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# A Kinetic Theory of Diffusely Reflecting Brownian Particles

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An analysis is made of the motion of a spherical Brownian particle whose surface can diffusely reflect the molecules of an equilibrium host gas. The analysis is based on Newton's second law and a limiting form of Markov's method. It is shown, both for specular and diffuse reflections, that equipartition of energy is a consequence of the dynamics and randomness of the motion. In addition, it is demonstrated that the diffusion coefficient can depend on the temperature of the particle. The entire analysis is restricted to the case for which the Knudsen number of the particle is large compared to unity.

**KEY WORDS:** Brownian motion; molecular diffusion; Einstein's diffusion coefficient; fluctuation-dissipation theorem; equipartition theorem; entropy; statistical mechanics.

## 1. INTRODUCTION

Recently, Harris$^{(1)}$ wrote that "a rigorous dynamical theory for the Brownian motion of assemblies of unstructured particles has been established within the framework of statistical mechanics." In support of this statement, we would like to add to his references the thorough study by Green$^{(2)}$ and a recent report by Mazo.$^{(3)}$ Harris proceeds to analyze the motion of structured Brownian particles ($B$ particles).

In this report, we shall analyze the motion of structured $B$ particles whose radius is small compared with the mean free path for the molecules of the equilibrium host gas. Actually, the analysis arose from the recent study by Shen and Slinn$^{(4,5)}$ of

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Brownian motion in a nonuniform gas, but in this paper the results will be illustrated only for the case of a uniform gas. The particular structure of the $B$ particle that will be considered differs from the structure studied by Harris in that we consider spherical particles whose surfaces can diffusely reflect the gas molecules. The gas itself is assumed to be composed of structureless molecules.

An outline of the present analysis is the following. First, Markov's method is slightly extended and then illustrated for a problem similar to the classic, rotary Brownian motion problem of Uhlenbeck and Goudsmit.(6) After a preliminary study is made of the stochastic force on a stationary, specularly reflecting $B$ particle, we proceed to remove these restrictions. Finally, some consequences of the new results are discussed.

## 2. MARKOV'S METHOD

Consider a $B$ particle of mass $M$ which is moving with velocity $\mathbf{V}$ through a uniform gas. It is assumed that Newton's second law adequately describes the motion of the particle. If the total force on the $B$ particle is separated into a continuous drag force $-M\beta\mathbf{V}$, where $\beta$ is the drag coefficient per unit mass, and a stochastic force $M\mathbf{A}$, which has zero mean, then Newton's second law becomes the Langevin equation:

$$d\mathbf{V}/dt = -\beta\mathbf{V} + \mathbf{A}(t) \qquad (1)$$

To analyze the motion of the $B$ particle, it is necessary to obtain a statistical description of the stochastic acceleration $\mathbf{A}$.

Actually, it is more useful to determine the probability density function (pdf) of the change in velocity

$$\mathbf{B} = \int_{t}^{t+\Delta t} \mathbf{A}(s)\, ds \qquad (2)$$

incurred during $\Delta t$ by the $B$ particle from random collisions with the gas molecules. Chandrasekhar(7) postulated that the pdf for $\mathbf{B}$ is

$$W(\mathbf{B}) = (4\pi kT\beta\,\Delta t/M)^{-3/2} \exp\{-M\,|\,\mathbf{B}\,|^2/4kT\beta\,\Delta t\} \qquad (3)$$

where $k$ is Boltzmann's constant and $T$ is the absolute temperature of the equilibrium environment. Earlier, Green(2) used Markov's and other methods to derive Eq. (3) for structureless $B$ particles with large Knudsen number. In the next section, we will present our own, independent derivation which differs in detail from Green's and which leads to the method that we shall use for structured $B$ particles.

Rather than seek the pdf, $W(\mathbf{B})$, for the change in velocity, it is more convenient to evaluate the closely related pdf for the total momentum $\mathbf{P}$ delivered during $\Delta t$ to the $B$ particle. If gas molecule $j$ delivers momentum $\mathbf{p}_j$ to the particle during $\Delta t$, then

$$\mathbf{P} = \sum_{j=1}^{N} \mathbf{p}_j \qquad (4)$$

where $N$ is the (unknown) total number of molecules that hit the $B$ particle during $\Delta t$. Each $\mathbf{p}_j$ depends on variables or "coordinates" $\mathbf{q}_j$ such as the molecule's speed $\xi$, its initial location, and its direction of travel. For a dilute gas in equilibrium, the pdf's $\tau_j(\mathbf{q}_j)$ of these coordinates are known.

Markov's result provides a method for calculating the pdf for $\mathbf{P}$ from knowledge of $\tau_j(\mathbf{q}_j)$, provided that the $\mathbf{p}_j$ are independent, random variables. This condition restricts our analysis to the case for which the movements of the gas molecules in the neighborhood of the particle are independent of one another. That is, it is required that the Knudsen number Kn (the ratio of the mean free path for the gas molecules, $\lambda$, to the radius of the particle $a$) be large compared to unity. Markov's result is

$$W(\mathbf{P}) = [1/(2\pi)^3] \int d\boldsymbol{\rho}\, A_N(\boldsymbol{\rho}) \exp\{-i\boldsymbol{\rho} \cdot \mathbf{P}\} \tag{5}$$

where

$$A_N(\boldsymbol{\rho}) = \prod_{j=1}^{N} \int d\mathbf{q}_j\, \tau_j(\mathbf{q}_j) \exp\{i\boldsymbol{\rho} \cdot \mathbf{p}_j(\mathbf{q}_j)\} \tag{6}$$

Except for the presence in Eq. (6) of $\mathbf{p}(\mathbf{q})$ rather than $\mathbf{q}$ alone, this is almost the familiar result$^{(8)}$ that the characteristic function for the sum of independent, random variables is the product of the characteristic functions of the elements of the sum.

Equation (6) will be modified slightly in a manner which was indicated by Chandrasekhar.$^{(7)}$ For the case when $\mathbf{q}_j$ and $\tau_j$ are the same for all $j$, then Eq. (6) becomes

$$A_N(\boldsymbol{\rho}) = \left[\int d\mathbf{q}\, \tau(\mathbf{q}) \exp\{i\boldsymbol{\rho} \cdot \mathbf{p}\}\right]^N \tag{7}$$

If $N$ is large enough, then, using the definition of the exponential

$$e = \lim_{h\to\infty} \left(1 + \frac{1}{h}\right)^h$$

and using

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

then Eq. (7) becomes

$$A_N(\rho) = \exp\{-C(\boldsymbol{\rho})\} \tag{8}$$

where

$$C(\boldsymbol{\rho}) = N \int d\mathbf{q}\, \tau(\mathbf{q})[1 - \exp\{i\boldsymbol{\rho} \cdot \mathbf{p}\}] \tag{9}$$

Equation (9) and a power series expansion of $C(\boldsymbol{\rho})$ in $\boldsymbol{\rho}$ will be utilized a number of times in the subsequent analysis.

Before continuing with the Brownian motion problem, it may be useful to illustrate the use of Markov's method by calculating the pdf for the number of molecules that, during $\Delta t$, strike one side of an area element $\Delta A$ which is immersed in a dilute gas in equilibrium. Let the total number of molecules that hit the plate during $\Delta t$ be $H$. If $h_j$ takes the numerical value 1 if molecule $j$ hits the plate and 0 if it does not, then

$$H = \sum_{j=1}^{N} h_j \tag{10}$$

where $N$ is the total number of molecules that could conceivably hit the plate during $\Delta t$.

To learn something about $N$, we remark that the velocity distribution function for the molecules of the gas will be taken to be Maxwellian. This admits the possibility that molecules have extremely large speeds, and thereby it is tempting to conclude that any molecule in the hemisphere of radius $R \to \infty$ above the plate could hit $\Delta A$ during $\Delta t$. Thus, it is suggested that

$$N = \tfrac{1}{2}(\tfrac{4}{3}\pi R^3)\,\bar{n} \gg 1 \tag{11}$$

where $\bar{n}$ is the mean number density of gas molecules. On the other hand, a more realistic estimate of $N$ incorporates the duration of the time interval, $\Delta t$. Thus, $N$ is of the order of $\bar{n}\bar{c}\,\Delta A\,\Delta t$, where the mean thermal speed of the molecules is

$$\bar{c} = (8kT/\pi m)^{1/2} \tag{12}$$

in which $m$ is the mass of a molecule of the gas. Equation (11) will be used in the sequel, but it is recognized that the use of the asymptotic expression, Eq. (8), for $A_N(\rho)$ implies a condition on $\Delta t$. This condition will be seen below.

The coordinates $\mathbf{q}_j$ upon which each $h_j$ depends are the molecule's speed $\xi$, its initial location $\mathbf{r} = (r, \theta, \omega)$, and its direction of travel. If the fluid is in equilibrium, then, by the theorem of detailed balance,(9) collisions between molecules need not be considered. The pdf for these coordinates is taken to be the product of the density functions:

$$\tau(\mathbf{q}) = 4\pi\left(\frac{\gamma}{\pi}\right)^{3/2} \xi^2 \exp\{-\gamma\xi^2\} \cdot \frac{dV}{4\pi R^3/6} \cdot \frac{d\Omega}{4\pi} \tag{13}$$

where $\gamma = m/2kT$. Thus, the speeds are assumed to have a Maxwellian distribution and the initial location (within volume element $dV$) and direction of travel (within solid angle $\Omega$) are assumed to be random. The statistical distribution of the coordinates is the same for all molecules.

The pertinent range of these coordinates can be determined from the following arguments. Molecule $j$, with speed $\xi$, could hit $\Delta A$ during $\Delta t$ only if it is within the distance $\xi\,\Delta t$ of the plate. In addition, its direction of travel must be within the solid angle $\Delta\Omega = \Delta A \cos\theta/r^2$ subtended at $r$ by the plate.

Substituting Eqs. (11) and (13) into Eq. (9) leads to

$$C(\rho) = \bar{n}\left(\frac{\gamma}{\pi}\right)^{3/2} \int_0^\infty d\xi\,\xi^2 \exp\{-\gamma\xi^2\} \int_0^{\xi\Delta t} dr\,r^2 \times \int_0^{\pi/2} d\theta\,\sin\theta \int_0^{2\pi} d\omega \int_0^{\Delta A\cos\theta/r^2} d\Omega[1 - \exp\{i\rho\}] \tag{14}$$

Thus, almost trivially,

$$C(\rho) = \overline{M}[1 - \exp\{i\rho\}] \tag{15}$$

where $\overline{M} = \bar{n}\bar{c}\,\Delta A\,\Delta t/4$. Finally, substituting Eq. (15) into (8) and the result into Eq. (5) gives

$$W(H) = \overline{M}^{H} e^{-\overline{M}}/\overline{M}! \tag{16}$$

Equation (16) is the familiar result[10] that the number of molecules that hit an area element during $\Delta t$ has a Poisson distribution with mean $\overline{M}$. It should be noticed that the more general result, that this number has a Bernoulli distribution, was not obtained. The reason for this was our use of the asymptotic formula for $A_N(\rho)$. However, it is well known that when the number of events is sufficiently large, that is, when $\overline{M}$ and therefore when $\Delta t$ is sufficiently large, then an adequate approximation to the Bernoulli distribution is the Poisson distribution. Furthermore, if $\overline{M}$ is large, then an acceptable approximation to the Poisson (or Bernoulli) distribution is the Gaussian distribution. This can be obtained either by expanding Eq. (16) or by expanding Eq. (9) in a power series in $\rho$ and integrating term by term. The latter method will be explored further in the next section.

## 3. STATIONARY PARTICLE—SPECULAR REFLECTIONS

Consider a spherical $B$ particle of radius $a$ that is 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 is exact provided $\mathbf{A}(t)$ is correct. In this section, the study of $\mathbf{A}(t)$ will be simplified through the assumption that the stochastic force on a moving $B$ particle is the same as the stochastic force on a stationary particle. In addition, it will be assumed that the gas molecules reflect specularly from the particle's surface. Both of these restrictions will be removed in the next section.

The method that will be used in this section to calculate the pdf of the total momentum transfer to a stationary $B$ particle is, first, to calculate the momentum transferred during $\Delta t$ to an area element $\Delta A$ 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 $(a, \Theta, \Phi)$ are the usual spherical coordinates of a point on the surface of the sphere, with respect to the origin of coordinates $(X, Y, Z)$ at the center of the sphere. Choose a second coordinate system $(x, y, z)$ at the area element with basis vectors $(\hat{\mathbf{k}}, \hat{\mathbf{i}}, \hat{\mathbf{j}}) = (\hat{\mathbf{e}}_R, \hat{\mathbf{e}}_\Theta, \hat{\mathbf{e}}_\Phi)$. Thus, $\hat{\mathbf{k}}$ is perpendicular to the area element. The momentum delivered during $\Delta t$ to the area element $\Delta A$ is given by Eq. (4). If the molecular collisions are specular, then (by definition)

$$\mathbf{p}_j = 2m\xi \cos\theta(-\hat{\mathbf{k}}) \tag{17}$$

where $\theta$ is the polar angle measured from the $z$-axis of a point $(r, \theta, \omega)$ within the gas.

Substituting Eq. (17) into (9) and using Eq. (13) for the pdf for the coordinates, there results

$$C(\boldsymbol{\rho}) = \bar{n}\left(\frac{\gamma}{\pi}\right)^{3/2} \int_0^{R\to\infty} dr\, r^2 \int_0^{\pi/2} d\theta \sin\theta \int_0^{2\pi} d\omega \int_{r/\Delta t}^{\infty} d\xi$$
$$\times \frac{\Delta A \cos\theta}{r^2}\, \xi^2 \exp\{-\gamma\xi^2\}[1 - \exp\{-i\boldsymbol{\rho}\cdot\hat{\mathbf{k}}\, 2m\xi\cos\theta\}] \tag{18}$$

Evaluating these integrals leads to

$$C(\boldsymbol{\rho}) = im(\pi/\gamma)^{1/2}\, \bar{M}\rho_z\, g(-m\rho_z\gamma^{-1/2}) \tag{19}$$

where

$$g(t) = \exp(-t^2)\,\mathrm{erfc}(-it) \tag{20}$$

is the error function with complex argument.(11) Now, substituting Eq. (19) into (5) and integrating over $\rho_x$ and $\rho_y$ gives

$$W(\mathbf{P}) = \frac{1}{2\pi}\,\delta(P_x)\,\delta(P_y) \int d\rho_z \exp(-i\rho_z P_z) \exp\{-im(\pi/\gamma)^{1/2}\,\bar{M}\rho_z g(-m\rho_z\gamma^{-1/2})\} \tag{21}$$

where the $\delta$'s are Dirac delta functions. Equation (21) 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 Eq. (21). Expanding $g(t)$ of Eq. (20) in the uniformly converging power series(11)

$$g(t) = \sum_{n=0}^{\infty} (it)^n/\Gamma(1 + n/2) \tag{22}$$

and keeping only the first two terms leads to

$$W(\mathbf{P}) = \frac{\delta(P_x)\,\delta(P_y)}{(2\pi\sigma^2)^{1/2}} \exp - \left\{\frac{(P_z - \mu)^2}{2\sigma^2}\right\} \tag{23}$$

where $\mu = -\bar{n}kT\,\Delta t\,\Delta A$ and $\sigma^2 = \pi\bar{M}(m\bar{c})^2$. Thus, to this approximation, the distribution is normal with mean $\mu$ and variance $\sigma^2$.

This procedure of expanding the characteristic function and integrating term by term is a standard method for generating the Edgeworth(12) or Bruns–Charlier(13) series. The conditions for it to yield an acceptable result are essentially those required for the central-limit theorem to be applicable. Green(2) has investigated this step in considerable detail. The general result is that the normal distribution, Eq. (23), is adequate, provided that the next term in the expansion, which is of order $\bar{M}^{-3/2}$, can be ignored compared to the term that has been retained. Thus, we require that $\bar{M}^{1/2} \gg 1$.

The total momentum, say $\mathbf{M}$, delivered to the sphere is given by

$$\mathbf{M} = \sum_{j=1}^{L} \mathbf{P}_j \tag{24}$$

where $\mathbf{P}_j$ is the momentum delivered to area element $j$ and $L = 4\pi a^2/\Delta A$. As was mentioned earlier, the $\mathbf{P}_j$ are taken to be independent, random variables. Instead of attempting to find the distribution of the total $\mathbf{M}$, it is convenient to study a component of $\mathbf{M}$ along some arbitrary direction $Z$. Thus, consider

$$M_Z = \sum_{j=1}^{L} P_j \cos \Phi_j \tag{25}$$

The components of $\mathbf{M}$ along mutually orthogonal directions $X$ and $Y$ will have distributions identical to that of $M_Z$.

From Eq. (23), each $P_j \cos \Phi_j$ will have a normal distribution with mean $\mu_j \cos \Phi_j$ and variance $\sigma_j^2 \cos^2 \Phi_j$, where

$$\sigma_j^2 = (\pi/4)\bar{n}\bar{c}\,\Delta t\,(m\bar{c})^2\,\Delta A_j \qquad \text{and} \qquad \mu_j = \bar{n}kT\,\Delta t\,\Delta A_j$$

To calculate $W(M_Z)$, it is necessary to evaluate, first,

$$A_L(\rho) = \exp\left\{i\rho \sum_{j=1}^{L} \mu_j \cos \Phi_j - \frac{\rho^2}{2} \sum_{j=1}^{L} \sigma_j^2 \cos^2 \Phi_j\right\} \tag{26}$$

In the limit as $L$ becomes large, the summations in Eq. (26) may be changed to integrals. Evaluating these and substituting the result into Eq. (5) results in

$$W(M_Z) = (2\pi\bar{\sigma}^2)^{-1/2} \exp\{-M_Z{}^2/2\bar{\sigma}^2\} \tag{27}$$

where $\bar{\sigma}^2 = \pi\bar{n}\bar{c}(4\pi a^2)\,\Delta t\,(m\bar{c})^2/12$.

If the particle were free to move and if it were to receive momentum $\mathbf{M}$, then its change in velocity could be found from the momentum by dividing the momentum by the mass of the particle. Therefore, from Eq. (27), the probability that during $\Delta t$ the particle's velocity changes by $\mathbf{B}$ to $\mathbf{B} + d\mathbf{B}$ as a result of the random collisions by the gas molecules is

$$W(\mathbf{B})\,d\mathbf{B} = d\mathbf{B}\left(4\pi \frac{kT}{M}\frac{\Delta t}{\tau}\right)^{-3/2} \exp\left\{-\,|\,B\,|^2/4\,\frac{kT}{M}\frac{\Delta t}{\tau}\right\} \tag{28}$$

where

$$\tau = 3M/m\bar{n}\bar{c}4\pi a^2 \tag{29}$$

This result is to be compared to Chandrasekhar's postulate, Eq. (3). The only difference is that in Eq. (28) $\tau$ appears in place of the $(1/\beta)$ of Eq. (3). Proceeding as in Chandrasekhar's review article, the velocity distribution function for a $B$ particle whose initial velocity is $\mathbf{V}_0$ is found to be

$$W(\mathbf{V}, t) = \exp\left\{\frac{|\,\mathbf{V} - \mathbf{V}_0 \exp(-\beta t)|^2}{(2kT/M)(1/\tau\beta)\{1 - \exp(-2\beta t)\}}\right\} \Big/ \left[2\pi \frac{kT}{M}\frac{1}{\tau\beta}\{1 - \exp(-2\beta t)\}\right]^{3/2} \tag{30}$$

Thus, the particle will eventually attain a Maxwellian velocity distribution if

$$\tau\beta = 1 \tag{31}$$

Equation (31) is satisfied; Epstein's drag coefficient $\beta$ for specular reflections of the molecules from a sphere in free-molecule flow(14) is exactly the above result, Eq. (29), for $1/\tau$.

That this formalism has predicted the drag coefficient from information that is available when the sphere is at rest [provided that Eq. (31) is enforced] is not too surprising. The fluctuation–dissipation theorem(15–17) predicts that properties characteristic of equilibrium fluctuations, such as the variance of Eq. (28), are related, simply, to the first-order term of the dissipative response of a thermodynamic system, such as the drag coefficient $\beta$. Einstein's relation for the diffusion coefficient, $D = kT/M\beta$, is the classic example of how fluctuations (manifested in $D$) are related to dissipation (described by $\beta$). Since both the fluctuation and the dissipation are caused by impacts of the fluid molecules on the particle, it is physically reasonable that the "coefficients" are related.

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 fluctuation. Thus, Einstein used Stokes' drag coefficient to determine the diffusion coefficient. Here, $\tau$ has been calculated and can be used to determine $\beta$. It would be interesting to determine if Stokes' drag coefficient could be derived in a similar manner. The second observation is that there is no *a priori* reason to assume $\tau\beta = 1$. Nevertheless, in the fundamental analyses of Brownian motion by Einstein,(18) Langevin,(19) Uhlenbeck and Ornstein,(20) and by Chandrasekhar,(7) essentially this assumption has been made and justified by invoking the equipartition theorem.(21,22) Above, we implicity invoked the equipartition theorem by requiring that the velocity distribution function, Eq. (30), becomes Maxwellian. But it is to be pointed out that here, both $\tau$ and $\beta$ could be calculated and do in fact satisfy $\tau\beta = 1$. In the next section, a more complete analysis will be given.

## 4. MOVING PARTICLE—DIFFUSE REFLECTIONS

In this section, the limitations of the previous section to specular reflections of the molecules and to a stationary $B$ particle will be removed. The motion of the particle is described by Newton's law

$$\mathbf{F} = M\, d\mathbf{V}/dt \tag{32}$$

where $\mathbf{F}$ is the sum of the forces applied to the particle from molecular encounters. In attempting to describe $\mathbf{F}$ statistically, it becomes apparent that it is unnecessary to utilize Langevin's separation of $\mathbf{F}$ into two parts. Instead, a description is sought for the pdf of the total change in momentum of the particle,

$$M\,\Delta\mathbf{V} = \sum_{j=1}^{N} \mathbf{F}_j\,\Delta t \tag{33}$$

that occurs during $\Delta t$. In this section, the mean and variance of $M\,\Delta\mathbf{V}$ will be calculated.

Consider a spherical $B$ particle whose velocity $\mathbf{V}$ is instantaneously in the $Z'$ direction of an inertial coordinate system ($X'$, $Y'$, $Z'$). Choose a second coordinate system ($X$, $Y$ $Z$) whose origin is at the center of the particle and whose axes are instantaneously parallel to the corresponding axes ($X'$, $Y'$, $Z'$). Finally, as in the previous section, choose a third coordinate system ($x, y, z$) with origin at position ($a$, $\Theta$, $\Phi$) on the surface of the sphere.

The momentum transferred to the particle during $\Delta t$ is, say,

$$\mathbf{M} = \sum_{j=1}^{N} \mathbf{P}_j \tag{34}$$

that is, the sum, over all molecules that hit the particle, of the momentum delivered by each. Now, Markov's method could be utilized to determine the pdf for $\mathbf{M}$ but, recognizing the difficulty that arose in the simpler calculation of the previous section, it seems advisable to invoke the central-limit theorem here from the outset. Consequently, Eq. (9) is expanded for small $\boldsymbol{\rho}$ and yields, when only the first two terms are retained

$$C(\boldsymbol{\rho}) = -i\boldsymbol{\rho} \cdot N\langle \mathbf{p} \rangle + (1/2)\, \boldsymbol{\rho} \cdot N\langle \mathbf{pp} \rangle \cdot \boldsymbol{\rho} \tag{35}$$

where

$$\langle \mathbf{p} \rangle = \int d\mathbf{q}\, (\mathbf{q})\, \mathbf{p} \tag{36}$$

$$\langle \mathbf{pp} \rangle = \int d\mathbf{q}\, (\mathbf{q})\, \mathbf{pp} \tag{37}$$

and in which it has been assumed that the pdf's, $\tau_j(\mathbf{q}_j)$, are the same for all $j$.

Since $N$ is the number of molecules that hit the particle during $\Delta t$ and since $\langle \mathbf{p} \rangle$ is the average momentum delivered by a single molecule, then $N\langle \mathbf{p} \rangle$ is the (total) mean momentum delivered to the particle during $\Delta t$. This is just the drag force on the particle multiplied by the time interval. For a sphere which is a perfect thermal conductor, whose Knudsen number is large compared to unity, and whose temperature $T_p$ is the same as the temperature of the environment $T$, Epstein's expression$^{(14)}$ yields

$$N\langle \mathbf{p} \rangle = -M\beta \mathbf{V}\, \Delta t\, [(1 + f\pi/8) + O(\gamma^{1/2} V)] \tag{38}$$

where $f$ is the fraction of the total number of molecules $N$ that are reflected diffusely. As Epstein has shown, the numerical factor $\pi/8$ changes slightly if different reflection models are used.

We shall now slightly extend Epstein's analysis by calculating $N\langle \mathbf{p} \rangle$ for a spherical particle whose temperature $T_p$ has not reached its equilibrium value $T$, the temperature of the gas. It will be assumed that the particle is a perfect thermal conductor so that $T_p$ is independent of position on the sphere. In addition, it will be assumed that the diffusely reflected molecules are perfectly "accomodated" to the temperature of the sphere.$^{(14)}$

To calculate $N\langle \mathbf{p} \rangle$ and $N\langle \mathbf{pp} \rangle$, consider first the incident molecules. If, with respect to ($X'$, $Y'$, $Z'$), the velocity of a gas molecule is $\boldsymbol{\xi}'$ and the velocity of the $B$ particle is $\mathbf{V}$, then with respect to the coordinate system $(X, Y, Z)$ fixed to the particle, the velocity of a molecule is

$$\boldsymbol{\xi} = \boldsymbol{\xi}' - \mathbf{V} \tag{39}$$

The velocity distribution function describing the incident molecules is

$$f_i = (\gamma_i/\pi)^{3/2} \exp\{-\gamma_i \boldsymbol{\xi}' \cdot \boldsymbol{\xi}'\} \tag{40}$$

Substituting Eq. (39) into (40) and expanding for small $\gamma^{1/2}V$ leads to

$$f_i = (\gamma_i/\pi)^{3/2} \exp\{-\gamma_i \boldsymbol{\xi} \cdot \boldsymbol{\xi}\}[1 - 2\gamma_i \boldsymbol{\xi} \cdot \mathbf{V}] \tag{41}$$

The number of molecules that during $\Delta t$ strike the area element at $(a, \Theta, \Phi)$ is

$$N_i = \Delta A\, \Delta t \int_{-\infty}^{+\infty} d\xi_x \int_{-\infty}^{+\infty} d\xi_y \int_{-\infty}^{0} d\xi_z\, (-\xi_z)\, \bar{n}_i f_i \tag{42}$$

That is,

$$N_i = \overline{M}[1 + (\pi\gamma_i)^{1/2}\, V \cos \Theta] \tag{43}$$

where

$$\overline{M} = (1/4)\, \bar{n}_i \bar{c}_i\, \Delta A\, \Delta t \tag{44}$$

The effective number density of diffusely reflected molecules $\bar{n}_r$ can be determined as follows. The velocity distribution function of the diffusely reflected molecules is

$$f_{rd} = (\gamma_r/\pi)^{3/2} \exp\{-\gamma_r \boldsymbol{\xi} \cdot \boldsymbol{\xi}\} \tag{45}$$

where

$$\gamma_r = m/2kT_p \tag{46}$$

Since a fraction $f$ of the total number of molecules is reflected diffusely, the remaining specularly, then the total number of molecules that are reflected is

$$N_r = \Delta A\, \Delta t \left[f \int_{(\xi_z>0)} d\boldsymbol{\xi}\, \bar{n}_r \xi_z f_{rd} + (1 - f) \int_{(\xi_z>0)} d\boldsymbol{\xi}\, \bar{n}_i \xi_z f_{rs}\right] \tag{47}$$

where the velocity distribution function for the specularly reflected molecules $f_{rs}$ is obtained from $f_i$ by replacing $\xi_z$ by $(-\xi_z)$ in Eq. (41). Equating the results given by Eqs. (43) and (47) gives

$$\bar{n}_r = \bar{n}_i (T/T_p)^{1/2}\, [1 + (\pi\gamma_i)^{1/2}\, V \cos \Theta] \tag{48}$$

The momentum delivered to area element $\Delta A$ during $\Delta t$ is

$$m\, \Delta A\, \Delta t \left[\bar{n}_i \int_{(\xi_z<0)} d\boldsymbol{\xi}\, (-\xi_z)\, \boldsymbol{\xi} f_i + \int_{(\xi_z>0)} d\boldsymbol{\xi}\, \xi_z \boldsymbol{\xi}\{(1 - f)\, \bar{n}_i f_{rs} + f n_r f_{rd}\}\right] \tag{49}$$

Evaluating these integrals and then integrating over the sphere gives

$$N\langle \mathbf{p}\rangle = -M\beta\mathbf{V}\, \Delta t\, [1 + f(\pi/8)(T_p/T)^{1/2}] \tag{50}$$

The difference between Eqs. (38) and (50) displays the effect on the drag force of the temperature of the particle.

To calculate $N\langle\mathbf{pp}\rangle$, it is convenient to consider the specularly and diffusely reflected molecules separately. The molecules that are reflected specularly deliver to $\Delta A$ during $\Delta t$

$$(1-f)\int_{(\xi_z<0)} d\boldsymbol{\xi}\, \bar{n}_i(-\xi_z)\, \Delta A\, \Delta t\, (2m\xi_z)^2\, \hat{\mathbf{k}}\hat{\mathbf{k}} f_i \tag{51}$$

Integrating this over the sphere yields

$$[N\langle\mathbf{pp}\rangle]_s = 2(1-f)(4/3)\,\pi a^2 m\bar{n}_i\bar{c}_i\,\Delta t\, kT_i\tilde{I} \tag{52}$$

where $\tilde{I}$ is the identity or metric tensor. To calculate the contributions from the molecules that are reflected diffusely, it is convenient to write

$$\begin{aligned}[N\langle\mathbf{pp}\rangle]_d &= [N\langle(\mathbf{p}_i+\mathbf{p}_r)(\mathbf{p}_i+\mathbf{p}_r)\rangle]_d \\ &= [N\langle\mathbf{p}_i\mathbf{p}_i\rangle]_d + 2[N\langle\mathbf{p}_i\mathbf{p}_r\rangle]_d + [N\langle\mathbf{p}_r\mathbf{p}_r\rangle]_d\end{aligned} \tag{53}$$

The first and third terms on the right-hand side of Eq. (53) are evaluated as in Eq. (51); for example, one first evaluates

$$\int_{(\xi_z>0)} d\boldsymbol{\xi}\, f\bar{n}_r\xi_z\, \Delta A\, \Delta t\, m^2\boldsymbol{\xi}\boldsymbol{\xi} f_{rd}$$

and then integrates over the sphere. The result is

$$[N\langle\mathbf{p}_r\mathbf{p}_r\rangle]_d = f(4/3)\,\pi a^2 m\bar{n}_i\bar{c}_i\,\Delta t\, kT_p\tilde{I} \tag{54}$$

The correlation term is evaluated from

$$(2/fN_i)\Big[\int_{(\xi_z<0)} d\boldsymbol{\xi}\, f\bar{n}_i\, \Delta A\, \Delta t\, (-\xi_z)\, m\boldsymbol{\xi} f_i\Big]\Big[\int_{(\xi_z>0)} d\boldsymbol{\xi}\, f\bar{n}_r\, \Delta A\, \Delta t\, \xi_z m\boldsymbol{\xi} f_{rd}\Big]$$

Summing this over the sphere gives

$$2[N\langle\mathbf{p}_i\mathbf{p}_r\rangle]_d = 2f(\pi/8)(T_p/T_i)^{1/2}\,(4/3)\,\pi a^2 m\bar{n}_i\bar{c}_i\,\Delta t\, kT_i\tilde{I} \tag{55}$$

In summary,

$$N\langle\mathbf{pp}\rangle = \frac{4}{3}\pi a^2 m\bar{n}_i\bar{c}_i\,\Delta t\, kT_i\tilde{I}\left[2-f+f\frac{T_p}{T_i}+2f\frac{\pi}{8}\left(\frac{T_p}{T_i}\right)^{1/2}\right] \tag{56}$$

The limitations on these results should be mentioned. It was not demonstrated explicitly, but, to obtain Eq. (56), terms $O(\gamma V^2)$ have been ignored. This is acceptable provided $(M/m) \gg 1$. Further, to satisfy the central limit theorem,

$$(1/4)\,\bar{n}\bar{c}\,\Delta t\, 4\pi a^2 \gg 1 \tag{57}$$

However, in Eq. (57), $\Delta t$ can not be chosen arbitrarily large because it was assumed that, during $\Delta t$, the mean velocity of the particle does not change significantly. Thus,

$$\Delta t \ll \beta^{-1} \simeq 3M/(4\pi a^2 m\bar{n}\bar{c}) \tag{58}$$

Combining Eqs. (57) and (58), it is seen that it is required that

$$(M/m)^{1/2} \gg 1 \tag{59}$$

Further, we mention again that $Kn \gg 1$.

A few comments on the correlation term, Eq. (55), might be in order. In an earlier analysis this term was ignored based on the (faulty) reasoning that since the *B* particle "Maxwellianized" the diffusely reflecting molecules, the incoming molecule's "memory" would be erased. Thereby, it was concluded that there would be no correlation between the molecule's incident and reflected motions. When this assumption did not lead to equipartition at equilibrium, it was thought that some phenomenon, such as an angular velocity of the particle, might have been overlooked. However, upon finding no phenomena that influenced the result, the above assumption was reexamined. It was finally realized that, of course, the molecules do "remember" where they hit on the surface of the particle. That is, since more molecules are incident on the windward than on the leeward side of the particle, the diffusely reflected molecules are not uniformly distributed over the sphere. Thus, although the motions of different molecules are independent of one another (and therefore Markov's method is still applicable), the incoming and outgoing portions of the trajectories of each molecule are correlated.

If Eqs. (50) and (56) are substituted into Eq. (35), and the result into Eqs. (8) and (5), then the probability that during $\Delta t$ the change in velocity of a Brownian particle is between $\mathbf{B}$ and $\mathbf{B} + d\mathbf{B}$ is found to be

$$W(\mathbf{B})\, d\mathbf{B} = \frac{d\mathbf{B}}{[4\pi(kT/M)(\Delta t/\tau^*)]^{3/2}} \exp\left\{\frac{-\,|\,\mathbf{B} + \beta^* \mathbf{V}\, \Delta t\,|^2}{4(kT/M)(\Delta t/\tau^*)}\right\} \tag{60}$$

Here,

$$\beta^* = \beta[1 + f(\pi/8)(T_p/T)^{1/2}] \tag{61}$$

and

$$(\tau^*)^{-1} = \beta[1 + (f/2)\{(T_p/T) - 1\} + f(\pi/8)(T_p/T)^{1/2}] \tag{62}$$

The subscript that was used to distinguish the incident molecules has been dropped. Notice that if there are no diffusely reflected molecules (that is, if, as in the last section, $f = 0$) or for arbitrary $f$, provided $T_p = T$, then Eqs. (61) and (62) yield

$$\tau^* \beta^* = 1 \tag{63}$$

Some consequences of Eqs. (60)–(62) will be discussed in the next section.

## 5. CONSEQUENCES

Following Chandrasekhar's presentation,⁽⁷⁾ Eq. (60) can be used to obtain a Fokker–Planck equation for diffusely reflecting *B* particles:

$$\frac{\partial W}{\partial t} + \mathbf{V} \cdot \nabla_R W = \beta^* \nabla_V \cdot W\mathbf{V} + \frac{kT}{M\tau^*} \nabla_V{}^2 W \tag{64}$$

Here, $W(\mathbf{R}, \mathbf{V}, t; \mathbf{R}_0, \mathbf{V}_0, t_0)\, d\mathbf{R}\, d\mathbf{V}$ is the probability that the $B$ particle is within the volume element $d\mathbf{R}\, d\mathbf{V}$ about the phase point $\mathbf{R}$, $\mathbf{V}$ at time $t$ if the particle were known to be at $\mathbf{R}_0$, $\mathbf{V}_0$ at time $t_0$. The solution to Eq. (64) in velocity space, subject to the initial condition

$$W(\mathbf{V}, t) \to \delta(\mathbf{V} - \mathbf{V}_0) \qquad \text{as} \quad t \to 0$$

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

$$W(\mathbf{V}, t) = \left[\frac{2\pi kT}{M\tau^*\beta^*}\{1 - \exp(-2\beta^* t)\}\right]^{-3/2} \exp\left\{\frac{-|\mathbf{V} - \mathbf{V}_0 \exp(-\beta^* t)|^2}{(2kT/M\tau^*\beta^*)\{1 - \exp(-2\beta^* t)\}}\right\} \tag{65}$$

Equation (65) is one of the main results of this analysis. Taking into account Eqs. (61) and (62), it is seen that, for $t \gg \beta^{-1}$, Eq. (65) predicts that the velocity distribution function for the $B$ particle becomes Maxwellian regardless of the number of diffusely reflected gas molecules, provided that the particle has come to its equilibrium temperature $T_p = T$. This result, that at equilibrium each degree of freedom of the $B$ particle attains its equipartition value of energy $kT/2$, 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. Thus, equipartition is a consequence of the dynamics and randomness of the motion and not of the specific molecular reflection mechanism under consideration.

The solution to Eq. (64) in phase space can also be obtained from Chandrasekhar's analysis (his equation 286). For $t \gg \beta^{-1}$, it becomes

$$W(\mathbf{R}, \mathbf{V}, t \gg \beta^{-1}) \to \frac{W(\mathbf{V})}{(4\pi D^* t)^{3/2}} \exp - \left\{\frac{|\mathbf{R} - \mathbf{R}_0|^2}{4D^* t}\right\} \tag{66}$$

In Eq. (66), a diffusion coefficient has been identified as

$$D^* = \frac{kT}{M\tau^*}\frac{1}{(\beta^*)^2} = \frac{kT}{M\beta^*}\frac{1 + \frac{1}{2}f[(T_p/T) - 1] + \frac{1}{8}f\pi(T_p/T)^{1/2}}{[1 + f(\pi/8)(T_p/T)^{1/2}]} \tag{67}$$

Two interesting features of Eq. (67) are the following. For $T_p \neq T$ and $f \neq 0$, it is seen that the diffusion coefficient depends on the temperature of the particle. This is reasonable because, if the temperature of the particle is, for example, greater than the temperature of the gas, then as the diffusely reflected molecules leave the particle's surface, they "kick back" harder than do specularly reflected molecules. Thereby, the diffusion coefficient would increase.

A second prediction from Eq. (67) is that, for $T_p = T$, regardless of $f$, Einstein's relation is regained:

$$D^* = kT/M\beta^* \tag{68}$$

In turn, this demonstrates that, to terms $O(\gamma V^2)$, the fluctuation–dissipation theorem is also extendable to those circumstances for which some parameter, such as $f$, external to the thermodynamic bath, influences the response of the thermodynamic system to an external perturbation. Perhaps this is a rather surprising result. However, it is not just the fluctuations of the thermodynamic system which are important (for they do not contain any information about $f$), but it is the fluctuations of the *influence* of the thermodynamic system on the external perturbation. Further, though, notice that, for the nonequilibrium situation, $T_p \neq T$, it would be necessary to know not only $\beta^*$ to obtain $D^*$, but also $f$ and $T_p$.

Finally, it might be of interest to add a few qualitative comments about the dependence of the entropy of the system on the parameter $f$. If Eq. (65) is used in Boltzmann's expression for the entropy (or $H$ function)$^{(23)}$

$$h = \int d\mathbf{V}\, W \log W \tag{69}$$

then an explicit dependence of the $B$ particle's entropy on $f$ and $T_p$ can be obtained. This is an illustration of Prigogine's discussion$^{(24)}$ of the dependence of entropy on "internal coordinates." From an information-theoretic interpretation of entropy, it is reasonable that the entropy of the system should depend on $f$ when $T_p \neq T$. For example, if $T_p \neq 0$, then, introducing a diffusely reflecting $B$ particle into a ($T = 0$)-beam of molecules will randomize their motion. Thus, the entropy of the gas molecules will increase as a function of how many gas molecules are reflected diffusely. A similar phenomenon, discussed by Sommerfeld,$^{(25)}$ occurs when a speck of soot is introduced into a chamber filled with electromagnetic radiation. The soot can transform the radiation field into blackbody radiation. In analogy to the above discussion, it can be said that, when the radiation field is not in equilibrium, then the entropy of the system depends on the amount of soot which is present. As a further extension of these concepts, it might be appropriate to determine the dependence of the entropy on the "coordinates" of Maxwell's familiar demon.$^{(26)}$

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