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Maxwell $\xrightarrow[t\to\infty]{}$ Boltzmann

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This paper presents a new approach to the solution of the Brownian motion problem in which a particle subject to Brownian forces is also subject to a potential. The dynamical description of this system is written in the form of a multiplicative, stochastic, differential equation. This equation is solved and the solution is simplified so that it may be written in terms of integrals of well-understood functions. Enough of the kinematic details of the system are revealed in this way to show that the infinite-time limit of this dynamical solution is a Maxwell–Boltzmann distribution. Although there are other approaches to this problem which yield the infinite-time limit directly, these methods cannot be extended to find the solution to this problem for finite times. In this paper the solution is exhibited for all times, and the details of the approach to the infinite-time limit are elucidated.

KEY WORDS: Brownian motion; Gaussian stochastic process; multiplicative stochastic process; Chandrasekhar–Kramers–Liouville equation.

1. INTRODUCTION

The subject of this paper is the problem of a particle under the influence of a bounded potential and interacting with a fluid of other particles. Some physical problems related to this one are chemical reaction rates,[1] macromolecular bonding in solution, ion mobility experiments and calculations, and the spectral linewidth of atoms.[2] Kramers has studied this problem in the high-viscosity limit and applied the results to the problem of chemical reaction rates. In this paper the problem is considered in a less restricted way.

The model which is used for the above problem is a particle in a box, where periodic boundary conditions are assumed, influenced by an external potential and a "Brownian" fluid. The "Brownian" fluid is considered to be composed of particles which make their presence known only through a stochastic force $\tilde{F}(t)$ and a damping coefficient α. It is assumed that initially

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the particle is described by a probability distribution which is Maxwellian in momentum space and arbitrary in position space.

This type of problem may be approached in several ways. For example, it is known that the Brownian motion will cause the momentum distribution to relax to a Maxwellian distribution. One may use this information to calculate the infinite-time limit of the position distribution. This approach has the advantage of being short and straightforward. It cannot, however, be extended to a calculation of the probability distribution at finite times. In particular, the distribution function is not a product of position and momentum distributions at finite times.

Another approach, the one used in this paper, is to write the dynamical equation governing the time evolution of the distribution function and find an expression for the distribution function at time t. From a stochastic analog of the Liouville equation,

$$\frac{\partial}{\partial t} D(r, p, t) = \left\{ -\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU(r)}{dr}\frac{\partial}{\partial p} - \frac{\partial}{\partial p}\left[-\frac{\alpha}{m} p + \tilde{F}(t) \right] \right\} D(r, p, t)$$

one may find the Chandrasekhar–Kramers–Liouville equation,[3]

$$\frac{\partial}{\partial t}\langle D(r, p, t)\rangle = \left[-\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU(r)}{dr}\frac{\partial}{\partial p} + \alpha \frac{\partial}{\partial p}\left(\frac{p}{m} + \beta^{-1}\frac{\partial}{\partial p} \right) \right] \langle D(r, p, t)\rangle$$

This equation has the solution

$$\langle D(r, p, t)\rangle = \exp\left[-\frac{pt}{m}\frac{\partial}{\partial r} + t\frac{dU(r)}{dr}\frac{\partial}{\partial p} + \alpha t \frac{\partial}{\partial p}\left(\frac{p}{m} + \beta^{-1}\frac{\partial}{\partial p} \right) \right] D(r, p, 0)$$

Attempts to immediately derive useful information from this solution are frustrated by the fact that the differential operators in the exponential do not commute with each other. At this point, the type of operator algebra more commonly used in quantum electrodynamics is brought in. The use of these operator techniques overcomes the commutativity difficulties, thereby strengthening the impression that these techniques are useful in other contexts, such as the present one. A disentanglement theorem, Eq. (13), is used to write the average phase space distribution in series form, Eqs. (16)–(18). The terms of this series are analyzed to all orders, Eq. (60), but the results have not been reduced to a simple form.

As the terms of this series are analyzed, several interesting facts appear. The first term in this series is the average phase space distribution for the free Brownian motion problem. In the arguments following Eq. (40), it is shown that the operator methods which are used in this paper lead to a solution of the free Brownian motion problem which is in some respects clearer than the results obtained by the usual methods.[4–6] In the solution of this part of the problem the exponential propagator operator for free Brownian motion [see Eq. (20)] is simplified to a form which is particularly easy to use.

The exponential propagator operator is equal to

$$\exp\left(-\frac{tp}{m}\frac{\partial}{\partial r}\right)\exp\left[t\alpha\frac{\partial}{\partial p}\left(\frac{p}{m}+\frac{1}{kT}\frac{\partial}{\partial p}\right)\right]\exp\left[\phi_1(t)\frac{p}{m}\frac{\partial}{\partial r}\right]$$
$$\times\exp\left[2\phi_2(t)\frac{1}{kT}\frac{\partial^2}{\partial p\,\partial r}\right]\exp\left[-\phi_3(t)\frac{2kT}{m}\frac{\partial^2}{\partial r^2}\right]$$

When the potential is present and the Nth term of the phase-space distribution series is analyzed in the limit $t\to\infty$, one finds a product of a polynomial in the potential of order N, $(1/kT)^N$, and the Maxwellian momentum distribution, Eq. (69). If one factored the momentum distribution out of the series, the series should sum to a Boltzmann distribution. In order to prove this, the Boltzmann distribution is written in terms of a power series in $1/kT$. The coefficients in these two power series appear very dissimilar and a complex combinatorial proof is required to show that these coefficients are in fact identical. In the next sections, some of the details of the calculations will be given.

2. DIFFERENTIAL EQUATIONS FOR THE MOTION

The time evolution of this system is given by the stochastic analog of the Liouville equation,

$$\frac{\partial}{\partial t}D(r,p,t)=\left\{-\frac{p}{m}\frac{\partial}{\partial r}+\frac{dU(r)}{dr}\frac{\partial}{\partial p}-\frac{\partial}{\partial p}\left[-\frac{\alpha}{m}p+\tilde{F}(t)\right]\right\}D(r,p,t) \quad (1)$$

where the stochastic properties of $\tilde{F}(t)$ are those of Brownian motion with "white noise":

$$\langle\tilde{F}(t)\rangle=0 \qquad \text{and} \qquad \langle\tilde{F}(t)\tilde{F}(s)\rangle=2(\alpha/\beta)\,\delta(t-s) \quad (2)$$

where $\delta(t-s)$ is the Dirac delta function. The damping parameter α from Eq. (1) is found in the autocorrelation formula for $\tilde{F}(t)$ and that is the fluctuation-dissipation relation which connects α and $\tilde{F}(t)$.[7] The time evolution of this system can also be given in additive stochastic form as

$$\dot{r}(t)=\frac{1}{m}p(t), \qquad \dot{p}(t)=-\frac{\alpha}{m}p(t)-\frac{dU(r)}{dr}r(t)+\tilde{F}(t)$$

Whether one models this problem with an additive stochastic equation or a multiplicative stochastic equation, the function of interest in this paper is not the phase space distribution, but the stochastic average of the phase space distribution. The time evolution for this distribution is given by the Chandrasekhar–Kramers–Liouville equation:

$$\frac{\partial}{\partial t}\langle D(r, p, t)\rangle = \left[-\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU(r)}{dr}\frac{\partial}{\partial p} + \alpha\frac{\partial}{\partial p}\left(\frac{p}{m} + \beta^{-1}\frac{\partial}{\partial p}\right)\right]\langle D(r, p, t)\rangle \tag{3}$$

which is derived from the Liouville equation in Ref. 8 and from the additive stochastic equations in Ref. 9. The solution to Eq. (3) is given by

$$\langle D(r, p, t)\rangle = \exp\left[-\frac{pt}{m}\frac{\partial}{\partial r} + t\frac{dU(r)}{dr}\frac{\partial}{\partial p} + \alpha t\frac{\partial}{\partial p}\left(\frac{p}{m} + \beta^{-1}\frac{\partial}{\partial p}\right)\right]D(r, p, 0) \tag{4}$$

Equation (3) is a caricature of the Boltzmann equation, which can be written

$$\frac{\partial}{\partial t}f(r, p, t) = \left(-\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU}{dr}\frac{\partial}{\partial p}\right)f(r, p, t) + \mathrm{coll}(f(r, p, t)) \tag{5}$$

in which $\mathrm{coll}(f(r, p, t))$ signifies the nonlinear integral operator for collisions in the Boltzmann equation. This operation is known to drive the momentum distribution toward a Maxwellian form,[3] so that

$$f(r, p, t) \xrightarrow[t\to\infty]{} A(r)W_m(p) \tag{6}$$

where $W_m(p)$ is the Maxwellian momentum distribution. Asymptotically $\mathrm{coll}(f(r, p, t)) = 0$ and $(\partial/\partial t)f(r, p, t) = 0$, so that

$$\left(-\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU}{dr}\frac{\partial}{\partial p}\right)A(r)W_m(p) = 0 \tag{7}$$

must hold and this implies that $A(r) = C\exp[-\beta U(r)]$, where C is an arbitrary constant. In Eq. (3) the operator $\alpha(\partial/\partial p)(p/m + \beta^{-1}\,\partial/\partial p)$ drives $\langle D(r, p, t)\rangle$ to the asymptotic form

$$\langle D(r, p, t)\rangle \xrightarrow[t\to\infty]{} A(r)W_m(p) \tag{8}$$

with $(\partial/\partial t)\langle D(r, p, t)\rangle = 0$. Therefore, again $A(r) = C\exp[-\beta U(r)]$ because both the Boltzmann equation and Eq. (3) contain the same streaming operator,

$$-\frac{p}{m}\frac{\partial}{\partial r} + \frac{dU}{dr}\frac{\partial}{\partial p}$$

In the following, the details of the dynamics of the approach to the Boltzmann distribution are examined. Operator techniques are used to show that a

[3] This argument for the Boltzmann equation appears in Ref. 10.

series representation of the Boltzmann distribution is obtained as the dynamical asymptotic limit of Eq. (4).

3. SIMPLIFICATION OF THE PROPAGATION OPERATOR

In the process of simplifying the exponential propagation operator, it will prove convenient to define several operators.

$$A = \frac{p}{m}\frac{\partial}{\partial r}, \qquad B = \alpha\frac{\partial}{\partial p}\left(\frac{p}{m} + \beta^{-1}\frac{\partial}{\partial p}\right)$$
$$C = 2\beta^{-1}\frac{\partial^2}{\partial p\,\partial r}, \qquad D = -\frac{2}{\beta m}\frac{\partial^2}{\partial r^2} \tag{9}$$

The following relations will also be useful:

$$[A, B] = -(\alpha/m)(A + C), \qquad [B, C] = -(\alpha/m)C, \qquad [A, C] = D$$
$$[A, D] = [B, D] = [C, D] = 0 \tag{10}$$

where [., .] denotes the commutator operator. Equation (4) may now be rewritten as

$$\langle D(r, p, t)\rangle = \exp\left[-t\left(A - B - \frac{dU(r)}{dr}\frac{\partial}{\partial p}\right)\right] D(r, p, 0) \tag{11}$$

The problem encountered in analyzing the action of the exponential operator is that the operators in the exponent do not commute,

$$\exp\left[-t\left(A - B - \frac{dU(r)}{dr}\frac{\partial}{\partial p}\right)\right] \neq \exp(-tA)\exp(tB)\exp\left[t\frac{dU(r)}{dr}\frac{\partial}{\partial p}\right] \tag{12}$$

There is, however, a "disentanglement" theorem (Ref. 7, p. 1925; Refs. 11, 12) from time-dependent perturbation theory which is quite useful in this case.

4. A DISENTANGLEMENT THEOREM AND EXTENSION OF GLAUBER'S THEOREM

4.1. Disentanglement Theorem

If R_1 and R_2 are noncommuting, differential operators, then

$$\exp[is(R_1 + R_2)]$$
$$= \exp(isR_1)\ \underset{\leftarrow}{T}\ \exp\left[i\int_0^s \exp(-is'R_1)\,R_2\exp(is'R_1)\,ds'\right] \tag{13}$$

where, for an operator $O(s)$ which does not commute with itself at different times,

$$\underset{\leftarrow}{T} \exp\left[\int_0^s O(s')\, ds'\right] = 1 + \sum_{n=1}^{\infty} \int_0^s ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n\, O(s_1)O(s_2)\cdots O(s_n) \tag{14}$$

Using this disentanglement theorem, one obtains from Eq. (11)

$$\langle D(r, p, t)\rangle = \exp[-t(A - B)]\, \underset{\leftarrow}{T} \exp\left\{\int_0^s \exp[s(A - B)] \times \frac{dU(r)}{dr}\frac{\partial}{\partial p} \exp[-s(A - B)]\, ds\right\} D(r, p, 0) \tag{15}$$

Using the definition of the time-ordered exponential, one may write the average distribution as a series

$$\langle D(r, p, t)\rangle = D_0 + \sum_{N=1}^{\infty} D_N \tag{16}$$

where

$$D_0 = \exp[-t(A - B)]D(r, p, 0) \tag{17}$$

and

$$D_N = \int_0^s ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{N-1}} ds_N \exp[-(t - s_1)(A - B)]\frac{dU(r)}{dr}\frac{\partial}{\partial p} \times \exp[-(s_1 - s_2)(A - B)]\cdots\frac{dU(r)}{dr}\frac{\partial}{\partial p}\exp[-s_N(A - B)]\, D(r, p, 0) \tag{18}$$

Operators of the form $\exp[-t(A - B)]$ appear several times in Eqs. (17) and (18), and the next step will be to factor this operator into a form in which each differential operator factor acts consecutively. In order to do this one needs the disentanglement theorem and a time-ordered extension of Glauber's theorem.[8]

4.2. Time-Ordered Extension of Glauber's Theorem

$$\underset{\leftarrow}{T} \exp\left\{\int_0^t ds\, [f(s) + g(s)]\right\} = \underset{\leftarrow}{T} \exp\left[\int_0^t ds\, f(s)\right] \times \underset{\leftarrow}{T} \exp\left[\int_0^t ds\, g(s)\right] \times \underset{\rightarrow}{T} \exp\left\{\int_0^t ds_1 \int_0^{s_1} ds_2\, [g(s_1), f(s_2)]\right\} \tag{19}$$

In this theorem f and g do not commute, but do commute with their commutator. Notice in particular the different senses of the time ordering in Eq. (19). However, as will soon be seen, all time orderings will vanish. Using these theorems, one obtains

$$\exp[-t(A - B)] = \exp(-tA)\exp(tB)\exp[\phi_1(t)A] \times \exp[\phi_2(t)C]\exp[\phi_3(t)D] \tag{20}$$

where

$$\phi_1(t) = -\int_0^t \frac{s\alpha}{m}\exp\left(-\frac{s\alpha}{m}\right) ds = t\exp\left(-\frac{t\alpha}{m}\right) + \frac{m}{\alpha}\left[\exp\left(-\frac{t\alpha}{m}\right) - 1\right] \tag{21}$$

$$\phi_2(t) = -\int_0^t \frac{s\alpha}{m}\cosh\frac{s\alpha}{m}\, ds = \frac{1}{2}[\phi_1(t) + \phi_1(-t)] \tag{22}$$

$$\phi_3(t) = -\frac{1}{6}t^3\frac{\alpha}{m} - \int_0^t ds' \int_0^{s'} ds''\, s'\frac{\alpha}{m}\left(\cosh\frac{s'\alpha}{m}\right)s''\frac{\alpha}{m}\exp\left(-\frac{s''\alpha}{m}\right) \tag{23}$$

and

$$\phi_3(t) = -\frac{1}{4}\left[\phi_1(t)\phi_1(-t) + \phi_1^2(t) + \frac{m}{\alpha}\phi_1(t) - \frac{m}{\alpha}\phi_1(-t)\right] \tag{24}$$

The commutativity difficulties have been overcome! The phase space distribution may now be written out in terms of exponential operator factors which act consecutively. Several lemmas will be useful in the further analysis of this problem.

Operator identities

1. $$\frac{\partial \exp(\phi A)}{\partial p} = \frac{\phi}{m}\frac{\partial}{r}\exp(\phi A) \tag{25}$$

2. $$\exp(tB)\frac{\partial}{\partial p} = \frac{\partial}{\partial p}\exp\left(-\frac{t\alpha}{m}\right)\exp(tB) \tag{26}$$

3. $$\exp[-t(A - B)]\frac{\partial}{\partial p} = \left[\frac{\partial}{\partial p}\exp\left(-\frac{t\alpha}{m}\right) + \frac{t - \phi_1(t)}{m}\frac{\partial}{\partial r}\right] \times \exp[-t(A - B)] \tag{27}$$

The action of operators on Maxwellian distributions

4. $$\exp\left(b\frac{\partial}{\partial p}\frac{\partial}{\partial r}\right)\exp(ar)\,W_m(p + q) = \exp(ar)\,W_m(p + q + ab) \tag{28}$$

5. $$\exp(tB)\,W_m(p + a) = W_m\left(p + a\exp\left(-\frac{t\alpha}{m}\right)\right) \tag{29}$$

Simple identities

6a. $$W_m(p)\exp(ap) = W_m\left(p - \frac{am}{\beta}\right)\exp\left(\frac{a^2 m}{2\beta}\right) \tag{30}$$

6b. $$W_m(p + b)\exp(ap) = W_m\left(p + b - \frac{am}{\beta}\right)\exp\left[\frac{a}{2\beta}(ma - 2\beta b)\right] \tag{31}$$

Lemmas 1, 2, and 5 are proved in Ref. 8. Lemma 3 is an application of Lemmas 1 and 2 to Eq. (20).

5. ANALYSIS OF THE SERIES EXPANSION OF D(r, p, t)

5.1. Analysis of D_0, the Simple Brownian Motion Case

In addition to being the first term in the expansion of the average phase space distributions for the problem under consideration, D_0 is also the average phase space distribution for a system which consists of a particle acted on by a "Brownian" fluid but not subject to any other forces. It will be seen that the present treatment will lead to familiar results. Using periodic boundary conditions, we assume the initial conditions to be

$$D(r, p, 0) = \sum_N L^{-1/2} C_N \exp\left(i\frac{2\pi}{L} rN\right) W_m(p) \tag{32}$$

where the initial spatial distribution $R(r, 0) = \sum_N L^{-1/2} C_N \exp[i(2\pi/L)rN]$ is Fourier-analyzed in a box L. Then D_0 may be written, using Eqs. (9) and (20), as

$$\begin{aligned} D_0 = L^{-1/2} \sum_N C_N \exp\left(i\frac{2\pi}{L} Nr\right) \exp\left[\frac{2\pi^2 N^2}{L^2 \beta m} 4\phi_3(t)\right] \\ \times \exp\left(-it\frac{2\pi}{L} N\frac{p}{m}\right) \exp(tB) \exp\left[i\phi_1(t)\frac{2\pi}{L} N\frac{p}{m}\right] \\ \times W_m\left(p + i\phi_2\frac{2\pi}{L} N\frac{2}{\beta}\right) \end{aligned} \tag{33}$$

or

$$\begin{aligned} D_0 = L^{-1/2} \sum_N C_N \exp\left(i\frac{2\pi}{L} rN\right) \\ \times W_m\left(p + \frac{i2\pi N}{\beta}\left\{t + [2\phi_2(t) - \phi_1(t)]\exp\left(-\frac{t\alpha}{m}\right)\right\}\right) \\ \times \exp\left[\frac{2\pi^2 N^2}{L^2 \beta m}\phi_4(t)\right] \end{aligned} \tag{34}$$

where

$$\phi_4(t) = 4\phi_3(t) + 4\phi_2^2(t) - [2\phi_2(t) - \phi_1(t)]^2 - t^2 - 2t[2\phi_2(t) - \phi_1(t)] \exp(-t\alpha/m) \tag{35}$$

$$\phi_4(t) = -2(tm/\alpha) + 2(m^2/\alpha^2)[1 - \exp(-t\alpha/m)] \tag{36}$$

One notes that in Eq. (34)

$$t + [2\phi_2(t) - \phi_1(t)] \exp(-t\alpha/m) = (m/\alpha)[1 - \exp(-t\alpha/m)] \tag{37}$$

Since Einstein's relation for the diffusion constant is

$$D = 1/\beta\alpha \tag{38}$$

one may write Eq. (34) as

$$D_0 = L^{-1/2} \sum_N C_N \exp\left(i\frac{2\pi}{L} rN\right) W_m\left(p + i\frac{2\pi}{L} Nm\left[1 - \exp\left(-\frac{t\alpha}{m}\right)\right] D\right) \times \exp\left\{-\frac{4\pi^2 N^2}{L^2} D\left[t - \frac{m}{\alpha} + \frac{m}{\alpha}\exp\left(-\frac{t\alpha}{m}\right)\right]\right\} \tag{39}$$

It is clear from the damping behavior of the last exponential that in the infinite-time limit one has

$$\lim_{t\to\infty} D_0 = L^{-1} W_m(p) \tag{40}$$

Thus, the average of the phase space distribution for a particle in a "Brownian" fluid but subject to no other forces relaxes to a distribution which is uniform in position space and Maxwellian in momentum space, as was expected. One should also note that Eq. (39) contains in the last exponential the term

$$D\left[t - \frac{m}{\alpha} + \frac{m}{\alpha}\exp\left(-\frac{t\alpha}{m}\right)\right]$$

which is the diffusive behavior of a particle.[13,14]

Equation (39) shows the advantage of calculating the phase space distribution rather than calculating the position distribution and momentum distribution separately. It also illustrates how information is lost when one contracts the description of a system. When one asks, "What is the average position distribution of such a system?," one obtains, by the methods normally used,[4–6] a Gaussian distribution of zero mean and a second moment of

$$2D\left[t - \frac{m}{\alpha} + \frac{m}{\alpha}\exp\left(-\frac{t\alpha}{m}\right)\right] \tag{41}$$

This is also the answer one obtains by integrating Eq. (39) over momentum space and transforming from Fourier components to position space.

On the other hand, one may ignore position information and ask the question, "What is the average momentum distribution?" Traditionally, the answer is, at all times, the Maxwellian distribution. In the present calculation, integrating Eq. (39) over position space yields a Maxwellian momentum distribution.

One may also inquire about conditional probabilities. What is the average position distribution of a particle at some time t, which is known to have a specific momentum p at time t? It is not the above Gaussian distribution, Eq. (41). The average momentum distribution at a specific position is not Maxwellian. Equation (39) makes these facts clear.

5.2. Analysis of D_1

We have

$$D_1 = \{\cdots\}_1 \int_0^t ds_1 \exp[-(t - s_1)(A - B)] \exp\left(i \frac{2\pi}{L} rk_1\right) \frac{\partial}{\partial p} \times \exp[-s_1(A - B)] \exp\left(i \frac{2\pi}{L} rN\right) W_m(p) \tag{42}$$

where

$$\{\cdots\}_1 = \sum_{k_1} \sum_{N} L^{-1} \hat{U}(k_1) C_N i \frac{2\pi}{L} k \tag{43}$$

Using the result which was obtained in the analysis of D_0, one may rewrite Eq. (42) as

$$D_1 = \{\cdots\}_1 \int_0^t ds_1 \exp[-(t - s_1)(A - B)] \frac{\partial}{\partial p} \exp\left[i \frac{2\pi}{L} r(N + k_1)\right] \times W_m(p + f(s_1, N)) F(s_1, N) \tag{44}$$

where

$$f(s_1, N) = (i2\pi Nm/L\beta\alpha)[1 - \exp(-s_1\alpha/m)] \tag{45}$$

and

$$F(s_1, N) = \exp[(2\pi^2 N^2/L^2 \beta m)\phi_4(s_1)] \tag{46}$$

One may now use Lemma 3, Eq. (27), and obtain

$$D_1 = \{\cdots\}_1 \exp\left[i \frac{2\pi}{L} r(N + k_1)\right] \int_0^t ds_1 \{\cdots\}_2 \times \exp\left[-(t - s_1) \frac{i2\pi}{L} (N + k_1) \frac{p}{m}\right]$$

$$\times \exp[(t - s_1)B] \exp\left[\phi_1(t - s_1)\frac{i2\pi}{L}(N - k_1)\frac{p}{m}\right]$$
$$\times \exp\left[\phi_2(t - s_1)i\frac{2\pi}{L\beta}(N + k_1)\,2\frac{\partial}{\partial p}\right]$$
$$\times \exp\left[\frac{2\pi^2}{L^2\beta m}4(N + k_1)^2\phi_3(t - s_1)\right] W_m(p + f(s_1, N))F(s_1, N) \quad (47)$$

where

$$\{\cdots\}_2 = \frac{\partial}{\partial p}\exp\left[-(t - s_1)\frac{\alpha}{m}\right] + \frac{t - s_1 - \phi_1(t - s_1)}{m}\,i\frac{2\pi}{L}(N + k_1) \quad (48)$$

Next D_1 is simplified and one obtains

$$D_1 = \sum_{k_1}\sum_{N} L^{-1}\hat{U}(k_1)C_N i\frac{2\pi}{L}k_1 \exp\left[i\frac{2\pi}{L}r(N + k_1)\right]$$
$$\times \int_0^t ds_1 \left\{\frac{\partial}{\partial p}\exp\left[-(t - s_1)\frac{\alpha}{m}\right] + \frac{t - s_1 - \phi_1(t - s_1)}{m}\,i\frac{2\pi}{L}(N + k_1)\right\}$$
$$\times W_m\left(p + f(s_1, N)\exp\left[-(t - s_1)\frac{\alpha}{m}\right] + f(t - s_1, N + k_1)\right)$$
$$\times F(t - s_1, N + k_1)F(s_1, N)$$
$$\times \exp\left(\frac{m}{\alpha}f(s_1, N)\frac{i2\pi}{Lm}(N + k_1)\left\{1 - \exp\left[-(t - s_1)\frac{\alpha}{m}\right]\right\}\right) \quad (49)$$

Now the infinite-time limit of D_1 will be examined and it will be found to depend on the initial spatial distribution only as far as the normalization. In the integrand, $\lim_{t\to\infty} F(t - s_1, N + k_1)$ is zero unless $s_1 \to \infty$ or $N + k_1 = 0$. If $N + k_1 = 0$, the integrand contains a term $\lim_{t\to\infty}\exp[-(t - s_1)\alpha/m]$ and the integrand is still zero unless $s_1 \to \infty$. If $s_1 \to \infty$, then the integrand is zero due to $F(s_1, N)$ unless $N = 0$. Therefore, only the $N = 0$ term in the sum over N contributes to the infinite-time limit of D_1. From normalization requirements, Eq. (32), $C_0 = L^{-1/2}$. We have

$$\lim_{t\to\infty} D_1 = L^{-1}\sum_{k_1} L^{-1/2}\hat{U}(k_1)\lim_{t\to\infty}\int_0^t ds_1 \exp[-(t - s_1)(A - B)]$$
$$\times i\frac{2\pi}{L}k_1 \exp\left(i\frac{2\pi}{L}rk_1\right)\frac{\partial}{\partial p}W_m(p) \quad (50)$$

Using the definition of A and the fact that $B\exp[i(2\pi/L)rk_1]\,W_m(p) = 0$, one may write Eq. (50) as

$$\lim_{t\to\infty} D_1 = L^{-1}\sum_{k_1} L^{-1/2}\hat{U}(k_1)\lim_{t\to\infty}\int_0^t ds_1\,(-\beta)\exp[-(t - s_1)(A - B)]$$
$$\times (A - B)\exp\left(i\frac{2\pi}{L}rk_1\right) W_m(p) \quad (51)$$

The integrand is now an exact differential! Integrating gives

$$\lim_{t\to\infty} D_1 = L^{-1}\sum_{k_1} L^{-1/2}\hat{U}(k_1)(-\beta)\left[\exp\left(i\frac{2\pi}{L}rk_1\right) - \delta(k_1)\right]W_m(p) \quad (52)$$

or

$$\lim_{t\to\infty} D_1 = -\beta L^{-1}W_m(p)[U(r) - \overline{U(r)}] \quad (53)$$

If one expands a Maxwell–Boltzmann distribution in powers of β, one finds the asymptotic limit of D_0 and D_1 for the first two terms. The proof of this appears later. In order to prove this relation to all orders, one must analyze D_n for arbitrary n.

5.3. Analysis of D$_n$

From what has been learned in the analysis of D_0 and D_1, D_n may now be evaluated. A very useful result may be abstracted from the analysis of D_1. From Eqs. (44) and (49), one may show

$$\begin{aligned}
&\exp\left[-t\left(i\frac{2\pi}{Lm}K - B\right)\right] W_m(p+b) \\
&= W_m\left(p + b\exp\left(-\frac{t\alpha}{m}\right) + f(t,K)\right)F(t,K) \\
&\times \exp\left(\frac{m}{\alpha}b\frac{i2\pi}{Lm}K\right)\left[1 - \exp\left(-\frac{t\alpha}{m}\right)\right]
\end{aligned} \quad (54)$$

From Eq. (18) one has

$$\begin{aligned}
D_N &= \sum_{k_1}\sum_{k_2}\cdots\sum_{k_N}\sum_{l} L^{-(N+1)/2}\hat{U}(k_1)\hat{U}(k_2)\cdots\hat{U}(k_N) \\
&\times C_l\left(i\frac{2\pi}{L}\right)^N k_1k_2\cdots k_N\int_0^t ds_1\int_0^{s_1} ds_2\cdots\int_0^{s_{N-1}} ds_N \\
&\times \exp[-(t-s_1)(A-B)]\exp\left(i\frac{2\pi}{L}rk_N\right)\frac{\partial}{\partial p} \\
&\times \exp[-(s_1-s_2)(A-B)]\exp\left(i\frac{2\pi}{L}rk_{N-1}\right)\frac{\partial}{\partial p}\cdots \\
&\times \exp\left(i\frac{2\pi}{L}k_1r\right)\frac{\partial}{\partial p}\exp[-s_N(A-B)]\exp\left(i\frac{2\pi}{L}rl\right)W_m(p)
\end{aligned} \quad (55)$$

Letting the A operators act, one obtains

$$D_N = \{\cdots\}_1 \int_0^t ds_1 \cdots \int_0^{s_{N-1}} ds_N$$
$$\times \exp\left\{-(t - s_1)\left[i\frac{2\pi}{Lm}p\left(l + \sum_{i=1}^{N} k_i\right) - B\right]\right\}$$
$$\times \frac{\partial}{\partial p}\exp\left\{-(s_1 - s_2)\left[i\frac{2\pi}{Lm}p\left(l + \sum_{i=1}^{N-1} k_i\right) - B\right]\right\}\frac{\partial}{\partial p}\cdots$$
$$\times \frac{\partial}{\partial p}\exp\left[-s_N\left(i\frac{2\pi}{Lm}pl - B\right)\right] W_m(p) \tag{56}$$

where

$$\{\cdots\}_1 = L^{-(N+1)/2}\left(\frac{i2\pi}{L}\right)^N \sum_l C_l \prod_{i=1}^{N} \sum_{k_1} \hat{U}(k_i)\exp\left(i\frac{2\pi}{L}rk_i\right) \tag{57}$$

Using Lemma 3, Eq. (27), one has

$$D_N = \{\cdots\}_1 \int_0^t ds_1 \cdots \int_0^{s_{N-1}} ds_N \{\cdots\}_2 \exp\left\{-(t - s_1)\left[i\frac{2\pi}{Lm}p\right.\right.$$
$$\times \left.\left.\left(l + \sum_{i=1}^{N} k_i\right) - B\right]\right\}\exp\left\{-(s_1 - s_2)\left[i\frac{2\pi}{Lm}p\left(l + \sum_{i=1}^{N-1} k_i\right) - B\right]\right\}$$
$$\times \cdots \exp\left[-s_N\left(i\frac{2\pi}{Lm}pl - B\right)\right] W_m(p) \tag{58}$$

where $\{\cdots\}_2$, the product obtained from commuting all the $\partial/\partial p$ operators to the left, is given by

$$\{\cdots\}_2 = \left\{\frac{\partial}{\partial p}\exp\left[-(t - s_1)\frac{\alpha}{m}\right]\right.$$
$$\left. + [t - s_1 - \phi_1(t - s_1)]\frac{i2\pi}{Lm}\left(l + \sum_{i=1}^{N} k_i\right)\right\}$$
$$\times \left\{\frac{\partial}{\partial p}\exp\left[-(t - s_2)\frac{\alpha}{m}\right]\right.$$
$$+ [t - s_1 - \phi_1(t - s_1)]\frac{i2\pi}{Lm}\left(l + \sum_{i=1}^{N} k_i\right)$$
$$\times \exp\left[-(s_1 - s_2)\frac{\alpha}{m}\right]$$
$$\left. + [s_1 - s_2 - \phi_1(s_1 - s_2)]\frac{i2\pi}{Lm}\left(l + \sum_{i=1}^{N-1} k_i\right)\right\}\cdots$$

$$\times \left\{\frac{\partial}{\partial p}\exp\left[-(t - s_N)\frac{\alpha}{m}\right] + [t - s_1 - \phi_1(t - s_1)]\frac{i2\pi}{Lm}\left(l + \sum_{i=1}^{N} k_i\right) \times \exp\left[-(s_1 - s_N)\frac{\alpha}{m}\right] + \cdots + [s_{N-1} - s_N - \phi_1(s_{N-1} - s_N)]\frac{i2\pi}{Lm}(l + k_1)\right\} \tag{59}$$

Using Eq. (54), one may rewrite Eq. (58) as

$$D_N = \{\cdots\}_1 \int_0^t ds_1 \cdots \int_0^{s_{N-1}} ds_N \times \{\cdots\}_2 W_m\left(p + f(s_N, l)\exp\left[-(t - s_N)\frac{\alpha}{m}\right] + f(s_{N-1} - s_N, l + k_1)\exp\left[-(t - s_{N-1})\frac{\alpha}{m}\right] + \cdots + f\left(t - s_1, l + \sum_{i=1}^{N} k_i\right)\right)\{\cdots\}_3\{\cdots\}_4 \tag{60}$$

where

$$\{\cdots\}_3 = F(s_N, l)F(s_{N-1} - s_N, l + k_1)\cdots F\left(t - s_1, l + \sum_{i=1}^{N} k_i\right) \tag{61}$$

and

$$\{\cdots\}_4 = \exp\left(\frac{i2\pi}{L} f(s_N, l)\left\{1 - \exp\left[-(s_{N-1} - s_N)\frac{\alpha}{m}\right]\right\}(l + k_1)\right) \times \exp\left(\frac{i2\pi}{L\alpha}\left\{f(s_N, l)\exp\left[-(s_{N-1} - s_N)\frac{\alpha}{m}\right] + f(s_{N-1} - s_N, l + k_1)\right\} \times \left\{1 - \exp\left[-(s_{N-2} - s_{N-1})\frac{\alpha}{m}\right]\right\}(l + k_1 + k_2)\right)\cdots \times \exp\left(\frac{i2\pi}{L\alpha}\left\{f(s_N, l)\exp\left[-(s_1 - s_N)\frac{\alpha}{m}\right] + f(s_{N-1} - s_N, l + k_1) \times \exp\left[-(s_1 - s_{N-1})\frac{\alpha}{m}\right] + \cdots + f\left(s_1 - s_2, l + \sum_{i=1}^{N-1} k_i\right)\right\} \times \left\{1 - \exp\left[-(t - s_1)\frac{\alpha}{m}\right]\right\}\left(l + \sum_{i=1}^{N} k_i\right)\right) \tag{62}$$

Equation (60) is an expression for the phase space distribution at any time t. In this expression all of the differential operators have acted, with the exception of some of the momentum operators. Even though there are N integrals yet to be performed, one may still find out a lot about the dynamics of the system by studying the form of the expression. The term $\{\cdots\}_3$ contains damping exponentials, which, for many terms in the sums over Fourier indices, provide for a contribution to the integrals only when the integration variable is near t. As t grows, this trend is enhanced. The limit of D_N for large t is now calculated using this approach.

From the form of D_n it may be argued that the only term in the sum $\sum_l$ that contributes to the infinite-time limit of D_n is the term $l = 0$. This is due to the product $\{\cdots\}_3$ which contains

$$\lim_{t\to\infty} F\left(t - s_1, l + \sum_{i=1}^{N} k_i\right) = 0$$

unless $s_1 \to \infty$. If $s_1 \to \infty$, then

$$\lim_{s_1\to\infty} F\left(s_1 - s_2, l + \sum_{i=1}^{N-1} k_i\right) = 0$$

unless $S_2 = \infty$. This process continues until $\lim_{s_N\to\infty} F(s_N, l) = 0$ unless $l = 0$.

This chain of argument may be broken at some point if there is a sum which is zero, $l + \sum_{i=1}^{N-j} k_i = 0$. In this case the time variable s_{j+1} is not required to become infinite. This type of problem also occurred in the evaluation of D_1; see the arguments following Eq. (49). In this case the argument is similar. The chain of argument is assumed to be intact up until this first break. Thus, the time variables $t, s_1, s_2, \ldots, s_j$ all become infinite while, s_{j+1} is allowed to remain finite. $\{\cdots\}_2$ contains the following term:

$$\begin{aligned}\Bigg\{\frac{\partial}{\partial p}\exp\left[-(t - s_{j+1})\frac{\alpha}{m}\right] &+ [t - s_1 - \phi_1(t - s_1)]\frac{i2\pi}{Lm}\left(l + \sum_{i=1}^{N} k_i\right)\\ &\times \exp\left[-(s_l - s_{j+1})\frac{\alpha}{m}\right] + \cdots + [s_l - s_{l+1} - \phi_1(s_l - s_{l+1})]\frac{i2\pi}{Lm}\\ &\times \left(l + \sum_{i=1}^{N-j} k_i\right)\Bigg\}\end{aligned} \tag{63}$$

The exponentials in this term all damp to zero and only the last term remains. This last term, however, contains $l + \sum_{i=1}^{N-j} k_i$, which was assumed to be zero. Thus one sees that all such breaks in the chain of argument which has been constructed lead, inevitably, to a zero contribution. It has been shown then that $\lim_{t\to\infty} D_N$ may be written in terms of only the normalization information from the initial spatial distribution,

$$\lim_{t\to\infty} D_N = \lim_{t\to\infty} L^{-1} \int_0^t ds_1 \cdots \int_0^{s_{N-1}} ds_N \exp[-(t - s_1)(A - B)] \frac{dU(r)}{dr} \frac{\partial}{\partial p} \times \cdots \frac{dU(r)}{dr} \frac{\partial}{\partial p} \exp[-s_N(A - B)]\, W_m(p) \tag{64}$$

Since

$$\frac{\partial}{\partial p} \exp[-s_N(A - B)]\, W_m(p) = \frac{\partial}{\partial p}\, W_m(p) = -\frac{\beta p}{m}\, W_m(p) \tag{65}$$

Eq. (64) may be written in a form similar to Eq. (50),

$$\lim_{t\to\infty} D_N = \lim_{t\to\infty} L^{-1} \int_0^t ds_1 \cdots \int_0^{s_{N-2}} ds_{N-1} \exp[-(t - s_1)(A - B)] \times \frac{dU(r)}{dr} \frac{\partial}{\partial p} \cdots \int_0^{s_{N-1}} ds_N \exp[-(s_{N-1} - s_N)(A - B)] \times (-\beta) A U(r) W_m(p) \tag{66}$$

Since $-BW_m(p) = 0$, this quantity may be added to the integrand, thereby making it an exact differential of s_N! Integrating, one has

$$\lim_{t\to\infty} D_N = \lim_{t\to\infty} L^{-1} \int_0^t ds_1 \cdots \int_0^{s_{N-2}} ds_{N-1} \times \exp[-t(t - s_1)(A - B)] \frac{dU(r)}{dr} \frac{\partial}{\partial p} \cdots \times (-B)\{1 - \exp[-s_{N-1}(A - B)]\} U(r) W_m(p) \tag{67}$$

The part of the integrand which uses the 1 in the last bracket is already in the form of Eq. (66) and this integration procedure can be iterated. The part of the integrand which uses $\exp[-s_{N-1}(A - B)]$ is of the form of Eq. (56) with $R(r)$ replaced by $U(r)$. It has been shown that in an equation of this form the function of r may be replaced by its normalization information,

$$\overline{\cdots} \int dU \equiv \overline{U} \equiv L^{-1} \int_0^L U(r)\, dr \tag{68}$$

As this procedure is repeated N times one obtains

$$\lim_{t\to\infty} D_N = L^{-1}(-\beta)^N \left[(1 - \overline{\cdots}) \int dU \right]^N W_m(p) \tag{69}$$

Thus,

$$\begin{aligned}
D_0 &= L^{-1}W_m(p) \\
D_1 &= -L^{-1}\beta[U(r) - \bar{U}]W_m(p) \\
D_2 &= \tfrac{1}{2}L^{-1}\beta^2(U^2 - \bar{U}^2 - 2U\bar{U} + 2U^2)W_m(p)
\end{aligned}$$

or

$$D_2 = \tfrac{1}{2}L^{-1}\beta^2[(U - \bar{U})^2 - \overline{(U - \bar{U})^2}]W_m(p) \tag{70}$$

Therefore one has

$$\lim_{t\to\infty} D(r, p, t) = L^{-1} \sum_{N=0}^{\infty} \beta^N K_N'(r) W_m(p) \tag{71}$$

where

$$K_N'(r) = (-1)^N \left[(1 - \overline{\cdots}) \int dU\right]^N \tag{72}$$

This is a Maxwell–Boltzmann distribution. This is a remarkable statement. Only upon close examination does Eq. (71) reveal itself to be a Maxwell–Boltzmann distribution. In order to prove this statement, one needs a power series in β which is equivalent to a Boltzmann distribution.

6. SERIES EXPANSION OF THE BOLTZMANN DISTRIBUTION

Theorem 1. The series expansion of the Boltzmann distribution is given by

$$\frac{\exp[-\beta U(r)]}{\int_0^L \exp[-\beta U(r)]\, dr} = L^{-1} \sum_{N=0}^{\infty} K_N(r)\beta^N \tag{73}$$

where

$$\begin{aligned}
K_N(r) = \frac{(-1)^N}{N!} \sum_{m=0}^{N} \frac{N!}{(N-m)!\, m!} [U(r) - \overline{U(r)}]^{N-m} \\
\times \sum_{\substack{\text{partitions} \\ \text{of } m}} \prod_{l=1}^{m} \frac{p!\, m!\, (-1)^p}{m_l!\, (l!)^{m_l}} \overline{\{[U(r) - \overline{U(r)}]^l\}^{m_l}}
\end{aligned} \tag{74}$$

In Eq. (74), $\overline{g(r)} = L^{-1}\int_0^L g(r)\, dr$ for any function $g(r)$, and the symbol

$$\sum_{\substack{\text{partitions} \\ \text{of } m}}$$

is the sum over all partitions of m into smaller integers l with multiplicity m_l such that

$$m = \sum_{l=1}^{m} l m_l \qquad \text{and} \qquad p = \sum_{l=1}^{m} m_l$$

Henceforth this summation symbol is used without explanation. Theorem 1 is proved in Ref. 8. In order to show that the term (71) is a Boltzmann distribution, one must show

$$K_N(r) = K_N'(r) \tag{75}$$

Proof of the Boltzmann Term. In this proof the method of induction is used. If the first several terms in the two series are examined, it is easily seen that they are identical. Assume

$$K_N(r) = K_N'(r)$$

Then one may write

$$K'_{N+1}(r) = -(1 - \overline{\cdots}) \int du\, K_N(r) \tag{76}$$

$$= \frac{(-1)^{N+1}}{N!} (1 - \overline{\cdots}) \sum_{m=0}^{N} \frac{N!}{m!\,(N-m)!} \frac{1}{N-m+1} (U - \overline{U})^{N-m+1}$$
$$\times \sum_{\substack{\text{partitions}\\ \text{of } m}} \prod_{l=1}^{m} \frac{p!\,m!\,(-1)^p}{m_l!\,(l!)^{m_l}} \overline{[(U - \overline{U})^l]}^{m_l} \tag{77}$$

Now one makes use of a combinatorial lemma which is proved in Ref. 8. This lemma is

$$-\sum_{m=0}^{N} (-1)^{N+1} \overline{[U(r) - \overline{U(r)}]^{N+1-m}} \sum_{\substack{\text{partitions}\\ \text{of } m}} \prod_{l=1}^{m} \frac{(-1)^p p!}{(N+1-m)!\,m_l!\,(l!)^{m_l}}$$
$$\times \overline{\{[U(r) - \overline{U(r)}]^l\}^{m_l}}$$
$$= (-1)^{N+1} \sum_{\substack{\text{partitions}\\ \text{of } N+1}} \prod_{l=1}^{N+1} \frac{(-1)^{p'} p'!}{m_l'!\,(l'!)^{m'_l}} \overline{\{[U(r) - \overline{U(r)}]^{l'}\}^{m_l'}} \tag{78}$$

Using this lemma, one obtains

$$K'_{N+1}(r) = (-1)^{N+1} \sum_{m=0}^{N} [U(r) - \overline{U(r)}]^{N+1-m}$$
$$\times \sum_{\substack{\text{partitions}\\ \text{of } m}} \prod_{l=1}^{m} \frac{(-1)^p p!}{(N+1-m)!\,m_l!\,(l!)^{m_l}} \overline{\{[U(r) - \overline{U(r)}]^l\}^{m_l}} (-1)^{N+1}$$
$$\times \sum_{\substack{\text{partitions}\\ \text{of } N+1}} \prod_{k=1}^{N+1} \frac{(-1)^p p!}{m_k!\,(k!)^{m_k}} \overline{\{[U(r) - \overline{U(r)}]^k\}^{m_k}} \tag{79}$$

or

$$K'_{N+1}(r) = K_{N+1}(r) \tag{80}$$

This completes the proof of the fact that the series (71) is a Maxwell–Boltzmann distribution.

7. CONCLUSION

This paper has presented a solution to the problem of the forced motion of a particle in a "Brownian" fluid. This was done using the disentanglement theorem, a time-ordered extension of Glauber's theorem, commutator operators, and other operator algebra. These techniques proved to be very powerful and it was shown that the solution may be written and simplified to the point such that information can be extracted from it. Specifically, it is shown from this solution that the infinite-time limit of the probability distribution for the particle is a Maxwell–Boltzmann distribution. An obvious extension of this problem is to specific potentials which have wide interest or applicability. The problem of an ion drifting under the influence of a constant electric field will be solved at all times in a paper in preparation.

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