^{-8}$ sec for a 100 Å particle) then the variation in r and/or t need not be large to hold ξ constant. More quantitatively, let $\Delta r|_t$ be the variation in r (with t fixed) that is required to hold ξ constant as u varies — at least as u varies

through those values that give dominant contribution to the integral. The latter can be estimated from (96) to be

$$\Delta u \doteq (kT/M)^{1/2} . \quad (107)$$

The corresponding Δr is, from (105),

$$\Delta r|_t \doteq \beta^{-1} \Delta u \doteq (D/\beta)^{1/2} . \quad (108)$$

In addition, as t increases r must increase even more than that given by (108) if ξ is to remain constant. For $\Delta t \doteq \beta^{-1}$, the corresponding Δr is

$$\Delta r \doteq K/\beta^2 . \quad (109)$$

Integrating (106) over all η and using the prediction (96) that W rapidly tends to zero for large u and, in addition, integrating over the possible distribution of initial velocities, then (106) becomes

$$\left(\frac{\partial}{\partial \xi} - \frac{K}{\beta_I} \frac{\partial}{\partial \xi} \right) w = \frac{\partial}{\partial \xi} \left[D_I \frac{\partial w}{\partial \xi} + \frac{w}{\beta_I} \frac{\partial}{\partial \xi} (\beta_I D_I) - \frac{Kw}{\beta_I} \right] . \quad (110)$$

The left-hand side of (110) is the time derivative of w , written for an observer moving along the trajectory $r + Kt/\beta_I = \text{constant}$. It is convenient to return to $\partial/\partial t$. The right-hand side of (110) contains not $\partial/\partial r$ but $\partial/\partial \xi$. However, if w , D_I and β_I change, but not significantly over distances Δr given by either (108) or (109), whichever is larger, then (110) can be approximated by

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial r} \left[D_I \frac{\partial w}{\partial r} + \frac{w}{\beta_I} \frac{\partial}{\partial r} (\beta_I D_I) - \frac{Kw}{\beta_I} \right] . \quad (111)$$

In an arbitrary coordinate system, (111) becomes the generalized Smoluchowski-Kramers equation

$$\frac{\partial w}{\partial t} = \nabla \cdot [\tilde{D} \cdot \nabla w + w(\nabla \cdot \tilde{D} - \vec{v}_d)] . \quad (112)$$

Here, to first order in gradients, the drift velocity is given by

$$\begin{aligned} \vec{v}_d = \vec{V}_f + \frac{\vec{q}}{5p} + \frac{\vec{f}(e)}{\beta^*} \cdot \left(\tilde{I} + \frac{\tilde{\tau}}{5p} \right) \\ + \tilde{D} \cdot \left[\frac{\nabla \beta^*}{\beta^*} - \frac{\nabla \cdot \tilde{\tau}}{5p} \right] . \end{aligned} \quad (113)$$

The diffusion coefficient appears as the second order tensor

$$\tilde{D} = D^* \left[\tilde{I} - \frac{1}{5p} \tilde{\tau} \right] . \quad (114)$$

If there is a number density, N , of noninteracting Brownian particles in the fluid and if the initial location of these particles is not known with certainty, then it is convenient to replace (112) by a convective-diffusion equation. Since

$$N(\vec{R}, t) = \int d\vec{R}_0 w(\vec{R}, t; \vec{R}_0, t_0) N(\vec{R}_0, t) , \quad (115)$$

then operating on (114) with the operator in (112) and utilizing (112) yields³²

$$\frac{\partial N}{\partial t} = \nabla \cdot \left[\tilde{D} \cdot \nabla N + N(\nabla \cdot \tilde{D} - \vec{v}_d) \right] , \quad (116)$$

in which $\vec{v}_d$ is given by (113). Equation (116) is the generalized (or corrected) convective-diffusion equation and can serve as a starting point for many investigations.

The tensorial character of the diffusion coefficient in (114) implies that in a flow in which there exist viscous stresses, Brownian particles do not diffuse spherically symmetrically. Surfaces of constant density, instead of spherical, are ellipsoidal about the mean position dictated by $\vec{v}_d$. The principal axes of these ellipsoids coincide with the principal axes that diagonalize the viscous stress tensor. The dependence of $\tilde{D}$ on $\vec{v}$ at least qualitatively explains the observations reviewed by Fuchs³² that the diffusion coefficient in a nonequilibrium environment depends on the mean flow velocity. Some quantitative predictions of (116) have been obtained but the bulk of them will be left for future work.

VIII. SUMMARY AND CONCLUSIONS

The objective of this research was to determine how the diffusion of submicron particles in air is affected by a nonequilibrium state of the air environment. However, before nonequilibrium effects could be studied, it was necessary to strengthen the foundations of the equilibrium theory. Einstein's method requires that both the fluid and the particles be in thermodynamic equilibrium. The methods of Chandrasekhar and his predecessors are appropriate for the study of the relaxation of the particle to equilibrium but an integral part of their theories is to assume what the equilibrium state will be. To circumvent this assumption, Markoff's method was used to determine the statistical properties of the stochastic force acting on a Brownian particle whose Knudsen number is large compared to one. This method was found to be suitable for both equilibrium and nonequilibrium environments.

In the case of an equilibrium environment, the statistical properties of the stochastic force were calculated for both specular and diffuse reflections of the molecules from the particle's surface. For specular reflection of the molecules from a stationary Brownian particle, the description of the stochastic force can be used to determine

the drag coefficient, provided equipartition is assumed. This is in accord with the fluctuation-dissipation theorem.

It was found to be unnecessary to utilize Langevin's separation of the total force acting on a Brownian particle which is in motion. Starting from Newton's second law and using the central limit theorem, a statistical description of the total force was obtained. For specular reflection of the molecules this led to the prediction, rather than the postulate, of equipartition at equilibrium and to the usual expression for the diffusion coefficient. However, for diffuse reflections some unexpected results appeared. The diffusion coefficient was found to depend on the temperature of the particle and on the number of molecules that are reflected diffusely. These results indicate a practical limitation to the fluctuation-dissipation theorem.

Once the method had been developed that gave a complete theory of the Brownian motion of a particle in an equilibrium environment, then nonequilibrium effects could be included. A new force appeared which describes what has been called the stressphoresis effect. The new Fokker-Planck equation was obtained and solved in velocity space. In the Smoluchowski and convective-diffusion equations, the diffusion coefficient appears as a second order tensor dependent upon the viscous stress tensor.

There are a number of avenues open for future work. The theory developed here is restricted to particles whose Knudsen number is large compared to one. It is expected that the more difficult, continuum regime will yield similar results but with Stokes' drag coefficient replacing Epstein's. Other significant studies would be to derive the new Smoluchowski equation from the Langevin equation and to compare the results obtained here with the predictions of the phenomenological theory of transport processes. In addition, there exist a host of practical problems that can be analyzed with the new convective diffusion equation and tested experimentally.

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