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Dynamical Study of Brownian Motion*

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We study the motion of a Brownian particle in a fluid from a dynamical point of view, i.e., without the *a priori* introduction of purely stochastic elements. The Brownian particle is distinguished primarily by having a mass M which is much greater than the mass of the fluid particles m . Our method consists of rewriting the Liouville equation for μ , the joint distribution of fluid and Brownian particle, as a pair of coupled equations for the distribution function of the Brownian particle f and the conditional distribution of the fluid $P = (\mu/f)$. The equation for P is then solved formally in a perturbation series in the square root of the mass ratio (m/M) , which is then substituted in the equation for f to obtain a collision term δf representing the effect of the fluid on f . We consider two situations: (1) A constant external force acts on the Brownian particle and f is stationary, the external force being balanced by δf , and (2) a general time-dependent f . We find in both cases, as expected, that to lowest order δf has the form of a Fokker-Planck type collision term, though in the second case this only holds for times much larger than the fluid relaxation time after an initial time at which μ is arbitrary. The next order terms in δf differ for the two cases. Furthermore, because of the limitations on the times at which δf is valid in the second case, $f(t)$ does not really obey a Markoffian equation to this order when the initial state is arbitrary. In the Appendixes we consider the formal structure of δf , the form of f in the stationary case, a "quasistochastic" model of Brownian motion, the motion of a composite Brownian particle, and the motion of a Brownian particle in a crystal. The latter makes contact with the work of Hemmer and Rubin.

I. INTRODUCTION

THE explanation of "Brownian motion" by Einstein and Smoluchowsky^{1,2} in terms of the kinetic theory and their quantitative prediction of its features did much to establish the molecular theory of matter. A more complete description of Brownian motion was given later by Langevin and others.² Since the dynamics of the motion of the fluid atoms, which cause the Brownian motion in the heavier, microscopically visible, particles was not introduced explicitly, their effect could only be represented schematically. Thus, all descriptions of Brownian motion were of a stochastic nature *ab initio*. Despite this indeterminacy in the motion of an individual Brownian

particle (B particle), it is still possible when there are a very large number of such particles to give a deterministic equation for the time evolution of their spatial and velocity distribution $f(\mathbf{R}, \mathbf{V}, t)$. Here $f(\mathbf{R}, \mathbf{V}, t)d\mathbf{R}d\mathbf{V}$ represents the fraction of B particles in the macroscopically very small volume element $d\mathbf{R}d\mathbf{V}$ which is sufficiently large though to contain many particles. As is well known, it is more convenient mathematically to work in terms of an ensemble of systems each containing one B particle (since we are assuming that in the real system the B particles move independently) with the distribution function defined in terms of probabilities, assumed to satisfy the same equation as the "coarse-grained" f defined above.³

When use is made, in devising the stochastic properties of the interaction between the fluid and B particles, of the central fact that the heavy mass of the B particles makes the fractional change in their velocities small (on a molecular time scale) and results also in their

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¹ Albert Einstein, *Investigations on the Theory of the Brownian Movement*, edited with notes by R. Furth (Dover Publications, Inc., New York, 1956).

² S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943); this article gives a complete review of the theory of Brownian motion and contains references to earlier work.

³ H. Grad, in *Encyclopedia of Physics*, edited by S. Flugge (Springer-Verlag, Berlin, 1958), Vol. XII, p. 205. H. Mori, I. Oppenheim, and J. Ross, in *Studies in Statistical Mechanics*, edited by J. de Boer and G. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962).

moving (on the average) at speeds far below those of the fluid molecules, there results the well-known Fokker-Planck equation for $f(\mathbf{R}, \mathbf{V}, t)$,^{2,4}

$$\begin{aligned} \frac{\partial f(\mathbf{R}, \mathbf{V}, t)}{\partial t} + \mathbf{V} \cdot \frac{\partial f}{\partial \mathbf{R}} + \frac{1}{M} \mathbf{X} \cdot \frac{\partial f}{\partial \mathbf{V}} \\ = \left[\zeta \frac{\partial}{\partial \mathbf{V}} \cdot (\mathbf{V} f) + D \nabla^2 f \right] \\ = D \frac{\partial}{\partial \mathbf{V}} \cdot \left[f \frac{\partial}{\partial \mathbf{V}} \ln(f/f_0) \right]. \quad (1.1) \end{aligned}$$

Here $\mathbf{X}$ is the external force acting on the B particle, M its mass; ζ is the friction and D the diffusion constant in velocity space, of the B particles in the fluid. We have eliminated the friction constants ζ from the second part of this equation through use of the Einstein relation,²

$$D = (kT/M)\zeta. \quad (1.2)$$

f_0 is the equilibrium distribution function of the B particles whose velocity part goes as $e^{-\frac{1}{2}\beta M V^2}$; $\beta = (kT)^{-1}$ is the reciprocal of the temperature of the host fluid. The right side of (1.1) represents the effect of the fluid on the B particles. It is a special case of a collision term which will be generally denoted by δf .

The purpose of this note is to dispense with the *a priori* introduction of a stochastic interaction. We shall, therefore, start with the Liouville equation for the distribution function μ of the whole system consisting of host fluid and B particle. A transport equation for f will then result, after integration over the variables of the fluid particles, in certain limits involving the size of the fluid and the time scale. Such limits are clearly necessary to derive an irreversible transport equation from a reversible Liouville equation and have been discussed extensively in the recent literature on irreversible processes.^{5,6}

The equation that we shall arrive at for f will be of the same form as (1.1) to the lowest order in mass ratio of fluid and B particle with an explicit, if unevaluated, molecular expression for D . We shall, however, also find higher order correction terms to (1.1). These higher order terms have relevance to the Kirkwood theory of liquids^{7,8} which uses the Fokker-Planck equation to describe the time evolution of the low-order distribution functions of a liquid. We shall also consider the case where the B particle has internal structure.

⁴ M. C. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945).

⁵ L. Van Hove, Physica **21**, 517, 901 (1955); **22**, 343 (1956); **23**, 441 (1957); I. Prigogine, *Nonequilibrium Statistical Mechanics*, (Interscience Publishers Inc., New York, 1962). E. Montroll, Suppl. Nuovo Cimento **16**, (1960).

⁶ W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

⁷ J. G. Kirkwood, J. Chem. Phys. **14**, 180 (1946); J. Ross, *ibid.* **24**, 375 (1956).

⁸ J. L. Lebowitz, H. L. Frisch, and E. Helfand, Phys. Fluids **3**, 1 (1960).

We shall consider first the case where the B particle is subject to some external force, such as a constant electric field $\mathbf{E}$, which does not act on the fluid particles. This will enable us to look at the equation satisfied by the stationary nonequilibrium distribution f , to terms linear in $\mathbf{E}$. This distribution represents a balance between the effect of the acceleration by $\mathbf{E}$ and the scattering by the fluid particles. It will thus contain the collision term representing the effect of the fluid but will avoid some of the difficulties encountered in deriving the general time-dependent equation for f .^{6,9} Our method here will be similar to that developed by Kohn and Luttinger⁶ for deriving the quantum transport equation of an electron moving in the field of stationary impurities. Discussion of the collision term for the time-dependent case will be left for Sec. V.

II. GENERAL FORMULATION

The Hamiltonian of our system, consisting of host fluid and B particle, exclusive of the external field, will have the form

$$\begin{aligned} H = \frac{1}{2} M V^2 + \left[\sum_{i=1}^N \frac{1}{2} v_i^2 + \sum_{i < j} \phi(r_{ij}) \right] + \sum_{i=1}^N u(\mathbf{R}_i) \\ = H_1 + H_l + U; \quad \mathbf{R}_i = \mathbf{r}_i - \mathbf{R}, \end{aligned} \quad (2.1)$$

where $\mathbf{r}_i$ and $\mathbf{v}_i$ are the position and velocity of the i th fluid particle. The three terms in H are, respectively, the kinetic energy of the B particle, the Hamiltonian of the N fluid particles (of unit mass), and the interaction between them. The whole system is enclosed in a periodic box of volume Ω . The joint distribution function of the whole system will obey the Liouville equation

$$(\partial \mu(x, y, t) / \partial t) + (\mu, H) + M^{-1} \mathbf{E} \cdot (\partial \mu / \partial \mathbf{V}) = 0, \quad (2.2)$$

where (μ, H) is the Poisson bracket between μ and H (expressed in terms of the velocity variables) and we have used x and y as abbreviations,

$$x = (\mathbf{R}, \mathbf{V}), \quad y = (\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{v}_1, \dots, \mathbf{v}_N). \quad (2.3)$$

Since we want to consider only terms which are linear in $\mathbf{E}$, we write

$$\mu = \mu_0 + \mu', \quad (2.4)$$

where

$$\mu_0 = Z^{-1} e^{-\beta H}, \quad Z = \int e^{-\beta H} dx dy,$$

and μ' is linear in $\mathbf{E}$. μ' will satisfy the equation

$$(\partial \mu' / \partial t) + (\mu', H) - \beta \mathbf{E} \cdot \mathbf{V} \mu_0 = 0. \quad (2.5)$$

The distribution function of the B -particle f , normalized to unity, is given by

$$f = \int \mu dy = f_0 + f'. \quad (2.6)$$

⁹ I. Prigogine and P. Resibois, Conference on Irreversible Thermodynamics held at Brown University in 1962 (unpublished).

Since we are dealing with a uniform system, f will be independent of $\mathbf{R}$, and will contain a normalization factor Ω^{-1} ,

$$f = \Omega^{-1} [\rho_0(\mathbf{V}) + \psi(\mathbf{V})], \quad (2.7)$$

where $(\rho_0 + \psi)$ is the velocity distribution of the B particle,

$$\rho_0 = (2\pi kT/M)^{-3/2} e^{-\frac{1}{2}\beta M V^2}, \quad (2.8)$$

$$\psi = \Omega \int \mu' dy = \int \mu' dy d\mathbf{R}. \quad (2.9)$$

Integrating Eq. (2.5) over y and $\mathbf{R}$ yields

$$\frac{\partial \psi}{\partial t} - \beta \mathbf{E} \cdot \mathbf{V} \rho_0 = -\frac{1}{M} \frac{\partial}{\partial \mathbf{V}} \cdot \left(\int \mu' \mathbf{F} dy d\mathbf{R} \right), \quad (2.10)$$

where

$$\mathbf{F} = -\frac{\partial U}{\partial \mathbf{R}} = \sum_{i=1}^N \frac{\partial u(\mathbf{R}_i)}{\partial \mathbf{R}_i}. \quad (2.11)$$

It is clearly the right side of (2.10) which will become the collision term, $\delta\psi$.

We introduce now the conditional distribution function $P(x, y, t)$ which gives the probability density of finding the fluid at y given that the B particle is at x ,

$$P(x, y, t) = \frac{\mu(x, y, t)}{f(x, t)} = P_0(1 + \xi), \quad (2.12)$$

where

$$P_0 = \frac{\mu_0(x, y)}{f_0} = \frac{e^{-\beta H}}{\int e^{-\beta H} dy} = C e^{-\beta(H+U)}, \quad (2.13)$$

and C is a constant for the uniform system. We also define

$$P_0(1 + \eta) = \frac{\mu'}{\int \mu' dy} = \frac{\mu'}{\psi/\Omega}. \quad (2.14)$$

From normalization we find

$$\int P_0 dy = 1, \quad (2.15)$$

$$\int P_0 \eta dy = 0. \quad (2.16)$$

Substituting (2.14) into (2.5) yields

$$\begin{aligned} \eta \frac{\partial \psi}{\partial t} + \psi \frac{\partial \eta}{\partial t} + \psi(\eta, H) &= -(\psi, H) - \eta(\psi, H) \\ &- \psi(\eta + 1)(\ln P_0, H) + \frac{1}{M} \frac{\partial}{\partial \mathbf{V}} \cdot \left(\int \mu' \mathbf{F} dy d\mathbf{R} \right), \end{aligned} \quad (2.17)$$

where Eq. (2.10) has been used to eliminate the field term from above. Now from (2.13)

$$(\ln P_0, H) = \beta \mathbf{F} \cdot \mathbf{V} = -\frac{1}{M} \mathbf{F} \cdot \frac{\partial}{\partial \mathbf{V}} \ln \rho_0 \quad (2.18)$$

and

$$\int P_0 \mathbf{F} dy = 0. \quad (2.19)$$

Dividing (2.17) by ψ and writing out explicitly some of the Poisson bracket expressions, we finally find

$$\begin{aligned} \eta \frac{\partial \ln \psi}{\partial t} + \frac{\partial \eta}{\partial t} + (\eta, H_2) &= -\frac{1}{M} \frac{\partial}{\partial \mathbf{V}} \ln(\psi/\rho_0) \cdot \mathbf{F} \\ &- \frac{1}{M} \left[\frac{\partial}{\partial \mathbf{V}} \ln(\psi/\rho_0) + \frac{\partial}{\partial \mathbf{V}} \right] \cdot [\mathbf{F} \eta - \langle \mathbf{F} \eta \rangle] \\ &- \left[\mathbf{V} \cdot \frac{\partial \eta}{\partial \mathbf{R}} \left\langle \mathbf{V} \cdot \frac{\partial \eta}{\partial \mathbf{R}} \right\rangle \right], \end{aligned} \quad (2.20)$$

where

$$\langle \dots \rangle = \int P_0 \dots dy,$$

and H_2 is the Hamiltonian of the fluid in the presence of a *fixed* B particle which thus serves as a source of external potential,

$$H_2 = H_1(y) + \sum u(\mathbf{r}_i - \mathbf{R}), \quad (2.21)$$

with $\mathbf{R}$ treated as a constant number (not a canonical coordinate). The Poisson bracket (η, H_2) in Eq. (2.20) thus contains derivatives only with respect to the fluid variables $(\mathbf{r}_i, \mathbf{v}_i)$. Use has also been made here of the relation

$$\mathbf{V} \cdot \int P_0 \frac{\partial \eta}{\partial \mathbf{R}} dy = -\beta \mathbf{V} \cdot \int P_0 \mathbf{F} \eta dy. \quad (2.22)$$

Had we kept the term $\mathbf{V} \cdot \partial \eta / \partial \mathbf{R}$ on the left side of (2.20), H_2 would have corresponded to the Hamiltonian of a fluid with a *uniformly* moving Brownian particle in it. We may now rewrite Eq. (2.10) in our new notation,

$$\frac{\partial \psi}{\partial t} - \beta \mathbf{E} \cdot \mathbf{V} \rho_0 = -\frac{1}{M} \frac{\partial}{\partial \mathbf{V}} \cdot (\psi \langle \mathbf{F} \eta \rangle). \quad (2.10')$$

III. STATIONARY DISTRIBUTIONS

The set of coupled equations (2.20) and (2.10') for ψ and η , which describe the linear deviation of μ from μ_0 , caused by $\mathbf{E}$, are completely general. We would like to specialize these equations now to find the final steady-state value of ψ in the presence of a constant $\mathbf{E}$. It is clear that in order to get a "sensible" result we will have to eliminate effects coming from the finiteness of the system. The latter effects will be of $O(N^{-1/3})$,

for any fixed time interval, and can be formally eliminated by going to the limit of $N \rightarrow \infty, \Omega \rightarrow \infty, N/\Omega = n$, remaining constant. In this limit η would become a function of infinitely many variables. We are, however, not interested in η itself, but rather in its integral which appears in (2.10'), which we expect to approach a value dependent only on n . Thus, in order to get a transport equation for ψ , we shall somehow have to solve for η (formally at least) before going to the limit of an infinite system, substitute that in (2.10'), and then go to this limit. In order not to get any spurious volume-dependent terms which would disappear later anyway, we will have to consider carefully the times at which we look at the system after some initial time at which the system was in equilibrium.

There are two, essentially equivalent, formal ways of setting up the steady-state problem in a way consistent with the conditions discussed above. These forms were discussed by Kohn and Luttinger⁶ and we shall adopt their methods here. One is to consider the electric field to rise adiabatically from zero at $t = -\infty$, to its final value E at $t = 0$.

$$\mathbf{E}(t) = e^{t/t_0} \mathbf{E}, \quad t < 0. \quad (3.1)$$

If the system was in equilibrium at $t = -\infty$, $\mu(-\infty) = \mu_0$, we would expect μ' to have a time dependence of the same form as $\mathbf{E}$,

$$\mu'(x, y, t) = e^{t/t_0} \mu'(x, y), \quad t \leq 0 \quad (3.2)$$

where we have kept the symbol μ' for the time-independent distribution. It follows from the definition of ψ and η that ψ will have the same time dependence as μ' , and η will be time-independent. Equations (2.10') and (2.20) would then become for $t \leq 0$,

$$\psi/t_0 - \beta \mathbf{E} \cdot \mathbf{V} \rho_0 = -M^{-1}(\partial/\partial \mathbf{V}) \cdot (\psi \langle \mathbf{F} \eta \rangle), \quad (3.3)$$

$$\left[\frac{1}{-t_0} + iL \right] \eta = M^{-1} \mathbf{A} \cdot \mathbf{F} + M^{-1} \mathbf{B} \cdot [\mathbf{F} \eta - \langle \mathbf{F} \eta \rangle] - \left[\mathbf{V} \cdot \frac{\partial \eta}{\partial \mathbf{R}} - \mathbf{V} \cdot \left\langle \frac{\partial \eta}{\partial \mathbf{R}} \right\rangle \right], \quad (3.4)$$

where L is the Hermitian operator,

$$iL(\cdots) = (\cdots, H_2), \quad (3.5)$$

$$\mathbf{A} = -\frac{\partial}{\partial \mathbf{V}} \ln \frac{\psi}{\rho_0}, \quad (3.6)$$

$$\mathbf{B} \cdot (\cdots) = \left[\frac{\partial}{\partial \mathbf{V}} \ln \frac{\psi}{\rho_0} + \frac{\partial}{\partial \mathbf{V}} \right] \cdot (\cdots).$$

Now if t_0 is chosen so as to be large compared to the relaxation time of the B -particle t_r , then ψ/t_0 is very small compared to the right side of (3.3); the term ψ/t_0 may then be neglected and ψ treated as a function independent of t_0 where it appears in (3.4). On the

other hand, we may not, for reasons discussed above, let t_0 go to infinity in Eq. (3.4). Rather we must have, as we shall see later, t_0 small compared to the time t_s which it takes a particle to cross the whole container, $t_s \sim \Omega^{1/3}$; we solve for η , substitute η in $\langle \eta \mathbf{F} \rangle$, then first let N and $\Omega \rightarrow \infty$, and then let $t_0 \rightarrow \infty$.

An alternative formulation of the problem (see Ref. 6, Appendix 3) is to consider the system to be in equilibrium at $t=0$ when the full electric field $\mathbf{E}$ is turned on. We now consider the Laplace average of the distribution $\mu(t)$,

$$\tilde{\mu}(t_0) = \frac{1}{t_0} \int_0^\infty e^{-t/t_0} \mu(t) dt = \mu_0 + \tilde{\mu}'(t_0), \quad (3.7)$$

and define the function $\tilde{\eta}$ by the relation

$$\tilde{\mu}' = (\tilde{\psi}/\Omega) P_0(1 + \tilde{\eta}), \quad (3.8)$$

where

$$\tilde{\psi} = -\frac{1}{t_0} \int_0^\infty e^{-t/t_0} \psi(t) dt. \quad (3.9)$$

The functions $\tilde{\psi}$ and $\tilde{\eta}$ then obey the set of Eqs. (3.3) and (3.4) with $\langle \cdots \rangle \rightarrow \langle \cdots \rangle_{av}$ [see (3.12)], and we may drop the bars and tildes. It is seen now that the neglect of the term ψ/t_0 on the left side of (3.3), for $t_0 \gg t_r$, is equivalent to saying that for such values of t_0 the right side of (3.9) is equal to the final stationary value of ψ , which is what we want. We also see that we will get the same value for η if we replace η/t_0 in (3.4) by $\partial \eta / \partial t$, solve for η as a function of t with the initial condition $\eta=0$ at $t=0$, and then take its Laplace average, treating ψ as a time-independent function throughout. Equations (3.3) and (3.4) now become

$$-\beta \mathbf{E} \cdot \mathbf{V} \rho_0 = -M^{-1}(\partial/\partial \mathbf{V}) \cdot (\psi \langle \mathbf{F} \eta \rangle_{av}), \quad (3.10)$$

$$\frac{\partial \eta}{\partial t} + iL\eta = M^{-1} \mathbf{A} \cdot \mathbf{F} + M^{-1} \mathbf{B} \cdot [\mathbf{F} \eta - \langle \mathbf{F} \eta \rangle_{av}] - \left[\mathbf{V} \cdot \frac{\partial \eta}{\partial \mathbf{R}} - \mathbf{V} \cdot \left\langle \frac{\partial \eta}{\partial \mathbf{R}} \right\rangle_{av} \right], \quad (3.11)$$

where

$$\langle \cdots \rangle_{av} = \left\langle \frac{1}{t_0} \int_0^\infty e^{-t/t_0} \cdots dt \right\rangle = \frac{1}{t_0} \int_0^\infty e^{-t/t_0} \langle \cdots \rangle dt, \quad (3.12)$$

and the initial condition is $\eta=0$ at $t=0$. Equations (3.10)–(3.11) are then essentially equivalent to Eqs. (2.17) and (2.10') if the time variation of ψ is neglected there on the basis that for $t \gg t_r$, ψ has already achieved its stationary value. For the quantities whose average we will be interested in, it will be possible in (3.12) to go to the limit of an infinite system, with t_0 fixed, then for $t_0 \gg t_r$ the averages will be independent of t_0 and we can go to the limit $t_0 \rightarrow \infty$ making $\langle \cdots \rangle_{av} = \langle \cdots \rangle$.

All our considerations so far have been completely general, assuming only the existence of a stationary ψ . In principle, we could now solve (3.11) for η , which

would be a functional of ψ , substitute that into (3.10), and obtain the desired solution. But this is no more than saying that given the Hamiltonian the time evolution of any system is solved in principle. What we desire is an explicit equation for ψ which will contain as few as possible parameters depending on the fluid. The form of ψ will then be determined even if these parameters cannot be computed exactly on a theoretical basis. Knowing the form of ψ will also tell us how these parameters may be determined experimentally from the properties of the steady state. For this to be the case, we need some iteration procedure for solving the above equations. When the interaction between the B particle and the fluid is weak, an expansion in $\mathbf{F}$ is appropriate. This would lead to a generalized form of the Kohn-Luttinger procedure (classically). We shall consider that separately.¹⁰ Here we are interested in an expansion in $M^{-1} \ll 1$. To accomplish this, we shall scale the velocity of the B particle to its root mean square speed in equilibrium $(\beta M)^{-1/2}$, i.e., we shall treat $\mathbf{V}$ as of order $M^{-1/2}$ in the ensuing expansion. This will give us the correct result for the most important part of the distribution function which is the part for which linearization in $\mathbf{E}$ is useful. It will, however, not necessarily tell us correctly the behavior of very fast B particles. We shall investigate this further later.

Introducing now the velocity $\mathbf{v}$,

$$\mathbf{V} = \mathbf{v}/\sqrt{M} = \gamma \mathbf{v}, \quad \gamma^2 = M^{-1}, \quad (3.13)$$

into Eqs. (3.10)–(3.11) yields

$$-\beta \mathbf{E} \cdot \mathbf{v} \rho_0(\mathbf{v}) = (\partial/\partial \mathbf{v}) \cdot (\psi(\mathbf{v}) \langle \mathbf{F} \eta \rangle_{\text{av}}), \quad (3.14)$$

$$(\partial \eta / \partial t) + iL\eta = \gamma \mathbf{A}(\mathbf{v}) \cdot \mathbf{F} + \gamma \Gamma(\mathbf{v}) \eta, \quad (3.15)$$

where

$$\Gamma(\mathbf{v}) \eta = \mathbf{B}(\mathbf{v}) \cdot [\mathbf{F} \eta - \langle \mathbf{F} \eta \rangle] - \left[\mathbf{v} \cdot \frac{\partial \eta}{\partial \mathbf{R}} - \left\langle \mathbf{v} \cdot \frac{\partial \eta}{\partial \mathbf{R}} \right\rangle \right], \quad (3.16)$$

$$\rho_0(\mathbf{v}) = (2\pi/\beta)^{-3/2} e^{-\frac{1}{2}\beta v^2}. \quad (3.17)$$

IV. EXPANSION IN POWERS OF γ

It is seen from Eqs. (3.14)–(3.15) that, for small values of γ , η will be of order γ , while ψ will go as γ^{-1} . We therefore write η as a power series in γ ,

$$\eta = \gamma \eta_1 + \gamma^2 \eta_2 + \dots \quad (4.1)$$

The η_i will satisfy the equations,^{10a}

$$\begin{aligned} (\partial \eta_1 / \partial t) + iL\eta_1 &= \mathbf{A}(\mathbf{v}) \cdot \mathbf{F}, \\ (\partial \eta_j / \partial t) + iL\eta_j &= \Gamma \eta_{j-1}, \quad j > 1. \end{aligned} \quad (4.2)$$

¹⁰ See also R. Brout, *Physica* **23**, 959 (1957). R. W. Zwanzig, *Phys. Fluids* **2**, 12 (1958); I. Prigogine and M. Toda, *Mol. Phys.* **1**, 48 (1958).

^{10a} Note added in proof. The η_j will themselves also be dependent on γ , due to the dependence of $\mathbf{A}$ and Γ on γ , $\eta_j = \eta_j^0 + \gamma \eta_j^{(1)} + \dots$, but this will come out in the final form of $\delta\psi$ and doesn't have to be written out explicitly.

When these η 's are substituted in (3.14), we get successive approximations to the equation satisfied by ψ . The time-dependent solution $\eta_1(t)$ of (4.2) may be written in the form

$$\begin{aligned} \eta_1(t) &= - \int_0^t e^{-iL(t-t')} \mathbf{F}(\mathbf{R}, \mathbf{r}) dt' \cdot \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{\psi}{\rho_0} \right) \\ &= - \int_0^t e^{-iL t_1} \mathbf{F}(\mathbf{R}, \mathbf{r}) dt_1 \cdot \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{\psi}{\rho_0} \right). \end{aligned} \quad (4.3)$$

Now $e^{iL t}$ is the translation operator in the phase space of the fluid, whose motion is governed by the Hamiltonian H_2 ,

$$e^{iL t} g(x, y) = g(x, y(t)), \quad (4.4)$$

where $y(t) = y_t(y, t; \mathbf{R})$ is the phase-space point to which the point y will have moved, under the influence of the Hamiltonian H_2 , during the time interval t . H_2 is the Hamiltonian of the fluid particles in the field of a fixed B particle and contains $\mathbf{R}$ as a parameter. Thus,

$$\eta_1(t) = - \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{\psi}{\rho_0} \right) \cdot \int_0^t \mathbf{F}(-t_1) dt_1, \quad (4.5)$$

where

$$\mathbf{F}(-t) = \mathbf{F}(\mathbf{R}, \mathbf{r}(-t)) = \sum_{i=1} \cdot \frac{\partial}{\partial \mathbf{R}} u(\mathbf{r}_i(-t) - \mathbf{R}). \quad (4.6)$$

The expectation value $\langle \mathbf{F} \eta \rangle$ will be given to lowest order^{10a} in γ , for $t_0 \rightarrow \infty$,

$$\begin{aligned} \langle \mathbf{F} \eta \rangle_{\text{av}} &= -\gamma \lim_{t_0 \rightarrow \infty} \left\{ \frac{1}{t_0} \int_0^\infty dt e^{-t/t_0} \int_0^t dt_1 \langle \mathbf{F} \mathbf{F}(-t_1) \rangle \right\} \cdot \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{\psi}{\rho_0} \right) \\ &= -\gamma \lim_{t_0 \rightarrow \infty} \left\{ \int_0^\infty dt e^{-t/t_0} \langle \mathbf{F} \mathbf{F}(-t) \rangle \right\} \cdot \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{\psi}{\rho_0} \right) \\ &= -\gamma \mathfrak{D} \cdot \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{\psi}{\rho_0} \right) \end{aligned} \quad (4.7)$$

with

$$\begin{aligned} \mathfrak{D} &= \lim_{t_0 \rightarrow \infty} \int_0^\infty e^{-t/t_0} \langle \mathbf{F} \mathbf{F}(-t) \rangle dt \\ &= \lim_{t_0 \rightarrow \infty} \int_0^\infty e^{-t/t_0} \langle \mathbf{F} \mathbf{F}(t) \rangle dt \\ &= \frac{1}{3} \lim_{t_0 \rightarrow \infty} \left\{ \int_0^\infty e^{-t/t_0} \langle \mathbf{F} \cdot \mathbf{F}(t) \rangle dt \right\} \mathfrak{d} = \mathfrak{D} \mathfrak{d}, \end{aligned} \quad (4.8)$$

where the second equality follows from the time reversibility of the equations of motion and the last

equality follows from the isotropy of the fluid; δ is the unit tensor. When (4.7) is substituted into (2.14), the right side will be recognized immediately as the usual Fokker-Planck equation, Eq. (1.1), with the diffusion tensor $D\delta$ (here a multiple of the unit tensor) defined in terms of the molecular variables,^{7,11} $D = M^{-2}\mathfrak{D}$. As mentioned before, the limit $t_0 \rightarrow \infty$ is to be taken *after* the size of the system has been made infinitely large which itself is done after the ensemble average is taken.

Proceeding in the same fashion yields

$$\begin{aligned}\eta_2(t) &= \int_0^t e^{-iL t_2} \eta_1(t-t_2) dt_2 \\ &= \int_0^t dt_2 e^{-iL t_2} \Gamma \left\{ \int_0^{(t-t_2)} \mathbf{F}(-t_1) dt_1 \cdot \mathbf{A} \right\}. \quad (4.9)\end{aligned}$$

Now P_0 commutes with H_2 and is thus a constant of the motion,

$$e^{-iL t} P_0 = P_0. \quad (4.10)$$

Similar expressions will also hold for $\mathbf{A}$ and $\mathbf{B}$ which do not depend on $\mathbf{R}$ (but only on $\mathbf{v}$). Equation (4.9) may, therefore, be written in the form

$$\begin{aligned}\eta_2(t) &= \int_0^t dt_2 \int_0^{(t-t_2)} dt_1 \{ \mathbf{F}(-t_2-t_1) \mathbf{F}(-t_2) \\ &\quad - \langle \mathbf{F}(-t_2-t_1) \mathbf{F}(-t_2) \rangle \} : \mathbf{B} \mathbf{A} \\ &\quad - \int_0^t dt_2 \int_0^{(t-t_2)} dt_1 e^{-iL t_2} \left[\frac{\partial}{\partial \mathbf{R}} \mathbf{F}(-t_1) \right. \\ &\quad \left. - \left\langle \frac{\partial}{\partial \mathbf{R}} \mathbf{F}(-t_1) \right\rangle \right] : \mathbf{A} \mathbf{v}. \quad (4.11)\end{aligned}$$

When this expression for η_2 is substituted into $\langle \mathbf{F} \eta_2 \rangle$, the latter vanishes. This follows from consideration of the transformation of variables upon reflection of all the fluid particles through $\mathbf{R}$ and simultaneous reversal of their velocities,

$$\mathbf{R}_i = \mathbf{r}_i - \mathbf{R} \rightarrow \mathbf{R} - \mathbf{r}_i' = -\mathbf{R}_i', \quad \mathbf{v}_i \rightarrow -\mathbf{v}_i'. \quad (4.12)$$

This transformation leaves P_0 unchanged, but changes $\mathbf{F}(-t)$ and $\langle \mathbf{F} \eta_2 \rangle$ into their negative. We may therefore conclude that $\langle \mathbf{F} \eta_2 \rangle$ vanishes. The same will be true for all even terms $\langle \mathbf{F} \eta_{2l} \rangle$.

The first correction to the Fokker-Planck equation will thus come, in a uniform system, from η_3 which

will consist of four terms

$$\begin{aligned}\eta_3(t) &= \int_0^t dt_3 e^{-iL t_3} \Gamma \eta_2(t-t_3) \\ &= \int_0^t dt_3 \int_0^{t-t_3} dt_2 \int_0^{t-t_3-t_2} dt_1 \left\{ \mathbf{a} : \left[\frac{\partial^3 (\psi/\rho_0)}{\partial \mathbf{v} \partial \mathbf{v} \partial \mathbf{v}} \right] \right. \\ &\quad \left. + \mathbf{b} : \left[\frac{\partial}{\partial \mathbf{v}} \left(\frac{\partial}{\partial \mathbf{v}} \left(\frac{\psi}{\rho_0} \right) \mathbf{v} \right) \right] + \mathbf{c} : \left[\frac{\partial^2 (\psi/\rho_0)}{\partial \mathbf{v} \partial \mathbf{v}} \right] \right. \\ &\quad \left. + \mathbf{d} : \left[\frac{\partial}{\partial \mathbf{v}} \left(\frac{\psi}{\rho_0} \right) \mathbf{v} \mathbf{v} \right] \right\} \frac{\rho_0}{\psi}, \quad (4.13)\end{aligned}$$

where $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, and $\mathbf{d}$ are third rank tensors which are independent of $\mathbf{v}$,

$$\begin{aligned}\mathbf{a} &= \mathbf{F}(-t_3-t_2-t_1) \mathbf{F}(-t_3-t_2) \mathbf{F}(-t_3) \\ &\quad - \langle \mathbf{F}(-t_3-t_2-t_1) \mathbf{F}(-t_3-t_2) \rangle \mathbf{F}(-t_3), \\ \mathbf{b} &= e^{-iL(t_3+t_2)} \left\{ \left[\frac{\partial}{\partial \mathbf{R}} \mathbf{F}(-t_1) - \left\langle \frac{\partial}{\partial \mathbf{R}} \mathbf{F}(-t_1) \right\rangle \right] \mathbf{F}(t_2) \right\}, \\ \mathbf{c} &= e^{-iL t_3} \left\{ \frac{\partial}{\partial \mathbf{R}} [\mathbf{F}(-t_2-t_1) \mathbf{F}(-t_2)] \right. \\ &\quad \left. - \left\langle \frac{\partial}{\partial \mathbf{R}} [\mathbf{F}(-t_2-t_1) \mathbf{F}(-t_2)] \right\rangle \right\}, \\ \mathbf{d} &= e^{-iL t_3} \left\{ \frac{\partial}{\partial \mathbf{R}} \left[e^{-iL t_2} \frac{\partial}{\partial \mathbf{R}} \mathbf{F}(-t_1) \right] \right. \\ &\quad \left. - \left\langle \frac{\partial}{\partial \mathbf{R}} \left[e^{-iL t_2} \frac{\partial}{\partial \mathbf{R}} \mathbf{F}(-t_1) \right] \right\rangle \right\}. \quad (4.14)\end{aligned}$$

It is seen from (4.13) and (4.14) that when values of η_i up to η_3 are used in (3.14) the resulting equation will still be linear in ψ , albeit it will be of fourth order in the velocity gradients. Part of the terms coming from $\langle \mathbf{F} \eta_3 \rangle$ may be combined with those obtained previously from $\langle \mathbf{F} \eta_1 \rangle$ to obtain again a Fokker-Planck equation with new values for the friction force and the diffusion tensor. The remaining terms lead to higher derivatives. More precisely, the term proportional to γ^3 on the right side of (3.14), which represents the effect of the fluid, may be written in the form

$$\begin{aligned}\delta_3 \psi &= \nabla \cdot (A_3^{(1)} \psi) + \frac{1}{2!} \nabla^2 : (A_3^{(2)} \psi) + \frac{1}{3!} \nabla^3 : (A_3^{(3)} \psi) \\ &\quad + \frac{1}{4!} \nabla^4 : (A_3^{(4)} \psi). \quad (4.15)\end{aligned}$$

Here $\nabla = \partial/\partial \mathbf{v}$; the superscript indicates the rank of the tensor and the subscript the power of γ involved.

¹¹ See also E. Helfand, *Phys. Fluids*, **4**, 1 (1961). For the general use of autocorrelation function expressions in irreversible processes see M. S. Green, *J. Chem. Phys.*, **20**, 1281 (1950) and the second reference in Ref. 3 and references cited there.

¹² R. W. Zwanzig, *Lectures in Theoretical Physics* (Interscience Publishers Inc., New York, 1961), Vol. 3, p. 106.

The velocity dependence of the A 's which is of $O(v^3)$ may be written out immediately in terms of the various tensor invariants since the only vector available is $\mathbf{v}$:

$$\begin{aligned} A_3^{(1)} &= (\alpha_1^{(1)} + \alpha_2^{(1)} v^2) \mathbf{v}, \\ A_3^{(2)} &= \alpha_1^{(2)} \mathbf{v} \mathbf{v} + (\alpha_2^{(2)} v^2 + \alpha_3^{(2)}) \delta, \\ A_3^{(3)} &= \alpha_2^{(3)} [\delta \times \mathbf{v}]_s, \\ A_3^{(4)} &= \alpha_4^{(3)} [\delta \times \delta]_s. \end{aligned} \quad (4.16)$$

Here the α 's are constants independent of $\mathbf{v}$, δ is the unit tensor of rank two, the cross indicates the direct product, and the subscript s indicates that the tensor be symmetrized in all indices. The numerical values of the α 's and β 's are linear combinations of the time integrals of the expectation values of F times the tensors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $\mathbf{d}$ appearing in (4.12). Thus,

$$\begin{aligned} \frac{1}{4!} \alpha_4 &= \lim_{t_0 \rightarrow \infty} \left\{ \frac{1}{t_0} \int_0^{t_0} dt e^{-t/t_0} \int_0^t dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \right. \\ &\quad \times [\langle F_x(-t_3) F_x(-t_2) F_y(-t_1) F_y \rangle \\ &\quad \left. - \langle F_x(-t_3) F_x(-t_2) \rangle \langle F_y(-t_1) F_y \rangle] \right\}, \end{aligned} \quad (4.17)$$

where x, y stand for components of the vector (*which are not summed over*), $x \neq y$.

V. TIME-DEPENDENT DISTRIBUTIONS

We now come to a discussion of the effect of the fluid on the time evolution of $f(\mathbf{R}, \mathbf{V}, t)$. In the absence of time-dependent forces, we expect that starting from an arbitrary initial state $f(\mathbf{R}, \mathbf{V}, 0)$, collisions with fluid particles will cause $f(t)$ to approach, as $t \rightarrow \infty$, a stationary value. There will be some changes, however, in the form of the collision term δf , when f is a function of t ; therefore, it differs from that arrived at in the last section for a stationary f . This will come from the fact that, as f keeps changing with time, the distribution of the fluid is not able to adjust itself to the instantaneous $f(t)$, as it does when f is stationary, but depends on the value of $f(t')$ over a time interval τ , the liquid relaxation time, prior to t . It is only when τ is small on the time scale in which f changes appreciably that a Markoffian transport equation in which the $\partial f(t)/\partial t$ depends only on $f(t)$ itself is possible. In our case τ is essentially the time interval over which $\langle \mathbf{F} \mathbf{F}(t) \rangle$ is significantly different from zero, while $(\partial \ln f / \partial t)^{-1}$ will be of order $t_r = \xi^{-1} \sim \gamma^{-2} \tau$ for a uniform system, $f(\mathbf{R}, \mathbf{V}, t) = f(\mathbf{V}, t)$, in which $V \sim \gamma$. When f has a slowly varying spatial dependence it is possible for the system to come to a "quasistationary" state in which $f(t)$ will be a "normal distribution" whose rate of change will be determined by the hydrodynamic equations and may be made very small.^{4,8} In either case, there will be corrections to the collision term δf appropriate for a stationary distribution of order $[\tau(\partial \ln f / \partial t)] \delta f$. For

the uniform case, these corrections will start as γ^3 , while in the quasistationary state they may be neglected to lowest order in the density gradient. In addition to these changes in δf , it is clear from the above discussion that for $t \lesssim \tau$ there will be no δf which can represent the effect of the fluid in terms of f , since for such times the fluid distribution will depend on its initial value at $t=0$, which is independent of f .

Let us consider first the spatially uniform case in the absence of an external field, where μ is only a function of $\mathbf{R}_i$ and r_{ij} and f is thus independent of $\mathbf{R}$, $f = f(\mathbf{V}, t)$. The ensemble density $\mu(x, y, t)$ will satisfy Eq. (2.2) with $\mathbf{E} = 0$. Defining the conditional distribution $P = P_0(1 + \xi)$ as in (2.12), we find the following coupled equations for f and ξ :

$$\partial f(\mathbf{v}, t) / \partial t = -\gamma (\partial / \partial \mathbf{v}) \cdot (f \langle \mathbf{F} \xi \rangle), \quad (5.1)$$

$$(\partial \xi / \partial t) + iL\xi = \gamma \mathbf{A} \cdot \mathbf{F} + \gamma \Gamma \xi - (\partial \ln f / \partial t) \xi. \quad (5.2)$$

L , $\mathbf{A}$, and Γ are the functions defined in Sec. III except that f and f_0 replace ψ and ρ_0 there.

Proceeding as before with an expansion of ξ and $\partial f / \partial t$ in powers of γ , we obtain to lowest order in γ ,

$$\begin{aligned} \frac{\partial f(\mathbf{v}, t)}{\partial t} &= -\gamma \frac{\partial}{\partial \mathbf{v}} (f \langle \mathbf{F} \xi(x, y, -t, 0) \rangle) \\ &\quad + \gamma^2 \frac{\partial}{\partial \mathbf{v}} \cdot \left\{ f_0 \int_0^t dt_1 \left[\langle \mathbf{F} \mathbf{F}(-t_1) \rangle \right. \right. \\ &\quad \left. \left. \cdot \frac{\partial}{\partial \mathbf{v}} \left(\frac{f(t-t_1)}{f_0} \right) \right] \right\}. \end{aligned} \quad (5.4)$$

We shall assume that $\xi(x, y, 0)$ is a function only of the r_{ij} and $\mathbf{R}_i$ and that its dependence on $\mathbf{R}_i$ is significant only for R_i in the range of $\mathbf{F}$, i.e., the fluid is homogeneous away from the B particle. Thus, when $t \gg \tau$ the first term will be (presumably) exponentially small and the integration in the second term may be extended to infinity with an error of order $\exp[-t/\tau]$. Also $f(t-t_1)$ may be expanded in a Taylor series about t . This yields again to lowest order in γ the Fokker-Planck equation

$$\begin{aligned} \frac{\partial f(\mathbf{v}, t)}{\partial t} &= \gamma^2 \mathfrak{D} : \frac{\partial}{\partial \mathbf{v}} \left[f \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{f}{f_0} \right) \right] + O(e^{-t/\tau}) \\ &= \gamma^2 \delta_1 f + O(e^{-t/\tau}). \end{aligned} \quad (5.5)$$

[The transition from (5.4) to (5.5) can also be accomplished by introducing formally the variable $s = \gamma^{-2} t$, then going to the limit $\gamma \rightarrow 0$, s remaining fixed.^{5,12}]

To obtain further terms in δf we will have to take into account terms coming from the expansion of $f(t-t_1)$ in (5.4) in addition to the terms obtained

previously for the stationary state. Thus, to order γ^4 ,

$$\begin{aligned} \frac{\partial f(\mathbf{v}, t)}{\partial t} = & \gamma^2 \delta_1 f + \gamma^4 \delta_3 f \\ & - \gamma^4 \frac{\partial}{\partial \mathbf{v}} \cdot \left\{ \mathbf{E} f_0 \frac{\partial}{\partial \mathbf{v}} \left[f_0^{-1} \mathfrak{D} \frac{\partial}{\partial \mathbf{v}} \left(f_0 \frac{\partial}{\partial \mathbf{v}} \left(\frac{f}{f_0} \right) \right) \right] \right\} \\ & + O(e^{-t/\tau}), \quad (5.6) \end{aligned}$$

where $\delta_3 f$ is given by (4.15), with f replacing ψ and (for normalization) f_0 replacing ρ_0 . The last term is the new one and $\mathbf{E}$ is defined as

$$\mathbf{E} = \int_0^\infty s \langle \mathbf{F} \mathbf{F}(-s) \rangle ds = (1/3) \int_0^\infty \langle \mathbf{F} \cdot \mathbf{F}(-s) \rangle ds \, \mathbf{\hat{s}}. \quad (5.7)$$

The integration in (5.7) has been extended to infinity on the assumption that this, like the transition from (5.4) to (5.5), produces an error of order $e^{-t/\tau}$. We must remember, however, that if we want to integrate equation (5.6) to obtain $f(t)$, for times of order $t_r \sim \gamma^{-2} \tau$, starting from some initial $f(\mathbf{v}, 0)$, then the terms which are of order $e^{-t/\tau}$ will also make contributions of order γ . Hence, if the collision terms are taken to order γ^4 we must not neglect these terms either. The evaluation of these terms though unfortunately requires a knowledge of ξ at $t=0$. Thus, unless f is known at some time $t, t \gg \tau$, i.e., at a time when the fluid distribution has already had a chance to adjust itself to f , the transport equation giving the effect of the fluid in terms of a time-independent collision operator δf is only useful to lowest order in γ .

When the distribution of B particles is not restricted to be uniform and we allow also the possibility that there is an external force $\mathbf{X}$ acting on them, the equation for $f(\mathbf{R}, \mathbf{V}, t)$ will have the form

$$\frac{\partial f}{\partial t} + \gamma \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{R}} + \gamma \mathbf{X} \cdot \frac{\partial f}{\partial \mathbf{v}} = \gamma \frac{\partial}{\partial \mathbf{v}} \cdot (f \langle \mathbf{F} \xi \rangle), \quad (5.8)$$

and the equation for ξ will remain the same as (5.2). An expansion in γ will yield to lowest order,

$$\begin{aligned} \frac{\partial f}{\partial t} + \gamma \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{R}} + \gamma \mathbf{X} \cdot \frac{\partial f}{\partial \mathbf{v}} = & - \gamma \frac{\partial}{\partial \mathbf{v}} \cdot (f \langle \mathbf{F} \xi(x, y-t, 0) \rangle) \\ & + \gamma^2 \frac{\partial}{\partial \mathbf{v}} \cdot \left\{ f_0 \int_0^t dt_1 \left[\langle \mathbf{F} \mathbf{F}(-t_1) \rangle \cdot \frac{\partial}{\partial \mathbf{v}} \left(\frac{f(t-t_1)}{f_0} \right) \right] \right\}. \quad (5.9) \end{aligned}$$

When the dependence of $\xi(x, y, 0)$ on $\mathbf{R}_i$ is limited to the vicinity of the B particle, $\mathbf{R}_i \sim 0$, the first term will again vanish for $t \gg \tau$. Similarly, the integration can be extended to infinity for $t \gg \tau$ and the integrand expanded about t to yield Eq. (1.1) to lowest order in γ .

When $\mathbf{X}$ is derivable from an external potential $\Phi(\mathbf{R})$, $\mathbf{X} = -\partial\Phi/\partial\mathbf{R}$, then the final stationary state will

be the equilibrium state,

$$\lim_{t \rightarrow \infty} f(\mathbf{R}, \mathbf{V}, t) = f_0 = C e^{-\beta\Phi(\mathbf{R})} \rho_0(\mathbf{v}), \quad (5.10)$$

where C is a normalization constant. (The requirement $\mathbf{X} = -\partial\Phi/\partial\mathbf{R}$ excludes constant fields in a periodic box.) Now since the collision term does not affect the density $n(\mathbf{R}, t)$ at all, there will be a new time scale T , for changes in n , determined by the density gradient and $\mathbf{X}$ (which we shall treat as quantities of the same order). When $T \gg t_r$ there will develop for $t \gg t_r$ a hydrodynamic domain in which f is a function of n , i.e., f will be a normal distribution $f(\mathbf{R}, \mathbf{V}, t) = f(\mathbf{V}, n(\mathbf{R}, t))$.^{4,8} The solution for f will then have the form of the Enskog solutions to the Boltzmann equation (though here n is the only conserved quantity),

$$f = f^{(0)} + f^{(1)} + \dots \quad (5.11)$$

The lowest order term in this solution is

$$f^{(0)} = n(\mathbf{R}, t) \rho_0(\mathbf{v}), \quad (5.12)$$

while $f^{(j)}$ will be proportional to the j th power of the density gradient (again $\mathbf{X}$ is treated as of the same order as $\partial n/\partial \mathbf{R}$). If we are interested in $f^{(1)}$, to all orders in γ , then $f(t-t_1)$ in (5.9) may be replaced by $f(t)$ and, in general, δf will have the same form as it has for the stationary state discussed in Sec. IV.⁹

VI. DISCUSSION

We have shown in this paper that the effect of the fluid on the distribution function of heavy particles, of mass M , and small velocities, $V \sim M^{-1/2}$, may be described to lowest order in M^{-1} , by a Fokker-Planck type collision term with a friction constant ζ defined in terms of molecular variables,

$$\zeta = M^{-1} \beta^{\frac{1}{2}} \int_0^\infty \langle \mathbf{F} \cdot \mathbf{F}(-t) \rangle dt. \quad (6.1)$$

In order for this to exist we must go to the limit $N \rightarrow \infty$, $\Omega \rightarrow \infty$, N/Ω constant, before extending the integration to infinity. This expression is to be compared, when applicable, with the hydrodynamic expression for the friction coefficient of a sphere of radius σ , Stokes' law,¹⁸

$$\zeta = M^{-1} 6\pi\eta\sigma, \quad (6.2)$$

where η is the viscosity of the fluid. For the hydrodynamic expression to be valid σ has to be much greater than the mean free path of the fluid particles (it is thus not valid for the Rayleigh model in which a sphere moves through a gas of noninteracting particles¹⁴).

¹⁸ See Ref. 1, note 6.

¹⁴ J. L. Lebowitz, Phys. Rev. **114**, 1192 (1959), and references cited there.

In order to compare (6.1) with (6.2), it is convenient to *define* a relaxation time τ by the relation

$$\int_0^\infty \langle \mathbf{F} \cdot \mathbf{F}(-t) \rangle dt = \tau \langle \mathbf{F} \cdot \mathbf{F} \rangle. \quad (6.3)$$

After some manipulation the average value of $\langle \mathbf{F}^2 \rangle$ may be put in the form

$$\langle \mathbf{F}^2 \rangle = 4\pi\beta^{-1}\rho \int_0^\infty G(R) [\nabla_R^2 U(R)] R^2 dR, \quad (6.4)$$

where ρ is the density of fluid particles and $G(R)$ is the radial distribution function between the B particle and a fluid particle, i.e., $\rho G(R)$ is the density of fluid particles a distance R from the B particle.

The "size" σ of the B particle enters into our analysis through the dependence of $U(R_i)$ on σ . If we assume that $U(R_i, \sigma) = U(R_i/\sigma)$ (an unlikely situation for true Brownian particles), then (6.4) becomes

$$\langle \mathbf{F}^2 \rangle = 4\pi\beta^{-1}\rho\sigma \int_0^\infty G(z, \sigma) \nabla^2 U(z) z^2 dz, \quad (6.5)$$

where we have introduced the dimensionless variable $z = R/\sigma$. Comparison of (6.2) with (6.3) and (6.5) yields for τ ,

$$\tau = \frac{3}{2}\eta \left[\int_0^\infty \rho G(z, \sigma) \nabla^2 U(z) z^2 dz \right]^{-1}. \quad (6.6)$$

We generally expect $G(z, \sigma)$ to depend only weakly on σ . When ρ is small, i.e., in a gas, $G \sim e^{-\beta U(z)}$, and $\eta \sim \frac{1}{2}\rho \bar{C}l$, where $\bar{C}$ is the mean speed and l the mean free path.¹⁵ Thus, in this case,

$$\begin{aligned} \tau &\sim (9/4)\bar{C}l \left[\int_0^\infty e^{-\beta U(z)} \nabla^2 U(z) z^2 dz \right]^{-1} \\ &= \frac{18}{\pi} \beta \left[\int_0^\infty e^{-\beta U} \nabla^2 U z^2 dz \right]^{-1} \tau_c, \end{aligned} \quad (6.7)$$

where $\tau_c = l/\bar{C}$ is the mean time between collisions of gas particles. The difference between τ and τ_c may perhaps be understood by considering that the density of gas particles and, hence, τ_c is changed in the vicinity of the B particle and also that the correlation of $\mathbf{F}$ persists for more than one mean collision time.

The scaling of the potential with σ as $U(R_i/\sigma)$ is appropriate for an atom and might be useful for discussing the motion of a neon atom in helium for example (though in this case Stokes' law would certainly not apply). In a true Brownian particle (i.e., colloidal particles of size $\sim 50\mu\mu$ or larger^{1,2}), the potential $U(R_i)$ is more likely to be of the form $U(R_i - \sigma)$, becoming

rapidly infinite for negative values of $R_i - \sigma$ and zero for positive values of $R_i - \sigma$. In the limit in which U becomes a step function at $R_i = \sigma$, i.e., the B particle is a hard sphere of radius σ , it might be possible to use quasihydrodynamic methods, i.e., a fluctuating pressure tensor,¹⁶ to evaluate (6.1). We are currently considering this as well as "many-body" diagram techniques for the evaluation of the force auto-correlation function. (Its evaluation in a one-dimensional crystal is presented in Appendix E.)

We may note here that the expression for the average force acting on the B particle, $\mathbf{F}_{av} = \langle \mathbf{F} \xi \rangle$, which is central in the derivation of the Fokker-Planck equation, can be put in the interesting form [cf. Eqs. (4.7) and (5.4)]

$$\mathbf{F}_{av}(\mathbf{p}) = \frac{D}{k} \frac{\partial}{\partial \mathbf{p}} [\mathcal{S}(\mathbf{p}) - \mathcal{S}_0(\mathbf{p})] \sim \left[\frac{d}{dt} \mathbf{p} \right]_{av}, \quad (6.8)$$

where $\mathbf{p} = M\mathbf{V}$ is the momentum of the B particle and

$$\mathcal{S}(\mathbf{p}) = -k \ln f(\mathbf{p}, \mathbf{R}) \quad (6.9)$$

is a kind of entropy density in the phase space of the B particle whose average value is the usual entropy.

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APPENDIX A: FORMAL STRUCTURE OF THE COLLISION TERM

According to the analysis of this paper, the effect of the fluid on the distribution of B particles may be represented in some cases to all orders in γ , in the form

$$\delta f = \sum_{n=1}^{\infty} \nabla_v^{(n)} \cdot [\mathbf{A}^{(n)}(\mathbf{v}) f], \quad (A1)$$

where $\mathbf{A}^{(n)}$ is an n th rank tensor independent of f . The right side of (A1) may be formally replaced by an integral operator acting on f ,^{14,17}

$$\delta f = \int [K(\mathbf{v}, \mathbf{v}') f(\mathbf{v}', \mathbf{R}, t) - K(\mathbf{v}', \mathbf{v}) f(\mathbf{v}, \mathbf{R}, t)] d\mathbf{v}'. \quad (A2)$$

The $\mathbf{A}^{(n)}$ are related to K by the relations,

$$\begin{aligned} \mathbf{A}^{(n)}(\mathbf{v}) &= (-1)^n \int K(\mathbf{v}', \mathbf{v}) (\mathbf{v}' - \mathbf{v})^n d\mathbf{v}' \\ &= (-1)^n \int K(\mathbf{z}; \mathbf{v}) \mathbf{z}^n d\mathbf{z}, \end{aligned} \quad (A3)$$

¹⁵ S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases*, (Cambridge University Press, New York, 1958).

¹⁶ L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon Press, Inc., New York, 1959), Chap. 17.

¹⁷ H. A. Kramers, *Physica* 7, 284 (1940); J. Keilson and J. E. Storer, *Quart. Appl. Math.* 10, 243 (1952).

and we have set

$$K(\mathbf{v}' - \mathbf{v}; \mathbf{v}) = K(\mathbf{v}', \mathbf{v}). \quad (\text{A4})$$

The function K is not uniquely determined by (A1) or (A2). This corresponds to the fact that $\mathbf{A}^{(0)}$ does not appear in (A1), or equivalently that we can modify $K(\mathbf{v}', \mathbf{v})$ by adding to it an arbitrary function,

$$\hat{K}(\mathbf{v}', \mathbf{v}) = K(\mathbf{v}', \mathbf{v}) + g(\mathbf{v})\delta(\mathbf{v} - \mathbf{v}'), \quad (\text{A5})$$

without changing (A2). Choosing $\mathbf{A}^{(0)}(\mathbf{v})$ arbitrarily for the moment, we may write

$$K(\mathbf{v}', \mathbf{v}) = (2\pi)^{-3} \int d\mathbf{k} [e^{i\mathbf{k}(\mathbf{v}' - \mathbf{v})}] \times \left[\sum_{n=0}^{\infty} \frac{(i\mathbf{k})^n}{n!} : \mathbf{A}^{(n)}(\mathbf{v}) \right]. \quad (\text{A6})$$

Alternatively, we may first use the $\mathbf{A}^{(k)}$, $k \leq n$, to find the value of the integral of the n th Hermite polynomial $H^{(n)}$, which is an n th rank tensor,¹⁸

$$B^{(n)} = \int K(\mathbf{z}; \mathbf{v}) H^{(n)}(\mathbf{z}) d\mathbf{z}. \quad (\text{A7})$$

The $H^{(n)}(\mathbf{z})$ are orthogonal with a weight factor $\rho_0(\mathbf{z})$, $\rho_0(\mathbf{z}) = (2\pi)^{-3/2} e^{-z^2/2}$,

$$\int H^{(l)}(\mathbf{z}) H^{(n)}(\mathbf{z}) \rho_0(\mathbf{z}) d\mathbf{z} = n! \delta_{nl}. \quad (\text{A8})$$

We thus have

$$K(\mathbf{z}; \mathbf{v}) = \sum_{k!} B^{(k)}(\mathbf{v}) \rho_0(\mathbf{z}) H^{(k)}(\mathbf{z}), \quad (\text{A9})$$

with

$$\mathbf{z} = \beta^{1/2}(\mathbf{v}' - \mathbf{v}). \quad (\text{A10})$$

The right side of (A2) has the structure of the usual linear transport equation when $K(\mathbf{v}', \mathbf{v}) d\mathbf{v}'$ is the transition probability per unit time from $\mathbf{v}$ to $d\mathbf{v}'$. That such an interpretation of the K constructed here be possible, it is necessary first, that the series (A6) or (A9) converge, and, in addition, it is also necessary that K be non-negative for all values of its arguments. This requirement on K sets up conditions on our choice of $\mathbf{A}^{(0)}(\mathbf{v})$ which it may or may not be possible to meet. The further requirement that $K(\mathbf{v}, \mathbf{v}')$ not contain $\delta(\mathbf{v} - \mathbf{v}')$ insures that the choice of $\mathbf{A}^{(0)}$, if at all possible, will be unique. If such a K can be found it will have the features of a stochastic kernel representing the effect of a heat bath, here the fluid, on the B particle.¹⁴ The distribution f will then satisfy some kind of H theorem which would assure the approach of f to a stationary state. As is well known, when δf is taken to lowest order in γ , i.e., the Fokker-Planck term, then f also satisfies an H theorem. We have not investigated

whether there exists such an H theorem when the series for δf is terminated at some higher power of γ .¹⁹

APPENDIX B: STATIONARY SOLUTION OF ψ

In order to get the form of the steady state ψ to the order in γ that we have been considering in Sec. IV, we write Eq. (3.14) in the form

$$-\beta \mathbf{E} \cdot \mathbf{v} \rho_0(\mathbf{v}) = \gamma \delta_1 \psi + \gamma^2 \delta_3 \psi + \dots, \quad (\text{B1})$$

and write ψ as an expansion in γ ,

$$\psi = \gamma^{-1} [\psi_1 + \gamma^2 \psi_3 + \dots]. \quad (\text{B2})$$

When (B2) is substituted into (B1) and equal powers of γ are equated, we obtain

$$\delta_1 \psi_1 \equiv \mathfrak{D} \cdot \left[\psi_1 \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{\psi_1}{\rho_0} \right) \right] = -\beta \mathbf{E} \cdot \mathbf{v} \rho_0(\mathbf{v}), \quad (\text{B3})$$

$$\delta_3 \psi_1 = -\delta_1 \psi_3 \equiv -\mathfrak{D} \cdot \left[\psi_3 \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{\psi_3}{\rho_0} \right) \right]. \quad (\text{B4})$$

The solution of (B3) is⁸

$$\psi_1(\mathbf{v}) = \mathfrak{D}^{-1} \mathbf{E} \cdot \mathbf{v} \rho_0(\mathbf{v}), \quad (\text{B5})$$

or in terms of the velocity variable $\mathbf{V}$:

$$\psi_1(\mathbf{V}) = \zeta^{-1} \beta \mathbf{E} \cdot \mathbf{V} \rho_0(V) + o(\gamma), \quad (\text{B6})$$

where ζ is the friction constant [cf. Eq. (1.2)], $\zeta = \gamma^2 \mathfrak{D} \beta^{-1} = \tau_r^{-1}$. In order to evaluate the term $\delta_3 \psi_1$, which is the inhomogeneous part of (B4), it is most convenient to look at (4.13) which already contains all the velocity dependence of δ_3 . When ψ_1 is substituted into the curly bracket of (4.13) the term multiplying $\mathbf{a}$ and $\mathbf{c}$ is seen to vanish and the rest becomes

$$\mathfrak{D}^{-1} [\mathbf{b} : \mathbf{E} \delta + \mathbf{d} : \mathbf{E} \mathbf{v} \mathbf{v}]. \quad (\text{B7})$$

The collision term $\delta_3 \psi_1$ can then be written in the form

$$\delta_3 \psi_1 = \nu_0 \mathbf{E} \cdot \mathbf{v} \rho_0(\mathbf{v}) + \nu_1 \left[\frac{1}{2} \beta v^2 - \frac{5}{2} \right] \mathbf{E} \cdot \mathbf{v} \rho_0(\mathbf{v}), \quad (\text{B8})$$

where ν_0 and ν_1 are two velocity-independent constants which can be expressed in terms of the force correlation functions. When (B8) is substituted in (B4) we obtain⁸

$$\psi_3(\mathbf{v}) = \beta \mathfrak{D}^{-1} \left[\nu_0 + \frac{1}{2} \beta \nu_1 \left(\frac{1}{2} v^2 - \frac{5}{2} \right) \right] \mathbf{E} \cdot \mathbf{v} \rho_0(\mathbf{v}). \quad (\text{B9})$$

The mean velocity of the B particles is

$$\begin{aligned} \langle \mathbf{V} \rangle &= \int \mathbf{V} \psi(\mathbf{V}) d\mathbf{V} = \zeta^{-1} / M (1 + \gamma^2 \nu_0) + O(\gamma^4) \\ &= \beta \mathfrak{D}^{-1} / (1 + \gamma^2 \nu_0) + O(\gamma^4). \end{aligned} \quad (\text{B10})$$

APPENDIX C: QUASISTOCHASTIC MODEL OF BROWNIAN MOTION

In this Appendix we shall consider a model which is midway between the usual model of Brownian motion, that of a stochastic force acting on the B particle, and

¹⁸ H. Grad, Comm. Pure Appl. Math. **2**, 325 (1949).

¹⁹ A. Siegel, J. Math. Phys. **1**, 378 (1960).

the analysis in this paper, where the motion of the B particle and fluid are governed by a definite Hamiltonian. We shall assume that the B particle interacts via a definite potential with one fluid particle but represent the effect of the rest of the fluid on this particle in a stochastic fashion. This model is of interest to us because the distribution $f(\mathbf{R}, \mathbf{V}, t)$ obeys equations formally similar to those developed in this paper with coefficients which may be evaluated explicitly in some cases.

The Hamiltonian of the B particle and one fluid particle, which together we shall call the system, has the form

$$H = \frac{1}{2} M \mathbf{V}^2 + \frac{1}{2} \mathbf{v}_1^2 + U(\mathbf{R} - \mathbf{r}_1), \quad (\text{C1})$$

where we have again set the mass of the fluid particle equal to unity. The joint distribution of B particle and fluid particle $\mu(\mathbf{R}, \mathbf{V}, \mathbf{r}_1, \mathbf{v}_1, t)$ will now obey a generalized Liouville equation which will take into account the effect of the rest of the fluid, the "reservoir," on the system,^{14,20}

$$\begin{aligned} \frac{\partial \mu}{\partial t} + (\mu, H) + M^{-1} \mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{V}} \\ = \int [K(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1', \mathbf{v}_1', \mathbf{R}, \mathbf{V}) \mu(\mathbf{R}, \mathbf{V}, \mathbf{r}_1', \mathbf{v}_1', t) \\ - K(\mathbf{r}_1', \mathbf{v}_1', \mathbf{r}_1, \mathbf{v}_1, \mathbf{R}, \mathbf{V}) \mu(\mathbf{R}, \mathbf{V}, \mathbf{r}_1, \mathbf{v}_1, t)] d\mathbf{r}_1' d\mathbf{v}_1'. \end{aligned} \quad (\text{C2})$$

In writing down the stochastic kernel K we have used explicitly our assumption that the reservoir does not act directly on the B particle but only on the fluid particle interacting with it. The form of the potentials U and of the kernel K are still at our disposal and we shall choose these to be as simple as possible. For U we will take a harmonic potential,

$$U(|\mathbf{R} - \mathbf{r}_1|) = \frac{1}{2} \omega_0^2 (\mathbf{R} - \mathbf{r}_1)^2 = \frac{1}{2} \omega_0^2 \mathbf{R}_1^2, \quad (\text{C3})$$

and K will be assumed to have a simple relaxational form

$$K(\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_1', \mathbf{v}_1', \mathbf{R}, \mathbf{V}) = \tau^{-1} P_0(\mathbf{R}, \mathbf{V}, \mathbf{r}_1, \mathbf{v}_1). \quad (\text{C4})$$

K tries to bring the conditional distribution of the fluid particle relative to the B particle, characterized by P , to its equilibrium value P_0 . It does this with a characteristic time, the fluid relaxation time, τ . The quantities P , P_0 , and ξ are defined as before,

$$P = \frac{\mu}{f} = P_0(1 + \xi); \quad (\text{C5})$$

$$f(\mathbf{R}, \mathbf{V}, t) = \int \mu(\mathbf{R}, \mathbf{V}, \mathbf{r}_1, \mathbf{v}_1, t) d\mathbf{r}_1 d\mathbf{v}_1,$$

²⁰ P. G. Bergmann and J. L. Lebowitz, Phys. Rev. **99**, 578 (1955); J. L. Lebowitz and P. G. Bergmann, Ann. Phys. (N.Y.) **1**, 1 (1957); J. L. Lebowitz and A. Shimony, Phys. Rev. **128**, 1945 (1962).

$$\begin{aligned} P_0 = \frac{\mu_0}{f_0} = \frac{e^{-\beta H}}{\int e^{-\beta H} d\mathbf{r}_1 d\mathbf{v}_1} = \left(\frac{2\pi}{\beta \omega_0} \right)^{-3} \\ \times \exp\left\{ -\beta \left[\frac{1}{2} \mathbf{v}_1^2 + \frac{1}{2} \omega_0^2 (\mathbf{R} - \mathbf{r}_1)^2 \right] \right\}, \\ f_0 = \Omega^{-1} \rho_0(\mathbf{V}). \end{aligned} \quad (\text{C6})$$

An alternative interpretation of our model is that there is a probability per unit time, τ^{-1} , that the fluid particle which interacts with the B particle is removed and replaced by another particle from the fluid. The probability distribution of this new particle is given by P_0 .

Equation (C2) now assumes the form

$$\begin{aligned} \frac{\partial \mu}{\partial t} + \mathbf{V} \cdot \frac{\partial \mu}{\partial \mathbf{R}} + \mathbf{v}_1 \cdot \frac{\partial \mu}{\partial \mathbf{r}_1} + M^{-1} \mathbf{F} \cdot \frac{\partial \mu}{\partial \mathbf{V}} - \mathbf{F} \cdot \frac{\partial \mu}{\partial \mathbf{v}_1} + M^{-1} \mathbf{E} \cdot \frac{\partial \mu}{\partial \mathbf{V}} \\ = f[P_0 - P]/\tau \\ = -P_0 f \xi / \tau, \end{aligned} \quad (\text{C7})$$

where, as before,

$$\mathbf{F} = -\partial U / \partial \mathbf{R} = \omega_0^2 (\mathbf{r}_1 - \mathbf{R}) = \omega_0^2 \mathbf{R}_1. \quad (\text{C8})$$

We shall now again consider the stationary distribution to terms linear in $\mathbf{E}$. It is not necessary to worry here about the system size going to infinity since that has already been accomplished by introducing the time-independent stochastic kernel K .²⁰ Consequently, it is also not necessary to introduce t_0 , it may be considered as infinite from the beginning. Introducing μ' , ψ , and η , as before, ψ and η will obey a set of coupled equations similar to (3.14)–(3.15),

$$-\beta \gamma \mathbf{v} \cdot \mathbf{E} \rho_0(\mathbf{v}) = -\gamma (\partial / \partial \mathbf{v}) \cdot (\psi(\mathbf{v}) \langle \mathbf{F} \eta \rangle), \quad (\text{C9})$$

$$(\partial \eta / \partial t) + iL\eta = \gamma \mathbf{A}(v) \cdot \mathbf{F} + \gamma \Gamma \eta - \eta / \tau. \quad (\text{C10})$$

The symbols have the same meaning here as before (though referring to one, rather than N fluid particles),

$$iL\eta(\mathbf{v}_1, \mathbf{R}_1, t) \equiv \mathbf{v}_1 \cdot \frac{\partial \eta}{\partial \mathbf{R}_1} - \omega_0^2 \mathbf{R}_1 \cdot \frac{\partial \eta}{\partial \mathbf{v}_1}, \quad (\text{C11})$$

and we need the solution of (C10) for $t = \infty$. The dissipative nature of the fluid is now lumped together schematically in the term $\tau^{-1}\eta$, i.e., it is the operator $(iL + \tau^{-1})$ which "corresponds" to the operator iL used previously. Expanding η as a power series in γ , we obtain as in (4.2), for $t = \infty$,

$$\eta_1 = -(\partial / \partial \mathbf{v}) \cdot \ln(\psi / \rho_0) \int_0^\infty ds e^{-s/\tau} \mathbf{F}(-s). \quad (\text{C12})$$

Due to the simplicity of the operator L we can find

here $\mathbf{F}(-t)$ explicitly. Indeed,

$$\begin{aligned} e^{-iLt}(\mathbf{r}_1 - \mathbf{R}) &= \mathbf{r}_1(-t) - \mathbf{R} = \mathbf{R}_1(-t) \\ &= \mathbf{R}_1 \cos \omega_0 t - \mathbf{v}_1 \omega_0^{-1} \sin \omega_0 t, \quad (\text{C13}) \\ e^{-iLt} \mathbf{v}_1 &= \mathbf{v}_1(-t) = \mathbf{v}_1 \cos \omega_0 t + \omega_0 \mathbf{R}_1 \sin \omega_0 t. \end{aligned}$$

Thus,

$$\eta_1 = -\frac{\tau \omega_0^2}{1 + \tau^2 \omega_0^2} [\mathbf{R}_1 - \tau \mathbf{v}_1] \cdot \frac{\partial}{\partial \mathbf{v}} \ln \left[\frac{\psi}{\rho_0} \right], \quad (\text{C14})$$

$$\langle \mathbf{F} \eta_1 \rangle = -\frac{\tau \omega_0^2 \beta^{-1}}{1 + \tau^2 \omega_0^2} \frac{\partial}{\partial \mathbf{v}} \ln \left[\frac{\psi}{\rho_0} \right] = -\mathfrak{D} \frac{\partial}{\partial \mathbf{v}} \ln \left[\frac{\psi}{\rho_0} \right], \quad (\text{C15})$$

$$\delta_1 \psi = \mathfrak{D} \frac{\partial}{\partial \mathbf{v}} \cdot \left[\frac{\psi}{\rho_0} \ln \left(\frac{\psi}{\rho_0} \right) \right]. \quad (\text{C16})$$

In a similar fashion we find

$$\begin{aligned} \eta_2(t) &= \frac{\omega_0^2 \tau^3}{(1 + 4\omega_0^2 \tau^2)(1 + \omega_0^2 \tau^2)} \\ &\times \{ \tau [\mathbf{v}_1 \mathbf{v}_1 - \omega_0^2 \mathbf{R}_1 \mathbf{R}_1] + \mathbf{v}_1 \mathbf{R}_1 \} : \left(\frac{\rho_0}{\psi} \right) \frac{\partial^2}{\partial \mathbf{v} \partial \mathbf{v}} \left(\frac{\psi}{\rho_0} \right). \quad (\text{C17}) \end{aligned}$$

We see here that $\langle \mathbf{F} \eta_2 \rangle$ will vanish [cf. discussion following Eq. (4.11)]. The next order contribution to the collision term will come from $\langle \mathbf{F} \eta_3 \rangle$ and will be

$$\begin{aligned} \delta_3 \psi &= \left(\frac{\tau^2 \omega_0^2}{1 + \tau^2 \omega_0^2} \right) \left(\frac{1 + 3\tau^2 \omega_0^2}{1 + 4\tau^2 \omega_0^2} \right) (\beta^2 \tau)^{-1} \\ &\times \frac{\partial^2}{\partial \mathbf{v} \partial \mathbf{v}} : \left[\rho_0 \frac{\partial^2}{\partial \mathbf{v} \partial \mathbf{v}} \left(\frac{\psi}{\rho_0} \right) \right]. \quad (\text{C18}) \end{aligned}$$

We note here that the terms in $\langle \mathbf{F} \eta_3 \rangle$ corresponding to $\mathbf{b}$ and $\mathbf{d}$ in Eq. (4.14) do not appear here because, as seen from (C13), $\partial \mathbf{F}(-t)/\partial \mathbf{R}$ is independent of $\mathbf{R}$ so that $\langle \mathbf{F} \mathbf{b} \rangle$ and $\langle \mathbf{F} \mathbf{d} \rangle$ vanish. This means that in an expansion of ψ in powers of γ , according to the method of Appendix B, $\delta_3 \psi_1$ and thus ψ_3 would be zero. The same will be true for all other ψ_l , $l > 1$. This can be verified directly for we can solve Eq. (C7) for the stationary state to terms linear in $\mathbf{E}$, without any expansion in γ ,

$$\begin{aligned} \mu = \mu_0 + \mu' = \mu_0 \left\{ 1 + \frac{1}{\tau} \int_0^\infty ds e^{-s/\tau} \left[\frac{\psi(\mathbf{v}'(-s))}{\rho_0(\mathbf{v}'(-s))} \right. \right. \\ \left. \left. + \gamma \tau \beta \mathbf{E} \cdot \mathbf{v}'(-s) \right] \right\}, \quad (\text{C19}) \end{aligned}$$

$$\psi = \int \mu' d\mathbf{v}_1 d\mathbf{r}_1 d\mathbf{R}, \quad (\text{C20})$$

where $\mathbf{v}'(-s)$ has the same meaning as $\mathbf{v}(-s)$ except that the motion now takes place under the influence of the whole Hamiltonian H , not just H_2 ; i.e., the position of the B particle is not held fixed. We find

$$\begin{aligned} \mathbf{v}'(-s) &= \mathbf{v} + \gamma m^* [(\mathbf{v}_1 - \gamma \mathbf{v})(1 - \cos \omega s) \\ &\quad - \omega \mathbf{R}_1 \sin \omega s], \quad (\text{C21}) \end{aligned}$$

where m^* is the reduced mass,

$$m^* = (1 + \gamma)^{-1} \quad (\text{since } m = 1), \quad (\text{C22})$$

and

$$\omega = \omega_0 (1 + \gamma^2)^{1/2}. \quad (\text{C23})$$

It can now be verified that

$$\psi(\mathbf{v}) = [\gamma \mathfrak{D}]^{-1} \mathbf{E} \cdot \mathbf{v} \rho_0(\mathbf{v}) = \psi_1(\mathbf{v}) \quad (\text{C24})$$

is a solution of Eqs. (C19)–(C20).

We can also work out for this model more explicitly the form of $\delta f(\mathbf{v}, t)$ for a uniform distribution in the absence of an external field,

$$\begin{aligned} \xi(t) &= \left[\frac{f(\mathbf{v}, 0)}{f(\mathbf{v}, t)} \right] e^{-t/\tau} \xi(\mathbf{v}_1(-t), \mathbf{R}_1(-t), \mathbf{v}, 0) \\ &- \gamma \left[\frac{f_0}{f} \right] \int_0^t dt_1 e^{-t_1/\tau} \mathbf{F}(-t_1) \cdot \frac{\partial}{\partial \mathbf{v}} \left[\frac{f(t-t_1)}{f_0} \right] + O(\gamma^2), \quad (\text{C25}) \end{aligned}$$

and for $t \gg \tau$, we find

$$\begin{aligned} \frac{\partial f(\mathbf{v}, t)}{\partial t} &= \gamma^2 \delta_1 f + \gamma^4 \left[\delta_3 f - \frac{(\beta^2 \tau^2)^{-1} (\omega_0^2 \tau^2)^2 (1 - \omega_0^2 \tau^2)}{(1 + \omega_0^2 \tau^2)^3} \right. \\ &\times \left. \frac{\partial}{\partial \mathbf{v}} \cdot \left\{ f_0 \frac{\partial}{\partial \mathbf{v}} \left[f_0^{-1} \frac{\partial}{\partial \mathbf{v}} \left[f_0 \frac{\partial}{\partial \mathbf{v}} \left(\frac{f}{f_0} \right) \right] \right] \right\} \right] + O(\gamma^6), \quad (\text{C26}) \end{aligned}$$

where $\delta_1 f$ and $\delta_3 f$ are given by Eqs. (C16) and (C18). The relaxation time t_r , which is the inverse of the friction constant ζ , is given in terms of τ and ω_0 ,

$$t_r = \frac{\tau}{\gamma^2} \left[\frac{\tau^2 \omega_0^2}{1 + \tau^2 \omega_0^2} \right]. \quad (\text{C27})$$

It is also possible for the model considered here, to write out more explicitly the exact equation satisfied by $f(\mathbf{v}, t)$, for an arbitrary $\mathbf{F}$,

$$\begin{aligned} \frac{\partial f(\mathbf{v}, t)}{\partial t} &= \frac{-\gamma}{\tau} \frac{\partial}{\partial \mathbf{v}} \cdot \int_0^t ds e^{-s/\tau} \int P_0(\mathbf{v}_1, \mathbf{R}_1) \mathbf{F}(\mathbf{R}_1) \\ &\times \exp \{ -\beta [v^2 - \mathbf{v}'^2(-s)] \} f(\mathbf{v}'(-s), t-s) d\mathbf{R}_1 d\mathbf{v}_1 \\ &- e^{-t/\tau} \gamma \frac{\partial}{\partial \mathbf{v}} \cdot \int \mathbf{F} \mu(\mathbf{v}_1'(-t), \mathbf{R}_1'(-t), \mathbf{v}'(-t), 0) \\ &\quad \times d\mathbf{R}_1 d\mathbf{v}_1, \quad (\text{C28}) \\ &= \gamma \frac{\partial}{\partial \mathbf{v}} \cdot \int_0^t ds e^{-s/\tau} \int \mathbf{F} \mu_0 \frac{d}{ds} \left[f(\mathbf{v}'(-s), t-s) / \right. \\ &\quad \left. f_0(\mathbf{v}'(-s)) d\mathbf{R}_1 d\mathbf{v}_1 + [\gamma e^{-t/\tau}] \right. \\ &\times \left. \left\{ \frac{\partial}{\partial \mathbf{v}} \int \mathbf{F} \mu_0 \xi(\mathbf{v}_1'(-t), \mathbf{R}_1'(-t), \mathbf{v}'(-t), 0) \right. \right. \\ &\quad \times \left. \left. \frac{f(\mathbf{v}'(-t), 0)}{f_0(\mathbf{v}'(-t))} d\mathbf{R}_1 d\mathbf{v}_1 \right\} \right], \end{aligned}$$

where the definitions of $\mathbf{v}'_1(-t)$ and $\mathbf{R}'_1(-t)$ are similar to that of $\mathbf{v}'(-t)$ given following Eq. (C19) and have the value, for $\mathbf{F}$ given in (C8),

$$\mathbf{v}'_1(-s) = \mathbf{v}_1 - m^*[(\mathbf{v}_1 - \gamma\mathbf{v})(1 - \cos\omega s) - \omega\mathbf{R}_1 \sin\omega s], \quad (\text{C29})$$

$$\mathbf{R}'_1(-s) = \mathbf{R}_1 \cos\omega s + \omega^{-1}[\gamma\mathbf{v} - \mathbf{v}_1] \sin\omega s. \quad (\text{C30})$$

When (C21), (C29), and (C30) are substituted in (C28), there results an expression for $\partial f(\mathbf{v}, t)/\partial t$ whose expansion in powers of γ for $t \gg \tau$ we have obtained in (C26).

APPENDIX D: COMPOSITE BROWNIAN PARTICLE

In this Appendix we shall consider the case in which the B particles are not simply mass points, but have some structure. For simplicity of notation we restrict ourselves to B molecules composed of two equal simple particles, “ B atoms,” having mass M , $M \gg m$ and interacting via a potential Φ . The distribution of the B molecules, assumed independent of each other, will be characterized by a distribution function f which is a function of the coordinates and velocities of both B atoms and the time t ,

$$f = f(x, t) = f(\mathbf{R}^{(1)}, \mathbf{R}^{(2)}, \mathbf{V}^{(1)}, \mathbf{V}^{(2)}, t). \quad (\text{D1})$$

The Hamiltonian of the full system will have a form similar to that given in Eq. (2.1),

$$H = H_{12} + H_t + \sum_{i=1}^N [u(\mathbf{R}_i^{(1)}) + u(\mathbf{R}_i^{(2)})], \quad (\text{D2})$$

where H_t is the same as in (2.1) and

$$H_{12} = \frac{1}{2}M\mathbf{V}^{(1)2} + \frac{1}{2}M\mathbf{V}^{(2)2} + \Phi(R^{12}), \quad (\text{D3})$$

$$\mathbf{R}_i^\alpha = \mathbf{r}_i - \mathbf{R}^\alpha, \quad \alpha = 1, 2.$$

The joint distribution μ will obey Eq. (2.2) (with $\mathbf{E} = 0$). The conditional distribution P is again defined by (2.12). However, unlike (2.13), P_0 will now depend on R^{12} ,

$$P_0 = \exp\{-\beta[H_t + U - \Psi(R^{12})]\}, \quad (\text{D4})$$

where

$$e^{-\beta\Psi} = \int e^{-\beta[H_t + U]} dy. \quad (\text{D5})$$

It is seen from (D5) that $\Psi + \Phi$ is equal to

$$(-\beta^{-1}) \ln n_2^0(R^{12}) + \text{constant},$$

where n_2^0 is the equilibrium value of the configurational distribution of the B particle. The equation for ξ and f may be written in a form analogous to (5.2) and (5.8) by letting $\mathfrak{R}$ and $\mathbf{v}$ stand for the six-dimensional position and reduced velocity vector of the B particle,

$$(\mathfrak{R}; \mathbf{v}) = (\mathbf{R}_1, \mathbf{R}_2; \mathbf{v}^{(1)}, \mathbf{v}^{(2)}), \quad (\text{D6})$$

$$\mathbf{v}^{(\alpha)} = \gamma^{-1/2} \mathbf{V}^{(\alpha)}.$$

We then have

$$\frac{\partial f(\mathfrak{R}, \mathbf{v}, t)}{\partial t} + (f, \mathcal{H}_1) = -\gamma \frac{\partial}{\partial \mathbf{v}} (f \langle \mathfrak{F} \xi \rangle), \quad (\text{D7})$$

$$\frac{\partial \xi}{\partial t} + iL\xi = \gamma \mathfrak{A} \cdot \mathfrak{F} + \gamma \Gamma \xi - \frac{\partial \ln f}{\partial t} \xi. \quad (\text{D8})$$

We have defined here an effective B -particle Hamiltonian $\mathcal{H}_1$, and an effective force $\mathfrak{F}$,

$$\mathcal{H}_1 = H_{12} + \Psi(R^{12}), \quad (\text{D9})$$

$$\mathfrak{F} = -(\partial/\partial \mathfrak{R})[U - \psi]. \quad (\text{D10})$$

The “effective” force (six-dimensional), $\mathfrak{F}$, acting on the B molecule is the direct product of the effective forces $\mathfrak{F}_1$ and $\mathfrak{F}_2$ acting on the B atoms. Proceeding now according to our method in Sec. V we obtain, to lowest order in γ , a generalized Fokker-Planck equation for f ,

$$\frac{\partial f}{\partial t} + (f, \mathcal{H}_1) = \gamma^2 \mathfrak{D}^{(6)} \cdot \frac{\partial}{\partial \mathbf{v}} \left[f \frac{\partial}{\partial \mathbf{v}} \ln \left(\frac{f}{f_0} \right) \right], \quad (\text{D11})$$

where $\mathfrak{D}^{(6)}$ is the six-dimensional tensor,

$$\mathfrak{D}^{(6)} = \lim_{t_0 \rightarrow 0} \int_0^\infty e^{-t/t_0} \langle \mathfrak{F} \mathfrak{F}(-t) \rangle dt. \quad (\text{D12})$$

In writing down the equation for f we have neglected the term coming from the initial value of ξ as we have done previously in going from (5.4) to (5.5). We are therefore assuming here, and this assumption is also made in treating $\mathbf{v}$ as being of order unity, that f changes on a time scale which is long compared to the fluid relaxation time. This may become unrealistic in cases where the internal velocities of the molecule are comparable to those of the fluid particles.

The tensor $\mathfrak{D}^{(6)}$ will generally be of the form

$$\mathfrak{D}^{(6)} = \begin{pmatrix} \mathfrak{D}_{11} & \mathfrak{D}_{12} \\ \mathfrak{D}_{12} & \mathfrak{D}_{11} \end{pmatrix}, \quad (\text{D13})$$

where $\mathfrak{D}_{\alpha\beta}$ is the three-dimensional tensor

$$\mathfrak{D}_{\alpha\beta} = \int_0^\infty \langle \mathfrak{F}_\alpha(-t) \mathfrak{F}_\beta \rangle dt$$

$$= A_{\alpha\beta}(R^{12}) \delta + B_{\alpha\beta}(R^{12}) [\mathbf{R}^{12} \mathbf{R}^{12} - \frac{1}{3}(R^{12})^2 \delta],$$

$$\alpha, \beta = 1, 2. \quad (\text{D14})$$

Here A and B are scalar functions of R^{12} .

It is possible now to introduce four relaxation times τ_i in analogy with the τ defined in Eq. (6.3). We define

the diagonal relaxation times τ_1 and τ_2 by the relations,

$$\begin{aligned} A_{11} &\equiv A_{22} = \frac{1}{3} \int_0^\infty \langle \mathfrak{F}_1(-t) \cdot \mathfrak{F}_1 \rangle dt \\ &= \frac{1}{3} \tau_1 \langle \mathfrak{F}_1 \cdot \mathfrak{F}_1 \rangle \\ &= \frac{1}{3} \tau_1 \beta^{-1} \left[\int \nabla^2 u(R_3^1) \frac{n_{(3)}^0(\mathbf{R}^1, \mathbf{R}^2, \mathbf{r}_1) d\mathbf{r}_1}{n_{(2)}^0(R^{12})} \right. \\ &\quad \left. - \nabla^2 \Psi(R^{12}) \right], \quad (\text{D15}) \end{aligned}$$

$$B_{11} = B_{22} = \frac{2}{3} \tau_2 \{ \langle \mathfrak{F}_1 \mathfrak{F}_2 \rangle - A_{11} \mathbf{1} \} : \mathbf{R}^{12} \mathbf{R}^{12} / (R^{12})^4. \quad (\text{D16})$$

τ_2 can also be expressed in terms of $n_{(3)}^0$. Relaxation times can also be assigned to the off-diagonal elements of $\mathfrak{D}_{\alpha\beta}$:

$$A_{12} = A_{21} = \frac{1}{3} \tau_3 \langle \mathfrak{F}_1 \cdot \mathfrak{F}_2 \rangle = -\frac{1}{3} (\tau_3 / \beta) \nabla^2 \Psi, \quad (\text{D17})$$

$$B_{12} = B_{21} = \frac{2}{3} \tau_4 \{ \langle \mathfrak{F}_1 \mathfrak{F}_2 \rangle - B_{12} \mathbf{1} \} : \mathbf{R}^{12} \mathbf{R}^{12} / (R^{12})^4. \quad (\text{D18})$$

Using this notation, the Fokker-Planck equation for f_2 may be expressed in terms of the τ_i 's and the equilibrium distributions $n_{(3)}^0$ and $n_{(2)}^0$.

The system we are considering might correspond to a dilute solution of heavy diatomic molecules, such as I_2 , in a gas like helium. The equation we shall obtain for f may then be suitable for discussing the dissociation rate of such molecules.²¹ Alternatively, we may consider f to represent the pair distribution function of Brownian particles in a fluid interacting with each other via a pair potential Φ . The equation obeyed by this f will be of the same form as in the first case if the density of the B particles is sufficiently low. Finally, in the Kirkwood theory, f would be the two-particle distribution in a liquid, the "host fluid" representing the influence of the other particles. Kirkwood made the further approximation of setting $\tau_3 = \tau_4 = 0$ and $\tau_1 = \tau_2 = \tau$, τ being defined by (6.3).

APPENDIX E: BROWNIAN MOTION IN A CRYSTAL

We shall discuss here the motion of a heavy particle in a crystalline lattice. This problem was investigated and solved in a very interesting series of papers by Rubin.²² Rubin considers an n -dimensional cubic crystal with nearest neighbor harmonic forces in which one particle has a mass M , which is larger than the masses of the other particles m , $m=1$. The forces between the B particle and the other particles is assumed to be the same as the force between two crystalline particles. Since this system has purely harmonic forces, the equations of motion can be solved exactly and one can

find the B -particle distribution for the case where the remainder of the lattice is initially in equilibrium. Rubin finds that in one and three dimensions the B -particle distribution f obeys a Fokker-Planck equation. In one dimension the equation is that appropriate to a free particle and in three dimensions that appropriate to a harmonically bound particle. The one-dimensional result was also obtained by Hemmer.²³ In two dimensions the situation is more complicated and somewhat paradoxical²⁴ and leads to the result that the B -particle distribution f does not obey a Fokker-Planck equation.

We will show first how the method developed in this paper for fluids can be generalized to include crystals. The formal application of our method always yields a Fokker-Planck equation for f to the lowest order in γ , $\gamma = M^{-1/2}$. In one and two dimensions this will be the equation appropriate for a free particle. In three dimensions the equation will be that appropriate to a harmonically bound particle with a restoring force equal to that found by Rubin. We shall also evaluate the friction constant in one dimension and show that it agrees with that obtained by Hemmer and Rubin. The failure of our expansion in two dimensions is not too surprising since in order to make our proofs rigorous, we would need (see Sec. V), the existence of an exponential relaxation for the light particles. This is believed correct for fluids, while for the simple crystals considered here the correlation functions decay essentially as $a(t)t^{-m/2}$, where $a(t)$ is an oscillatory function of the time (with a characteristic frequency of the crystal) and m is the dimensionality of the system.²⁵ We are currently carrying through the detailed computations for two- and three-dimensional lattices.

The main difference between the treatment of a fluid and a crystal is that in the latter there is an underlying lattice. The potential energy of the system is a function of the displacements $\mathbf{r}_i$ of each particle from its own lattice point and of the displacement $\mathbf{R}$ of the B particle from its lattice point which is not symmetric in the indexes i . Also the equilibrium distribution of the B particle $f_0(\mathbf{R}, \mathbf{V})$ is no longer independent of $\mathbf{R}$ even in the absence of an external field. This latter situation is similar to that encountered in Appendix D and the modification in the general treatment of Secs. II and VI will be similar to that done in Appendix D.

We write the Hamiltonian of the whole system in a form analogous to (D2),

$$\begin{aligned} H &= \frac{1}{2} M \mathbf{V}^2 + \sum_{i=1}^N \frac{1}{2} v_i^2 + \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) + U(\mathbf{R}, \mathbf{r}_1, \dots, \mathbf{r}_N) \\ &= H_1 + H_e + U. \quad (\text{E1}) \end{aligned}$$

The equilibrium distributions of the whole system μ_0 , of the B -particle f_0 , and the conditional distribution

²¹ T. Bak and J. L. Lebowitz, *Discussions Faraday Soc.* **33**, 189 (1962); *Phys. Rev.* **131**, 1138 (1963).

²² R. J. Rubin, *J. Math. Phys.* **2**, 373 (1961).

²³ P. C. Hemmer, *Det. Fysiske Seminar i Trondheim* **2**, (1959).

²⁴ See Sec. VC in Ref. 22.

²⁵ P. Mazur and E. W. Montroll, *J. Math. Phys.* **1**, 70 (1960).

P_0 are written as

$$\mu_0 = Z^{-1} e^{-\beta H}, \quad (\text{E2})$$

$$f_0 = \int \mu_0 d\mathbf{r}_1 \cdots d\mathbf{r}_N d\mathbf{v}_1 \cdots d\mathbf{v}_N \\ = Z^{-1} \exp\{-\beta[H_1 + \Psi(\mathbf{R})]\}, \quad (\text{E3})$$

$$P_0 = \mu_0 / f_0 = \exp\{-\beta[H_c + U - \Psi]\} \\ = \exp\{-\beta[H_2 - \Psi]\}. \quad (\text{E4})$$

Proceeding now as in Appendix D we obtain, to lowest order in γ , a Fokker-Planck (F.P.) equation for $f(\mathbf{R}, \mathbf{V}, t)$,

$$\frac{\partial f(\mathbf{R}, \mathbf{V}, t)}{\partial t} + \mathbf{V} \cdot \frac{\partial f}{\partial \mathbf{R}} + M^{-1} \mathbf{F}' \cdot \frac{\partial f}{\partial \mathbf{R}} \\ = M^{-2} \mathfrak{D} \cdot \frac{\partial}{\partial \mathbf{V}} \left[f \frac{\partial}{\partial \mathbf{V}} \ln \left(\frac{f}{f_0} \right) \right], \quad (\text{E5})$$

where

$$\mathbf{F}'(\mathbf{R}) = -\partial \Psi(\mathbf{R}) / \partial \mathbf{R} = \beta^{-1} \partial \ln f_0 / \partial \mathbf{R} \quad (\text{E6})$$

is the average force acting on the B particle, at $\mathbf{R}$, in equilibrium and $\mathfrak{D}$ is given as in (D12) by

$$\mathfrak{D} \equiv \lim_{t_0 \rightarrow \infty} \int_{t_0}^{\infty} e^{-t/t_0} \langle \mathfrak{F}(t) \mathfrak{F} \rangle dt, \quad (\text{E7})$$

with

$$\mathfrak{F} = -(\partial / \partial \mathbf{R}) [U(\mathbf{R}, \mathbf{r}_1, \cdots, \mathbf{r}_N) - \Psi(\mathbf{R})]. \quad (\text{E8})$$

$\mathfrak{F}(t)$ is to be computed as before from the evolution of the crystal under the influence of the Hamiltonian $H_2 = H_c + U$ with $\mathbf{R}$ kept as a fixed parameter. $\mathfrak{D}$ can thus depend on $\mathbf{R}$.

It is seen from (E5) that when $\mathbf{F}'$ vanishes, i.e., f_0 is independent of $\mathbf{R}$, the evolution of $f(t)$ is determined by a F.P. equation appropriate for a free particle while if f_0 is a Gaussian in $\mathbf{R}$, f obeys a F.P. equation appropriate for a harmonically bound particle. Now it has been shown by Peierls²⁶ and Montroll²⁷ that in the limit of the crystal becoming large, i.e., $N \rightarrow \infty$ (the limit in which we are interested), f_0 will be independent of $\mathbf{R}$ in one and two dimensions and will be Gaussian in three dimensions. Equation (E5) thus agrees with the results of Rubin in one and three dimensions. [The value of the force $\mathbf{F}'$ given by (E6) is correct in all cases where the F.P. equation is valid since it is determined by the requirement that $f(t)$ approach f_0 as $t \rightarrow \infty$.]

We shall now evaluate $\mathfrak{D}$ for a one-dimensional lattice with nearest neighbor forces. The displacement of the particles from their equilibrium positions will be denoted by x_i ; $i=0, \cdots, 2L+2$, and with $x_{L+1} \equiv X$, the displacement of the B particle. We shall choose the

boundary conditions to be such that the end particles are fixed, $x_0 = x_{2L+2} = 0$. (This avoids the problem of the motion of the lattice as a whole which has to be taken account of in a rather cumbersome way when periodic boundary conditions are used.) Thus, $N=2L$, and H is given by

$$H = \frac{1}{2} \sum_{j=1}^{2L+1} [1 - (M-1)\delta_{L+1,j}] v_j^2 \\ + \frac{1}{2} k \sum_{j=0}^{2L+1} (x_{j+1} - x_j)^2, \quad (\text{E9})$$

where k is the force constant and

$$x_0 = x_{2L+2} = 0, \quad (\text{E10})$$

x_{L+1} , v_{L+1} being the position and velocity of the B -particle X , V . It will be shown that

$$f_0 = \left(\frac{2\pi}{\beta} \right) \left(\frac{L+1}{2kM} \right)^{1/2} \\ \times \exp \left\{ -\frac{1}{2} \beta \left[M V^2 + \frac{2k}{(L+1)} X^2 \right] \right\}, \quad (\text{E11})$$

so that

$$\partial \Psi / \partial X = -2kX / (L+1) \quad (\text{E12})$$

and

$$\mathfrak{F} = k \{ (x_{L+2} - X) + (x_L - X) + 2X / (L+1) \}. \quad (\text{E13})$$

We have to find $\mathfrak{F}(t)$ when X is kept fixed. It is clear that keeping $x_{L+1} = X$ fixed separates the lattice into two parts of L particles each with fixed ends. Introducing the variables u_j and y_j ,

$$u_j = x_{j+(L+1)} - X \left(1 - \frac{j}{L+1} \right), \\ y_j = x_j - X \frac{j}{L+1}, \quad j=0, \cdots, L+1, \quad (\text{E14})$$

we may write H_2 , the Hamiltonian of the lattice with $x_{L+1} = X$,

$$H_2 = \left\{ \frac{1}{2} \sum_{j=1}^L \dot{y}_j^2 + \frac{1}{2} k \sum_{j=0}^L (y_{j+1} - y_j)^2 \right\} \\ + \left\{ \frac{1}{2} \sum_{j=1}^L \dot{u}_j^2 + \frac{1}{2} k \sum_{j=0}^L (u_{j+1} - u_j)^2 \right\} \\ + kX^2 / (L+1), \quad (\text{E15})$$

with the boundary conditions

$$y_0 = y_{L+1} = u_0 = u_{L+1} = 0.$$

Equation (E11) for f_0 follows immediately from (E15).

²⁶ R. Peierls, Suppl. Helv. Phys. Acta 2, 81 (1936).

²⁷ E. W. Montroll, in *Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability* (University of California Press, Berkeley, 1956), Vol. 3, p. 209.

The force $\mathfrak{F}$ will now be

$$\mathfrak{F} = k(u_1 + y_L) \quad (\text{E16})$$

and

$$\begin{aligned} \langle \mathfrak{F}(t) \mathfrak{F} \rangle &= k^2 \langle [u_1(t) + y_L(t)] [u_1 + y_L] \rangle \\ &= 2k^2 \langle u_1(t) u_1 \rangle. \end{aligned} \quad (\text{E17})$$

The second equality follows from the fact that the y 's and u 's are independent of each other. The evolution of $u_1(t)$ proceeds according to the Hamiltonian in the second curly bracket on the right-hand side of (E15).

We can evaluate (E17) by introducing the normal coordinates²⁷ η_s ,

$$u_j = \sum_{s=1}^N \eta_s \sin(\pi j s / L + 1), \quad (\text{E18})$$

which satisfy the equations

$$\ddot{\eta}_s = -4k \sin^2\left(\frac{\pi s}{L+1}\right) \eta_s = -\omega_s^2 \eta_s. \quad (\text{E19})$$

This yields, using the independence of the η_s ,

$$\begin{aligned} \langle u_1(t) u_1 \rangle &= \frac{2\beta^{-1}}{(L+1)} \sum_{s=1}^L \left[\sin^2\left(\frac{\pi s}{L+1}\right) \frac{\cos \omega_s t}{\omega_s^2} \right. \\ &\quad \left. + \sin\left(\frac{\pi s}{L+1}\right) \frac{\sin \omega_s t}{\omega_s^2} \right], \end{aligned} \quad (\text{E20})$$

$$\begin{aligned} &\xrightarrow{L \rightarrow \infty} \frac{2\beta^{-1}}{\pi k} \int_0^\pi \cos^2\left(\frac{1}{2}\Phi\right) [\cos[2\sqrt{k} + \sin(\frac{1}{2}\Phi)] \\ &\quad + \sin[2\sqrt{k} + \sin(\frac{1}{2}\Phi)]] d\Phi, \end{aligned}$$

and

$$\mathfrak{D} = 2\beta^{-1} \sqrt{k}, \quad (\text{E21})$$

which agrees with the result of Hemmer and Rubin. We note that the relaxation time τ defined in (6.3) is given here by

$$\tau = k^{-1/2}. \quad (\text{E22})$$