Bogolyubov-Born-Green–Kirkwood-Yvon equations, self-diffusion, and 1/*f* noise in a slightly nonideal gas

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The hypothesis of "molecular chaos" fails when applied to the spatially inhomogeneous evolution of a low-density gas, because this hypothesis is incompatible with a "collisional" description of the interaction of the particles. The failure of molecular chaos means that there is a statistical correlation among colliding and closely spaced particles in configuration space. This circumstance is taken into account in the collisional approximation (in the kinetic stage of the evolution) and in the limit of an infinitely small gas parameter to derive an autonomous system of coupled kinetic equations for the many-particle distribution functions of closely spaced particles from the Bogolyubov-Born-Green-Kirkwood-Yvon equations. This system of equations reduces to the Boltzmann equation only in the homogeneous case. It is used to analyze the statistics of the Brownian motion of a test gas particle. It is shown that there exist fluctuations with a $1/f$ spectrum in the diffusion coefficient and the mobility. The physical cause of these fluctuations is the randomness of the spread of particle encounters in the value of the impact parameter. This randomness makes the rate and effectiveness of collisions random.

1. INTRODUCTION

The kinetic theory of slightly nonideal gases as it exists today rests on the antiquated hypothesis of "molecular chaos," which asserts that the particles entering a collision are statistically independent and which makes it possible to reduce the exact Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) equations to the classical model Boltzmann equation.[1–3] Molecular chaos has not been proved, and it can be justified essentially only for the special case of the spatially homogeneous evolution of a gas.[2–6] In general, the molecular-chaos argument involves arbitrary assumptions. For example, it is sometimes identified with the circumstance that in a sufficiently low-density gas the colliding particles do not have an intersecting dynamic past. Generally speaking, however, as was emphasized many years ago,[4] the absence of a dynamic correlation by no means implies the absence of a statistical correlation from the standpoint of the probability laws which pertain to an ensemble of systems. It is also unjustified to identify molecular chaos with the condition that the statistical correlations decouple for particles which are infinitely far apart, since in actuality the particles arrive at a collision not from "infinity" but from a distance which is only on the order of or less than the mean free path λ_0 (in practice, molecular chaos is postulated even for distances on the order of the interaction radius $r_0 \ll \lambda_0$).

On the other hand, it is not terribly difficult to identify a factor which would cause molecular chaos to fail in the inhomogeneous, nonequilibrium case. In an inhomogeneous gas the configuration dependence of the distribution function carries statistical information not only about the instantaneous coordinates of the particles but also, indirectly, about their past diffusive displacements (since the size of the variations in the gas constitutes a natural reference scale for displacements). The displacement of each particle, on the other hand, is closely correlated with fluctuations in the rate of collisions of this particle. To the extent that these fluctuations have a temporal dimension, the displacement of each particle is thus also correlated with the given collision. The binary distribution function for the particles going into a collision is thus actually a conditional probability distribution under the condition that a mutual collision is realized in a fixed and small space-time region. Because of this circumstance alone, a given distribution function cannot in general be factored into a product of one-particle distribution functions which would furnish unconditional information about displacements and coordinates.

The question is thus the extent to which the fluctuations in the collision rate of an arbitrary particle of a gas are "long-lived." A natural source of such fluctuations is the random nature of the impact parameter in an encounter of particles (we will be using the work "encounter" to mean both an interaction event proper and simply the process in which particles come to a distance from each other comparable to the interaction radius r_0). It is totally obvious that this source of fluctuations does not reduce completely to ordinary fluctuations of the local gas density. Depending on the random distribution of encounters in the value of the impact parameter, the collision rate may vary from one time interval to another. The thermodynamic state of the gas, on the other hand, is indifferent to these variations since in any case they will not interfere with a local randomization of the gas over a finite time on the order of the mean free time τ_0. Consequently, there is no relaxation mechanism which would tend to establish a certain distribution (histogram) of values of the impact parameter, and in this sense the relaxation time (or smoothing time) of this distribution is infinitely long. Arguments of this sort show that fluctuations in the collision rate (and thus in the kinetic coefficients of the gas which are associated with this rate) are of a long-lived "flickering" nature.[7–11]

In order to deal with these fluctuations we must abandon the idea of starting off with molecular chaos; i.e., we must treat a binary distribution function of particles which are encountering each other (in the sense explained above) as an autonomous statistical characteristic of the gas which determines a local average over the ensemble of the rates of encounters and, in particular, collisions proper. According

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to the BBGKY equations, the evolution of this distribution becomes coupled with the evolution of the higher-order distribution functions for "clusters" of $n>2$ particles which encounter each other and which are close together. One might sugest that, taken together, they reflect the statistics of the distribution of encounters in the impact parameter and thus the collision rate.

In Sec. 2 we show that in the relatively crude kinetic "collisional" description of the interparticle interaction the BBGKY chain generates a separate system of evolution equations for these special distribution functions of particles which are encountering each other. The structure of these equations is such that it forbids Boltzmann molecular chaos in a spatially inhomogeneous gas. The only possibility is a weakened version of the molecular chaos hypothesis (examined in Sec. 3) which incorporates a statistical correlation of particles in configuration space.

Such a weakened hypothesis, however, is sufficient for deriving a closed (although infinite) system of kinetic equations. As is shown in Sec. 4 in the example of self-diffusion, these equations predict flicker fluctuations in the transport coefficients of a gas. This result, discussed in Sec. 5, supports the fundamental conception of $1/f$ noise which was proposed in Ref. 7 and 8.

2. COLLISIONAL APPROXIMATION

Since the BBGKY equations cannot be solved rigorously, we appeal to the idea of an asymptotic separation of the space-time scales into "collisional" and "kinetic"categories. This idea was proposed by Bogolyubov[1] and arises in a natural way in the limit of a low-density gas ($\lambda_0=\text{const}$, $\mu\equiv r_0/\lambda_0\sim\rho r_0^3\to 0$, where ρ is the average density of the gas). In other words, we assume, following Ref. 1, that in a sufficiently late stage of the evolution of the gas the many-particle distribution functions F_n are like F, in that they preserve only the slow time dependence which is characterized by the kinetic scales, $\gtrsim\tau_0=\lambda_0/v_0$ [$v_0=(T/m)^{1/2}$ is the thermal velocity]. In order to implement this approach in practice we have to specify the approximate asymptotic form in which we are seeking a solution of the BBGKY equations. For this purpose, Bogolyubov[1] introduced the asumption that all of the F_n are local (in terms of the time) functionals of the one-particle distribution function F_1. That assumption makes the hypothesis of molecular chaos unavoidable, but that hypothesis is not imposed by the original equations. The "slowness" of F_n, however, gives us a longer list of possibilities. We will accordingly discuss a less rigid formulation of the separation of scales.

To find the distribution function for clusters of closely spaced particles it is natural to express the interparticle distances $q_{ij}=q_i-q_j$ (q_i are coordinates) in units of r_0, while the position of the center of mass of a cluster as a whole, $q^{(n)}=(1/n)\Sigma_j q_j$, is expressed in units of λ_0. Putting the particle velocities in dimensionless form by dividing by the thermal scale value v_0, and putting the time in dimensionless form by dividing by the mean free time τ_0 (in accordance with the presumed slowness of the variation of the distribution function), we can write the following expression for the volume-normalized distribution functions:

$$F_n(t, q^{(n)}, q_{ij}, v_j)=v_0^{-3n}\tilde{F}_n\left(\frac{t}{\tau_0}, \frac{q^{(n)}}{\lambda_0}, \frac{q_{ij}}{r_0}, \frac{v_j}{v_0}\right). \qquad (1)$$

The separation of scales presupposes that in a certain asymptotic sense the "reduced" distribution functions of close-lying particles $\tilde{F}_n$, do not depend on the gas density ρ, i.e., do not contain the gas parameter μ as a special independent argument. Let us examine the consequences of this—still preliminary—suggestion by substituting (1) into the BBGKY equations.

To exhibit the scale value r_0 explicitly it is convenient to specify the interparticle interaction force to be $(T/r_0)f(q_{ij}/r_0)$. We can always choose r_0 and λ_0 in such a way that the relation $\lambda_0=1/\rho r_0^2$ holds. We introduce $z_n=q^{(n)}/\lambda_0$, $x_{ij}=q_{ij}/r_0$, while we retain the earlier notation for the dimensionless time, t/τ_0, and the dimensionless velocity v_j/v_0. The BBGKY equations can then be put in the following form without difficulty:

$$\left(\frac{\partial}{\partial t}+u_n\frac{\partial}{\partial z_n}+\mu^{-1}L_n'\right)\tilde{F}_n$$
$$=\sum_{j=1}^{n}\frac{\partial}{\partial v_j}\int f(x_{n+1,j})\tilde{F}_{n+1}dx_{n+1,j}dv_{n+1}\equiv J_n, \qquad (2)$$

where L_n' (which acts on the functional dependence on x_{ij} and v_j) is the Liouville operator of the relative motion and the n-particle interaction, which is found from the complete n-particle Liouville operator by eliminating the center-of-mass motion. In addition,

$$u_n\equiv\frac{1}{n}\sum_{j=1}^{n}v_j$$

is the velocity of the center of mass of the cluster.

It can be seen from (2) that, at a formal level, a strict independence of $\tilde{F}_n$ from μ would be expressed as the following requirement, which is a supplement to the original equations, (2):

$$L_n'\tilde{F}_n=0. \qquad (3)$$

This requirement would eliminate the contribution of the "fast" relative motion. The physical meaning of this requirement is easily understood: It asserts that the different dynamic states of a set of n close-lying particles which can be observed in the course of the encounters and interactions of these particles are realized at identical probabilities in the statistical ensemble. In other words, the different dynamic phases or stages of a collision (in particular, the in-states and out-states) are represented in equal proportions in the ensemble.

This statistical property is essentially a necessary expression of the "collisional" nature of the evolution of the gas and, correspondingly, of the possibility of a relatively crude description of this evolution in terms of collisions (a description in terms of collisions replaces a detailed description of the interaction geometry and of the instantaneous dynamic states by the statistics of coupled collisions, which are characterized as a whole by only the initial and final states). We would thus expect that the exact solution of the BBGKY equations would go in the direction of the asymptotic expression (3), so that requirement (3) should be thought of as more appropriate than the collisional-approximation basis which was proposed in Ref. 1 [an alternative to (3) would render the concept of collisions in applicable in

general; this would contradict elementary physical considerations].
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At the same time, we see that the equality in (3) does not hold in the strict sense, if only because the principle of separation of scales suggested above concerns only interparticle distances which are not too large, at any rate, $|q_{ij}| \ll \lambda_0$ (or, in dimensionless variables, $|x_{ij}| \ll \mu^{-1}$). We will thus move on to a more correct treatment of this separation of scales. For this purpose it is quite sufficient to understand (3) as the condition that the quantity $\mu^{-1} L_n' \tilde{F}_n$ (or the quantity $L_n' F_n$, in terms of the original dimensional variables) is small in comparison with the other terms of the n-th BBGKY equation. Furthermore, it is sufficient that (3) hold only on the average over some range of interparticle distances with a linear scale a much larger than r_0 but much smaller than λ_0. A natural choice for a, and one which is unambiguous in order of magnitude, is the average distance between neighboring particles: $a = \rho^{-1/3}$ (or, in dimensionless form, $a/r_0 = \mu^{-1/3}$).

In the limit $\mu \to 0$ this region (the "collision volume") becomes infinitely large on the scale of r_0, but it shrinks to a point at the scale of λ_0. In this case one can ignore the vanishingly small ($\lesssim a/\lambda_0 \sim \mu^{2/3}$) difference between the centers of masses of the configurations which figure on the left and right sides of (2), and we can replace the chain of variables z_n by the single common variable z: the coordinate of a physically small collision volume. Whether particles belong to the same such volume would then be taken as a measure of the closeness of the particles.

We will use a superior bar to specify this averaging, and we will denote the result of the averaging of $\tilde{F}_n$ by $A_n = \overline{\tilde{F}_n}$. By virtue of the definition of a distribution function, $A_n = A_n(t, z, v_1, \ldots, v_n)$ depends on only t, z, and the velocities v_j. It characterizes a local average density of the number of n-particle encounters. According to the discussion above, in place of (3) we then have $\overline{L_n' F_n} = 0$ in terms of the original dimensional variables or, in terms of dimensionless variables,

$$\overline{\mu^{-1} L_n' \tilde{F}_n} = 0. \tag{4}$$

Using (4), we can put Eqs. (2) in the form

$$\left(\frac{\partial}{\partial t} + u_n \nabla \right) A_n = \bar{J}_n, \tag{5}$$

where $\nabla = \partial/\partial z$, and where the limit $\mu \to 0$ is to be understood as in (4).

It is thus clear that in the general inhomogeneous case, with $\nabla A_n \neq 0$, the solution (5) cannot be written as a product of one-particle distribution functions,

$$A_n(t, z, v_1 \ldots v_n) \neq \prod_j A_1(t, z, v_j),$$

since the inertial terms $u_n \nabla A_n$ generate a statistical correlation of close-lying particles (because of their drift with respect to the density variation, together with the collision volume). As a consequence, the circumstance that particles belong to the same collision event or encounter establishes a definite statistical relationship between them. From the probabilistic point of view, of course, there is no fundamental difference between encounters and collisions proper.

We thus arrive at the conclusion that in an inhomogeneous situation the collisional approximation—by virtue of its very nature—contradicts the hypothesis of molecular chaos, since switching to a discussion in terms of collisions automatically supposes the elimination of the relative motion from the equations for the distribution functions which characterize the collision number density. As a result, even in the hydrodynamic state, the evolution of the gas is described by the infinite system of equations (5).

On the other hand, the collisional nature of the evolution does not prevent factorization of the n-particle distribution functions $F_n(t, q_1 \ldots q_n, v_1 \ldots v_n)$ if the particles are sufficiently far apart from each other. If, while taking the limit $r_0/\lambda_0 \to 0$ ($\lambda_0 = \text{const}$), we hold the interparticle distances q_{ij} fixed in units of λ_0, we find from the BBGKY equations some equations for F_n which have the factorized solution $F_n = \Pi_j F_1(t, q_j, v_j)$. In the equation for F_1, however, the binary distribution function has a different type of limit: a limit taken while q_{12} is fixed in units of r_0, i.e., $F_2|_{q_2 = q_1}$. As a result, we find the chain (5).

The switch to a common spatial variable z in (5) is of course possible only under the condition $|q^{(n)} - q^{(n+1)}| \ll 1$, where **1** is the length scale of the variation. We also need to require that the average volume of a cluster of n close-lying particles, which has a value $\lesssim na^3$, be smaller than $\mathbf{1}^3$. Each of these conditions is satisfied by an infinite margin in the limit under consideration here if the scale value **1** is specified in units of λ_0 [since we have $na^3/\mathbf{1}^3 = n\mu^2(\lambda_0/\mathbf{1})^3 \to 0$], and neither restricts the numbers of distribution functions A_n which are "tied" to a given coordinate z.

3. WEAKENED MOLECULAR CHAOS

The relations (4), which determine the collisional approximation, double as a mechanism for reducing the right sides of (2) and (5) to collisional form. In particular, with $n = 2$, Eq. (4) becomes

$$\overline{\mu^{-1} L_2' \tilde{F}_2} = a^{-3} \mu^{-1} \int\limits_{|q_{21}| < a} L_2' \tilde{F}_2 \, dq_{21} = \int\limits_{|x_{21}| < a/r_0} L_2' \tilde{F}_2 \, dx_{21} = 0,$$

or, after we take the limit $\mu \to 0$,

$$\int\limits_{|x_{21}| < \infty} \left[(v_2 - v_1) \frac{\partial}{\partial x_{21}} + f(x_{21}) \left(\frac{\partial}{\partial v_2} - \frac{\partial}{\partial v_1} \right) \right] \tilde{F}_2 \, dx_{21} = 0.$$

Hence we find from (2) the right side $\bar{J}_1 \equiv J_1$ of the first of equations (5) in the form of the integral

$$\bar{J}_1 = \int dv_2 (v_2 - v_1) \oint ds \, \tilde{F}_2$$

over an infinitely remote surface $|x_{21}| = \infty$ (with a normal vector $\mathbf{ds}$), so that $\bar{J}_1$ is determined by the particle flux going into the collision volume $|x_{21}| < \infty$ from the surrounding gas.

Depending on the sign of the scalar product $(\mathbf{v}_2 - \mathbf{v}_1)\mathbf{ds}$, the distribution function $\tilde{F}_2$ describes either the in-state or out-state of particle 2 with respect to particle 1. We denote by $A^{\text{in}}{}_2$ the values of $\lim\limits_{\mu \to 0} \tilde{F}_2$ on that part of the boundary surface $|q_{21}| \simeq a$ which corresponds to in-states. The boundary values for the out-states can then be expressed in terms of A_2^{in} with the help of the two-particle scattering matrix. The quantity $\bar{J}$ then acquires the standard form of a collision integral:

$$\left(\frac{\partial}{\partial t}+u_1\nabla\right)A_1=\int dv_2\hat{S}_{12}A_2^{in}.$$

Here $\hat{S}_{ij}$ is the ordinary "Boltzmann" collision operator for the collision of particles i and j. The action of this operator is defined by[1-3]

$$\hat{S}_{ij}\psi(v_iv_j)=|v_i-v_j|\int d^2b[\psi(v_i'v_j')-\psi(v_iv_j)],$$

where b is a two-dimensional impact-parameter vector, and v'_i and v'_j are the initial velocities which correspond to the final velocities v_i and v_j.

Correspondingly, we can use (4) to transform all of the $\bar{J}_n$ which appear in (5). Since in the limit $\mu\to 0$ the functions A_n are determined by the average of $\bar{F}_n$ over an infinite [$3(n-1)$ − dimensional] region of dimensionless interparticle distances, we are left as a result with the contribution of only the collisionless n-particle configurations. Correspondingly, only binary collisions contribute to $\bar{J}_n$: collisions between one of the n particles which figure on the left side of expression (5) and an "external" $(n+1)$st particle, which represents the rest of the gas. We therefore find a result which we could have predicted earlier:

$$\left(\frac{\partial}{\partial t}+u_n\nabla\right)A_n=\sum_{j=1}^{n}\int dv_{n+1}\hat{S}_{j,n+1}A_{n+1}^{in}, \qquad (6)$$

where A^{in}_{n+1} represents the boundary distribution function similar to A^{in}_2 which describes configurations in which the external particle is in an infinitely remote in-state with respect to the given n particles.

In order to derive a closed system of equations from (6) we need to relate the boundary distribution functions A^{in}_{1+n} on the right side to the functions on the left side. In this step—after the switch to a collisional form of the equations—we need to invoke the concept of molecular chaos. Specifically, we assume that, because of its particular role, the external $(n+1)$st particle has no velocity correlation with the other particles:

$$A_{n+1}^{in}(t,z,v_1\dots v_n|v_{n+1})=A_1(t,z,v_{n+1})A_n'(t,z,v_1\dots v_n).$$

This velocity factorization does not mean an absolute statistical independence, however, since it still allows a spatial correlation, by virtue of which the function A'_n may differ from A_n (according to the definition, A'_n is the conditional n-particle distribution under the condition that a collision with an additional particle is realized).

In its "pure" form the correlation of particles in configuration space is described by a distribution function integrated over all velocities. Since the particles in all of the configurations under consideration are infinitely close together from the standpoint of the kinetic scale value λ_0, the degree of spatial correlation must be the same in them. This assertion is expressed by the relation

$$\int A_{n+1}^{in}dv_1\dots dv_{n+1}=\int A_{n+1}\,dv_1\dots dv_{n+1},$$

which makes it possible to relate A^{in}_{1+n} to A_{n+1}. This equation essentially expresses the conservation of the number of particles in the collision processes (since A_{n+1} is an indirect characteristic of an intermediate stage of the collision). It is easy to see that the simplest form of the realtionship is described by

$$A_n'(t,z,v_1\dots v_n)=\int A_{n+1}(t,z,v_1\dots v_n,v_{n+1})dv_{n+1}\left(\int A_1(t,z,v)dv\right)^{-1}$$

or, equivalently,

$$A_{n+1}^{in}(t,z,v_1\dots v_n|v_{n+1})=\frac{A_1(t,z,v_{n+1})}{\int A_1(t,z,v)\,dv}\int A_{n+1}(t,z,v_1\dots v_n,v_{n+1})dv'_{n+1}. \qquad (7)$$

This relationship does not touch on the correlation of closely spaced particles in a cluster.

Expression (7) is a weakened version of the hypothesis of molecular chaos. It incorporates the spatial statistical correlation of the colliding particles; i.e., it asserts that they are independent only in momentum space—not in configuration space.

Along with (7), Eqs. (6) form a closed—we wish to stress this closure—chain of kinetic equations. In the uniform limit this chain permits the completely factored solution $A_n(t,v_1\dots v_n)=\Pi_jA_1(t,v_j)$ and is equivalent to the Boltzmann equation

$$\frac{\partial}{\partial t}A_1(t,v_1)=\int dv_2\,\hat{S}_{12}A_1(t,v_1)A_1(t,v_2).$$

Incidentally, this solution follows simply from the first of Eqs. (7) when we note that the condition for a mutually consistent normalization of the set of distribution functions,

$$\Omega^{-1}\int F_{n+1}\,dq_{n+1}\,dv_{n+1}=F_n$$

(Ω is the total, infinite volume of the system), can be reduced in the uniform case to the local form $\int F_{n+1}dv_{n+1}=F_n$. We then find the equality $\int A_{n+1}dv_{n+1}=A_n$ and from (7) we find

$$A_2^{in}(t,v_1|v_2)=A_1(t,v_1)A_1(t,v_2).$$

In the nonuniform case the latter relations no longer hold, since the exact global form of the mutual-consistency condition cannot be replaced by a spatially local form. The evolution of the one-particle distribution function is determined by the entire infinite chain of Eqs. (6), (7), and it becomes definitely non-Markovian, in contrast with the evolution in the Boltzmann model. Understandably, the non-Markovian nature then leads to a low-frequency temporal dispersion of the spatially nonlocal kinetic transport coefficients of the gas. In turn, this dispersion may serve as a source of information about the low-frequency fluctuations of the kinetic coefficients, as we will see below. The spatial nonuniformity of the gas is of course in no way the reason for these fluctuations (the fluctuations exist in both a uniform state and an equilibrium state)—only the means by which they are manifested in the simultaneous distribution functions of the gas because these distribution functions depend on the kinetic coefficients in a nonuniform, nonequilibrium state.

4. 1/f NOISE OF SELF-DIFFUSION

To analyze self-diffusion we need to eliminate from the kinetic equation the hydrodynamic modes which are asso-

ciated with the five integrals of motion of the system as whole. This can be done easily by taking the formal approach of Ref. 2: replacing the probability distribution of the external particle in the collision integral by an equilibrium one-particle distribution function, i.e., in our notation, replacing (7) by

$$A_{n+1}^{in}(t, z, v_1 \dots v_n | v_{n+1}) = A_0(v_{n+1}) \int A_{n+1}(t, z, v_1 \dots v_n, v'_{n+1})\, dv'_{n+1}, \quad (8)$$

where $A_0(v) \equiv (2\pi)^{-3/2}\exp(-v^2/2)$ is the equilibrium Maxwellian velocity distribution.

Physically, this replacement describes a situation in which the gas is in an equilibrium state in the macroscopic thermodynamic sense. There is simply a deviation from the statistical equilibrium with regard to some specified "test" particle and its immediate surroundings. The statistical state of the surroundings will be described by the set of distribution functions which stand on the left sides of (5) and (6). The rest of the gas serves as a heat reservoir. If the one-particle distribution function in this chain belongs to the test particle, the higher-order distribution functions will understandably correspond to a cluster of the test particle and $n-1$ other particles of the surroundings. We assign the index 1 to our test particle.

We also make use of the Green-Kubo theorem, according to which[6] the generalized diffusion coefficient $\hat{D}(\tau, \nabla)$ which figures in the general nonlocal form of the self-diffusion equation,[12]

$$\frac{\partial}{\partial t} W(t, R) = \nabla \int_0^t \hat{D}(t-\tau, \nabla) \nabla W(\tau, R)\, d\tau \quad (9)$$

($\nabla = \partial/\partial R$), for the probability density $W(t, R)$ for a displacement of an R-particle gas (over a time t) can be linked with the linear response of the distribution function of the test particle to an infinitely weak (potential) external force $f_{ex}(q_1)$ which acts on it (this force is "turned on" at an arbitrary time $t = 0$, before which the gas was in all respects at equilibrium). Specifically, it is a straightforward matter to show that the following relation holds (Sec. 1 of the Appendix):

$$\int_0^\infty dt\, e^{-pt} \int dq_1 e^{-ikq_1} \int v_1 F_1(t, q_1, v_1)\, dv_1 = T^{-1} D(p, ik)\, [p + k^2 D(p, ik)]^{-1} \tilde{f}_{ex}(k), \quad (10)$$

where $\tilde{f}_{ex}(k)$ is the Fourier transform of $f_{ex}(q_1)$ and

$$D(p, \nabla) \equiv \int_0^\infty e^{-p\tau} \hat{D}(\tau, \nabla)\, d\tau.$$

To find the response we need to add terms $m^{-1} f_{ex}(q_1) \partial F_n / \partial v_1$ to the left side of the BBGKY equations. After a transformation to the collisional asymptotic behavior, these terms take the form (in dimensionless notation $f_{ex}(z) \partial A_n / \partial v_1$ in (6). The replacement of q_1 by z in the argument of f_{ex} presupposes that the change in f_{ex} over length scales $\lesssim a$ is small and that the external force has only a slight effect on the dynamics of the collisions. These assumptions are legitimate in the limit $(a/T) f_{ex} \to 0$ and $\mu \to 0$ if, for example, the length scale of the inhomogeneity is $|k|^{-1} \gtrsim \lambda_0$. After (8) is substituted into (6), the Boltzmann collision integral on the right sides transforms into a generalized Fokker-Planck operator Λ (a "Boltzmann-Lorentz collision operator"[2])

$$\Lambda_j \psi \equiv \int dv_{n+1} \hat{S}_{j\, n+1} \psi A_0(v_{n+1}).$$

As a result we find the equations (in terms of dimensionless variables)

$$\left(\frac{\partial}{\partial t} + \frac{1}{n}\sum_{j=1}^n v_j \nabla + f_{ex}(z) \frac{\partial}{\partial v_1}\right) A_n = \sum_{j=1}^n \Lambda_j \int A_{n+1}\, dv_{n+1} \quad (11)$$

with the equilibrium initial conditions

$$A_n|_{t=0} = A_n^0 \equiv \prod_{j=1}^n A_0(v_j).$$

In principle, D can be found by analyzing the evolution of an initial deviation from equilibrium (thermal perturbation) in the absence of an external force. That approach, however, is less convenient since it requires a special consideration of the initial stage of the evolution, preceding the collisional asymptotic region.

Transforming to the linear response, we set $A_n = A_n^0 + \varphi_n$, $\varphi_n \to 0$, and we take a Fourier transform in z along with a Laplace transform in t. Denoting the Fourier transform of φ by $\tilde{\varphi}_n$, we find from (11)

$$\left(p + \frac{ik}{n}\sum_{j=1}^n v_j\right) \tilde{\varphi}_n = \sum_{j=1}^n \Lambda_j \int \tilde{\varphi}_{n+1}\, dv_{n+1} + v_1 \tilde{f}_{ex} p^{-1} A_n^0. \quad (12)$$

Since these equations cannot be solved in their general form, we will simplify the problem. First, we restrict the analysis to the first two terms in the expansion of D in the gradient in the inhomogeneity:

$$D(p, ik) = D_0(p) + (ik)^2 D_1(p) + \dots$$

Second, we choose the simplest possible model form for the operator Λ, i.e., the Einstein-Fokker-Planck diffusion operator:

$$\Lambda_j = \gamma\left(\frac{\partial}{\partial v_j} v_j + \frac{\partial^2}{\partial v_j^2}\right)$$

[we have used $\Lambda_j A_0(v_j) = 0$].

In reality, of course, an operator of this type could not be found from any interaction potential (since it corresponds formally to scattering through infinitely small angles). This circumstance, however, should not affect the qualitative side of the results, since all that is required of Λ is that it play the role of a "relaxer" which causes the velocity distribution to relax to equilibrium. This choice is convenient in that all the eigenfunctions Λ are products of $A_0(v)$ and polynomials. We know that the operator Λ corresponding to a Maxwellian interaction potential has the same property.[2] Accordingly, the calculations below can be generalized to this case. The Einstein-Fokker-Planck operator has a further advantage, however: It makes it possible to separate variables and to work with only the projections of all of the vector variables onto the wave vector of the variation, k, i.e.,

to formally reduce the problem to a one-dimensional problem (for a potential external force, the vector f_{ex} is also parallel to k). We will accordingly treat all the variables as scalars in the discussion below.

We expand the response function in the gradient of the variation:

$$\tilde{\varphi}_n = \sum_{N=0}^{\infty} (ik)^N C_n^{(N)} p^{-1} \tilde{f}_{ex}.$$

Using (10) to relate this series to the expansion of the diffusion coefficient, we find

$$D_0 = \int v_1 C_1^{(0)}\, dv_1, \quad D_1 + D_0^2/p = \int v_1 C_1^{(2)}\, dv_1 \equiv \delta_1.$$

Substituting the same series into (12), we find the system of equations

$$pC_n^{(0)} = \sum_{j=1}^{n} \Lambda_j \int C_{n+1}^{(0)}\, dv_{n+1} + v_1 A_n^0,$$

$$pC_n^{(N)} = \sum_{j=1}^{n} \Lambda_j \int C_{n+1}^{(N)}\, dv_{n+1} - C_n^{(N-1)} n^{-1} \sum_{j=1}^{n} v_j.$$

The first group of equations can be solved easily with this choice of Λ: we find

$$C_n^{(0)} = v_1 A_n^0 (p+\gamma)^{-1}, \quad D_0(p) = (p+\gamma)^{-1}. \tag{13}$$

The solution of the second group for $C_n^{(1)}$ should be sought in the form

$$C_n^{(1)} = \left(\alpha_n v_1 \sum_{j=1}^{n} v_j + \beta_n \right) A_n^0 D_0,$$

where α_n and β_n are functions of p alone. For them we find the equations

$$p\beta_n = 2\gamma\alpha_{n+1}, \quad p\alpha_n = -2\gamma\alpha_{n+1} - 1/n,$$

and then

$$\alpha_n = -\frac{1}{p} \sum_{j=n}^{\infty} \frac{1}{j} \left(-\frac{2\gamma}{p} \right)^{j-n}, \quad \alpha_n + \beta_n = -\frac{1}{pn}.$$

We now consider the functions

$$\delta_n = \int v_1 C_n^{(2)}\, dv_1 \ldots dv_n,$$

the first of which determines the unknown function D_1. Multiplying the chain of equations for C_n^2 by v_1, and integrating over all velocities, we find, after some straightforward calculations,

$$p\delta_n = -\gamma\delta_{n+1} - n^{-1}[(n+2)\alpha_n + \beta_n] D_0.$$

Substituting the expressions found above for α_n and β_n into this equation, we find δ_1 in the form of a repeating sum:

$$D_1 + \frac{D_0^2}{p} = \frac{D_0}{p^2} \sum_{n=1}^{\infty} (-X)^{n-1} \left[\frac{1}{n^2} + \frac{n+1}{n} \sum_{j=n}^{\infty} \frac{1}{j} (-2X)^{j-n} \right],$$

where $X \equiv \gamma/\rho$. Using the identity

$$n^{-1} X^{n-1} = X^{-1} \int_0^X y^{n-1}\, dy,$$

we can transform the series over n into a form which can easily be summed. We find as a result

$$D_1 + \frac{D_0^2}{p} = \frac{D_0}{p^2 X} \int_0^X \sum_{n=1}^{\infty} (-y)^{n-1} \left[\frac{1}{n} + \frac{n+1}{n} \sum_{j=n}^{\infty} (-2y)^{j-n} \right] dy$$

$$= \frac{D_0}{p\gamma} \int_0^{\gamma/p} \left\{ \frac{\ln(1+y)}{y} + \frac{1}{1+2y} \left[\frac{\ln(1+y)}{y} + \frac{1}{1+y} \right] \right\} dy. \tag{14}$$

We have gone into the details of the calculations to demonstrate the general characteristic structure of the p dependence of the response; this structure would be the same for another choice of the operator Λ. Let us examine the behavior of the diffusion coefficient at low frequencies, i.e., the functional dependence at $|p| \ll \gamma$. From (13) and (14) we find $D_0 = 1/\gamma$ and

$$D(p, ik) \approx D_0 \left[1 + (ik)^2 \frac{D_0}{2p} \left(\ln^2 \frac{\gamma}{p} + c \right) + \ldots \right], \tag{15}$$

where c is a numerical constant, in this limit. Switching to the dimensional notation, we must evidently set $D_0 = v_0^2 \tau_0/\gamma = (T/m)\tau_m$ and replace γ by $\gamma/\tau_0 \equiv 1/\tau_m$ in the argument of the logarithm, where τ_m is a momentum relaxation time.

We turn now to the statistical characteristics of the diffusive ("Brownian") motion of the test particle, which is described by the diffusion equation (9). Knowing the first N terms of the expansion of the diffusion coefficient $D(p, ik)$ in ik, we can in principle find the first $N+2$ moments of the displacement:

$$M_n(t) = \int R^n W(t, R)\, dR.$$

From (9) we have

$$\int_0^{\infty} M_2(t) e^{-pt}\, dt = \frac{2}{p^2} D_0(p),$$

$$\int_0^{\infty} M_4(t) e^{-pt}\, dt = \frac{24}{p^2} \left[D_1(p) + \frac{D_0^2(p)}{p} \right].$$

Now taking the inverse Laplace transform for long time intervals $t \gg \tau_m$, and using (14) and (15), we find $M_2(t) \approx 2D_0 t$ ($D_0 \equiv T\tau_m/m$) and

$$M_4(t) \approx 3M_2^2(t) + 6D_0^2 t^2 \left[\ln^2 \frac{t}{\tau_m} + c' \ln \frac{t}{\tau_m} + c'' \right], \tag{16}$$

where c' and c'' are numerical constants [which are determined by the inverse transform of $D_1(p)$].

Let us compare this result with that which we would have derived under the canonical hypothesis of molecular chaos, i.e., from the inhomogeneous Boltzmann-Lorentz equation. In this case we would have had a single closed equation

$$(p + ikv_1)\tilde{\Phi}_1 = \Lambda_1 \tilde{\Phi}_1 + v_1 \tilde{f}_{ex} p^{-1} A_0(v_1)$$

in place of (12). It then follows that for an arbitrary operator Λ we ultimately have the asymptotic behavior $M_2(t) \approx 2D_0 t$ and

$$M_4(t) \approx 3M_2^2(t) + \text{const}\, \lambda_0^2 D_0 t. \tag{17}$$

If Λ is chosen in the form of an Einstein-Fokker-Planck operator we find const = 0, and the value of D_0 [which can be defined as the limit of the ratio of $M_2(t)/2t$ at $t \gg \tau_m$]—i.e., the diffusion coefficient of the text particle—is the same as that found above.

The second term on the right sides of (16) and (17) is the fourth cumulant of the displacement, $\varkappa_4(t) \equiv M_4(t) - 3M_2^2(t)$. It is, as we know, a measure of the "non Gaussianness" of the displacement. In particular, it shows how substantially the (random) diffusion coefficient $\tilde{D}$ measured from a single realization of the displacement can differ from D_0, which characterizes the average over the ensemble of realizations.[7-9] The asymptotic expression (17), $\varkappa_4(t) \propto t$, derived in the "Boltzmann" model of self-diffusion, means that the random walk of the test particle is described completely by the one statistical parameter D_0.

This is no longer the case, however, if we have $\varkappa_3(t) \propto t^\gamma$, where $\gamma > 1$. An asymptotic expression of this type means that it is no longer possible to pack the time evolution of an arbitrary typical realization in a single parameter D_0. It is not difficult to verify that this asymptotic behavior is statistically equivalent to the existence of flicker fluctuations of the diffusion coefficient with an $\omega^{-(\gamma-1)}$ low-frequency spectrum (Refs. 7–11).

In the model under consideration here, in contrast with the Boltzmann model, we arrive at specifically this sort of situation, since we have $\varkappa_4(t) \propto t^2 \ln^2(t/\tau_m)$ by virtue of (16). It can be described [if we ignore the relatively small terms proportional to t in $\varkappa_4(t)$] over a fairly coarse time scale as a Gaussian random walk with a random diffusion coefficient $\tilde{D} = \tilde{D}(t)$. Taking $\tilde{D}$ as referring to the entire interval over which the characteristic is observed, we find

$$W(t, R) = \langle (4\pi t\tilde{D}(t))^{-1/2} \exp[-R^2/4t\tilde{D}(t)] \rangle$$

for the corresponding "doubly random" process and thus

$$M_2(t) = \langle 2t\tilde{D}(t) \rangle, \; M_4(t) = 3\langle (2t\tilde{D}(t))^2 \rangle,$$

where the angle brackets mean an average over the ensemble of realizations, and $\langle \tilde{D} \rangle = D_0$. Correspondingly, interpreting the asymptotic expression (16) in terms of the spectral density $S_D(\omega)$ of fluctuations of the diffusion coefficient, we find, for $\omega\tau_m \ll 1$ (see the Appendix),

$$D_0^{-2} S_D(\omega) \approx \frac{\pi}{\omega} \ln \frac{1}{\omega\tau_m}. \tag{18}$$

The "diffusion rate" is thus a random process with a $1/f$ spectrum. Let us discuss this result.

A measurement of the spectrum of fluctuations in a diffusion coefficient is nothing but a measurement of the equilibrium average value of a certain fourth-degree power-law functional of the particle velocity. An experiment of this type is not merely a thought experiment; it has been carried out (see the bibliography in Refs. 7 and 8). However, it is vastly simpler to represent a measurement of an ordinary quadratic spectrum of fluctuations in a drift velocity under the influence of an external force, i.e., fluctuations in mobility. Natural considerations suggest that these fluctuations should, at least at sufficiently low frequencies, be a statistical copy of the fluctuations in the diffusion coefficient. In Sec. 3 of the Appendix we prove that this is indeed the case for the system under consideration here (an "Einstein relation for fluctuations" holds).

From the standpoint of a fundamental experimental test of the theory it is interesting to extend the theory to a two-component or multicomponent gas, in particular, a weakly ionized gas. It can be shown that the spectrum of fluctuations in the diffusion coefficient for the particles of one of the components in a mixture as the generalized flicker form $\propto \omega^{-\alpha}$, where the exponent has a value in the interval $1 \leqslant \alpha < 2$, depending on the ratio of the masses and momentum relaxation times. Consequently, and in contrast with the fluctuation mechanism, a spectrum of the type in (18) is not a universal spectrum and shares this status with the spectrum $\propto \omega^{-1}[\ln(1/\omega\tau_0)]^{-2}$ found in the phenomenological theory[1)] (Refs. 7, 9, and 11).

The spectrum (18), like the asymptotic expression (16), provides evidence that the fluctuations in the diffusion coefficient and the mobility are of a statistically time-dependent and nonergodic nature. This statement means that in a determination of these quantities from a specific realization of the motion of a particle the mean square deviation (in the sense of an average over the ensemble of realizations) of the result does not decrease but instead increases with increasing length of the observation. The probabilistic aspects of such a behavior were studied in Refs. 9 and 11. It is important to emphasize here that this statistical time variation bears no relation to any thermodynamic time variation since relations (15) and (16) refer to a gas in thermodynamic equilibrium. The time variation is manifested only in the form of the dependence on the duration of the observation of the test particle—in absolutely no way in the dependence on the time at which the observation begins. It would be useful to keep in mind this possibility in principle of time-varying fluctuations in kinetic coefficients in a thermodynamically steady-state or equilibrium system while interpreting experiments.

5. CONCLUSION

The $1/f$ self-diffusion noise found here is a property of an infinitely low-density gas. In other words, by virtue of its nature the noise mechanism is independent of the gas density and is not related to any dynamic multiparticle correlations (through repeated collisions, for example). Fluctuations in the rate and effectiveness of the collisions of any gas particle with other particles due to the random nature of the geometric factors in the encounter of the particles is a unique source of noise of this type. If this source of randomness is to be converted into the mechanism for a specifically $1/f$ noise, the system would have to forget the number and rate of various types of collisions of the given particle in the past.[9-11] More rigorously, the loss of memory about the past implies the property of a mixing of the paths traced out by the system in the complete $6N$-dimensional phase space. For a gas, this property has already been proved by Krylov.[4] In the same paper, Krylov essentially showed that in general it is specifically because of mixing that the time-average frequency at which certain events are repeated on a specific phase path does not necessarily have to be the same as the average value over the ensemble of paths, no matter how long the averaging time. A paradoxical point is that although a random behavior of this sort results from a loss of memory it can be described by just those statistical correlations which are infi-

nitely long-lived.

In the derivation of kinetic equations, however, some assumption or other is always made in order to replace the actual random rate of elementary kinetic events by some value which is an average over the ensemble of paths. In particular, in the derivation of the Boltzmann equation this role was essentially assigned to molecular chaos (Refs. 9 and 10; see also Ref. 4). This decisive hypothesis is thus incorporated even in the "zeroth" approximation, of an infinitely low-density gas. When repeated collisions and various types of many-particle "ring" processes in a gas with a finite μ are subsequently taken into account, the chaos will of course be disrupted. As a result, we know that fluctuations will appear in the kinetic coefficients with characteristic hydrodynamic scales and spectra. However, the source of low-frequency fluctuations pointed out above will be lost.

In this paper we have attempted to analyze as rigorously as possible specifically the zeroth approximation from the standpoint of the overall spatially inhomogeneous situation. A generalization of the classical Boltzmann equation to the inhomogeneous case through a mechanical assignment of a drift term has attracted critical comments several times in the past (see Ref. 5, for example). The infinite chain of kinetic equations found is nothing but the inhomogeneous formulation of the Boltzmann equation which is rigorous in principle (formulated in accordance with the concept of collisions).

We would also like to take note of the relationship between the kinetic model which has been constructed and the formally exact generalized, temporally nonlocal (non-Markovian) kinetic equation for the one-particle distribution function which is derived by the method of projection operators.[6] Balescu[6] has shown that the assumption of analyticity (that it is legitimate to expand a Laplace transform in a series) of the operator kernel of this equation reduces it to a Boltzmann equation in the limit of an infinitely low-density gas. Accordingly, if the latter is incorrect the problem must lie in a nonanalytic nature of the kernel. An asymptotic expression of the type in (15) indicates that this is indeed the state of affairs. Consequently, the model which has been constructed agrees with the abstract theory of Ref. 6.

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APPENDIX

1. The application at $t=0$ of the force field $f_{ex}(r) = -dU(r)/\partial r$, which acts on the test particle, is described by the Hamiltonian

$$H(t)=H_0+U(q_1)\theta(t)=H_0+\sum_k \frac{ik\tilde{f}_{ex}(k)}{k^2\Omega}e^{ikq_1}\theta(t)$$
$$\equiv H_0-\sum_k X_k(t)Q_k,$$

where $\theta(t)$ is the step function, H_0 is the Hamiltonian of the gas, and $Q_k \equiv e^{ikq_1}$ and $X_k(t) \equiv -[ik\tilde{f}_{ex}(k)]k^{-2}\Omega^{-1}\theta(t)$ play the standard roles of generalized macroscopic variables and the conjugate external dynamic forces. Let us consider the "fluxes"

$$J_k \equiv \frac{d}{dt}Q_k = ikv_1 e^{ikq_1},$$

where v_1 is the velocity of the text particle. According to the exact Green-Kubo equations (the fluctuation-dissipation relations), to first order in the forces we have

$$\langle J_k(t)\rangle = \frac{1}{T}\sum_{k'}\int_{-\infty}^{t}\langle J_k(t), J_{k'}(t')\rangle_0 X_{k'}(t')\,dt',$$

where $\langle\ldots\rangle_0$ means an average over the equilibrium ensemble of phase paths of the system (which corresponds to the original, equilibrium Gibbs ensemble of inital states), and $\langle\ldots\rangle$ means a nonequilibrium average. In our case, taking account of the homogeneity and isotropy of the equilibrium state of the gas, we find, for $t=0$.

$$\int v_1 e^{-ikq_1}F_1(t,q_1,v_1)\frac{dq_1}{\Omega}dv_1 \equiv \langle v_1(t)e^{-ikq_1(t)}\rangle$$
$$=\frac{1}{T}\int_0^t \langle v_1(t)\exp\{-ik[q_1(t)-q_1(t')]\}v_1(t')\rangle_0\,dt'\,\tilde{f}_{ex}(k)\Omega^{-1}. \quad (A1)$$

The probability distribution of the displacement of a test particle which is undergoing a random walk in an equilibrium gas is given by

$$W(t-t_0,R)=\langle\delta(q_1(t)-q_1(t_0)-R)\rangle.$$

We apply the differential operator $\partial^2/\partial t\partial t_0$ to it; then seting $t_0=0$, we take Laplace transforms in t and Fourier transforms in R. Using $\langle v_1\rangle_0=0$, we find

$$p[p\tilde{W}(p,ik)-1]=-k\int_0^\infty dt\,e^{-pt}\langle v_1(t)$$
$$\times\exp\{-ik[q_1(t)-q_1(0)]\}v_1(0)\rangle_0 k, \quad (A2)$$

where $\tilde{W}(p,ik)$ is the transform of probability density $W(t,R)$. For it we find from (9) the identity

$$p\tilde{W}(p,ik)-1=-kD(p,ik)k\tilde{W}(p,ik),$$

which, combined with (A2), gives us

$$D(p,ik)[p+kD(p,ik)k]^{-1}$$
$$=\frac{1}{p}\int_0^\infty dt\,e^{-pt}\langle v_1(t)\exp\{-ik[q_1(t)-q_1(0)]\}v_1(0)\rangle_0. \quad (A3)$$

Now taking Laplace transforms in (A1) and comparing the result with (A3), we find Eq. (10).

We thus see that by applying a spatially nonuniform force to a test particle of a gas we can in principle extract from the linear response not only the self-diffusion coefficient $D(p,0)$ but also the entire probability law for self-diffusion.

2. The asymptotic expression found for $\varkappa_4(t)$ indicates a time-dependent behavior of the fluctuations in a diffusion coefficient which is measured from an observation of a single realization of the motion of a test particle. In other words, it indicates that the results of the observation cannot be averaged over time. Accordingly, $\tilde{D}(t)$ should be treated as a time-dependent random process. Since at $t \lesssim \tau_m$ we have $M_{2n}(t) \propto t^{2n}$, this process begins at a zero value, $\tilde{D}(0)=0$. The spectrum for a process of this sort is known to be determined in terms of a structure function:

$$\langle(\bar{D}(t)-\bar{D}(0))^2\rangle=2\int_0^\infty(1-\cos\omega t)S_D(\omega)\frac{d\omega}{2\pi}.$$

For $t\gg\tau_m$ we find from this expression, (16), and the expression for $M_4(t)$, after differentiating with respect to t,

$$\frac{1}{\pi}\int_0^\infty\sin\omega t\omega S_D(\omega)\,d\omega=\frac{d}{dt}(M_4(t)/12t^2)\approx D_0^2t^{-1}\ln\frac{t}{\tau_m}.$$

The spectrum (18) follows immediately.

3. Let us assume that a constant force f is turned on at the time $t=0$. This force acts on the test particle and does not depend on the spatial position of the particle, q_1. We denote by $W(t, R; f)$ the distribution of the subsequent displacement $R(t)\equiv q_1(t)-q_1(0)$. According to the fluctuation-dissipation relations[2)] we have

$$W(t, R; f)\exp(-fR/T)=W(t, -R; f). \tag{A4}$$

It is not difficult to rewrite this exact equality in the form (for brevity, we omit the arguments t and f)

$$W(R)-W(-R)=\operatorname{th}\frac{fR}{2T}[W(R)+W(-R)]. \tag{A5}$$

Multiplying (A5) by R, and integrating over R, we find a corollary of (A4):

$$\langle R(t)\rangle=\left\langle R(t)\operatorname{th}\frac{fR(t)}{2T}\right\rangle. \tag{A6}$$

We now take the third derivative of (A6) with respect to the force at the point $f=0$:

$$\frac{\partial^3}{\partial f^3}\langle R(t)\rangle|_{f=0}=\frac{3}{2T}\frac{\partial^2}{\partial f^2}\langle R^2(t)\rangle|_{f=0}-\frac{1}{4T^3}\langle R^4(t)\rangle_0. \tag{A7}$$

Let us discuss this general relation as it pertains to our system. The average displacement

$$\langle R(t)\rangle=\int_0^t\langle v_1(t')\rangle dt'$$

under the influence of a coordinate-independent force $f_{ex}=f=\text{const}$ is determined by the homogeneous solution of Eqs. (11). In the homogeneous case, however, they evidently reduce to the ordinary Boltzmann-Lorentz equation. We can thus assert that the average drift velocity $\langle v_1(t)\rangle$ reaches saturation at $t\gtrsim\tau_m$. Consequently, the left side of (A7) increases linearly with the time. The last term in (A7), however, which contains the fourth moment of the equilibrium displacement, $\langle R^4(t)\rangle_0=M_4(t)$, increases far more rapidly according to (16). Accordingly, to within a relatively small increment this term is the same as the first term on the right. As a result we find from (A6) and (A7), in the lower orders in the force,

$$\langle R(t)\rangle=\frac{f}{2T}M_2(t)\approx\frac{D_0}{T}ft,$$

$$\langle R^2(t)\rangle\approx M_2(t)+\frac{f^2}{12T^2}M_4(t)\approx 2D_0t+\frac{f^2t^2}{T^2}\langle\bar{D}^2(t)\rangle. \tag{A8}$$

On the other hand, we can write

$$\langle R(t)\rangle=t\langle\mu(t)\rangle f,\quad \langle R^2(t)\rangle=M_2(t)+t^2\langle\mu^2(t)\rangle f^2,$$

where $\mu(t)$ is the mobility referred to the entire observation interval as a whole.

A comparison with (A8) shows that the Einstein relation between the diffusion coefficient and the mobility holds not only in the ordinary sense (for quantities averaged over the ensemble of realizations) but also for their fluctuations. Correspondingly, (18) simultaneously refers to relative fluctuations of the (linear) mobility. A similar circumstance, concerning the spectral intensity of electrical noise and conductivity, has been confirmed experimentally in the Voss-Clark experiment.[8]

[1)] The model of Ref. 7 is based to a large extent on the restrictive assumption of an asymptotic "decay of correrlations," which presupposes that the spectrum $S_D(\omega)$ is a steady (intergrable) spectrum. This restriction is not physically necessary,[9] in contradiction of the original assumption in Ref. 7.

[2)] See, for example, Ref. 13 and the corresponding use of the fluctuation-dissipation relations in Ref. 8.

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