BBGKY EQUATIONS, SELF-DIFFUSION AND 1/F NOISE IN A SLIGHTLY NONIDEAL GAS

YURIY E. KUZOVLEV

Abstract. The hypothesis of “molecular chaos” is shown to fail when applied to spatially inhomogeneous evolution of a low-density gas, because this hypothesis is incompatible with reduction of interactions of gas particles to “collisions”. The failure of molecular chaos means existence of statistical correlations between colliding and closely spaced particles in configuration space. If this fact is taken into account, then in the collisional approximation (in the kinetic stage of gas evolution) in the limit of infinitely small gas parameter the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of equations yields an autonomous system of kinetic equations for the many-particle distribution functions of closely spaced particles. This system of equations can produce the Boltzmann equation only in the homogeneous case. It is used to analyze statistical properties of Brownian motion of a test gas particle. The analysis shows that there exist fluctuations with a 1/f spectrum in the diffusivity and mobility of any particle. The physical cause of these fluctuations is randomness of distribution of particles’ encounters over the impact parameter values and, consequently, randomness of the rate and efficiency of collisions.

In essence, this is reprint of the like author’s paper published in Russian in [Zh. Eksp. Teor. Fiz. 94 (12), 140-156 (Dec. 1988)] and translated into English in [Sov. Phys. JETP 67 (12), 2469-2477 (Dec. 1988)] twenty years ago but seemingly still unknown to those to whom it might be very useful. The footnotes contain presently added comments.

1. INTRODUCTION

The today’s kinetic theory of weakly nonideal gases as before 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, 2, 3]. Meanwhile, the molecular chaos never has been proved and, in fact, can be justified only for the special case of spatially homogeneous gas evolution [2, 3, 4, 5, 6]. As for the general case, any reasonings in favor of the molecular chaos involve

2000 Mathematics Subject Classification. 37A60, 76R50, 82C22, 82C40, 82C41.
Key words and phrases. BBGKY equations, molecular random walks, self-diffusion, Brownian motion, 1/f diffusivity and mobility fluctuations, 1/f-noise, kinetic theory of fluids, dynamical foundations of kinetics.
other arbitrary assumptions. For example, it is sometimes identified with those facts that in a sufficiently low-density gas the colliding particles do not have an intersecting dynamic past. However, as was emphasized many years ago [4], generally the absence of dynamic correlations by no means implies the absence of statistical correlations from the standpoint of the probability laws which pertain to an ensemble of dynamic systems. It is also incorrect to identify molecular chaos with the decoupling of statistical correlations for infinitely far spaced particles, since in actuality the particles arrive at a collision not from infinity but from a distance which is only on the order or less than the mean free path $\lambda_0$ (moreover, in practice, molecular chaos is being postulated even for distances on the order of the interaction radius $r_0 \ll \lambda_0$).

On the other hand, it is not difficult to indicate why the molecular chaos can fail in inhomogeneous non-equilibrium situations. Notice that, first, in spatially inhomogeneous gas configurational (spatial) dependencies of distribution functions (DF) carry statistical information not only about the instantaneous coordinates of gas particles but also, indirectly, about their past diffusive displacements, or “Brownian paths” (since the non-homogeneity constitutes a natural reference scale for the displacements). Second, the displacement of each particle is closely correlated with fluctuations in the rate of collisions of this particle and consequently is correlated, to the extent of duration of these fluctuations, with next collisions. Therefore the pair (two-particle) DF for pre-colliding particles (i.e. particles going into mutual collision) actually represents a conditional probability distribution under the conditions that a new collision realizes

---

1Another example of the arbitrary assumptions is replacement of the BBGKY hierarchy by so called “hard sphere BBGKY hierarchy” which has no substantiation but was exploited in the Lanford’s attempt to substantiate the Boltzmann equation (although for absurdly small evolution time only) [O.E.Lanford, “Time evolution of large classical systems”, in “Dynamical systems, theory and applications”, ed. J.Moser, Lectures Notes in Physics, vol.38, 1975; “On a derivation of Boltzmann equation”, in “Nonlinear phenomena. 1. The Boltzmann equation”, eds. J.L.Lebowitz, E.W.Montroll, N.-H., Amsterdam, 1983; H.Spohn,“Theory of fluctuations and Boltzmann equation”, ibid.]. In fact, the “hard sphere BBGKY hierarchy” is a “hand-made” probabilistic model which does not follow from the Liouville equation even in the limit of infinitely hard repulsion. The present paper helps to comprehend why it is so (for detail, see [Yu.Kuzovlev, “On Brownian motion in ideal gas and related principles”, arXiv: 0806.4157] and footnotes below).
and it takes place in a given small space-time region. Even because of this circumstance alone, generally the mentioned DF can not be factored into the product of one-particle DF which would furnish only unconditional information about the coordinates and displacements.

The question thus is the extent to which the fluctuations in the collision rate of an arbitrary gas particle are “long-living”. A natural source of these fluctuations is the randomness of the impact parameter in an encounter of two particles (we will be using the word “encounter” to mean both a factual interaction of particles and their mere passing at a relative distance comparable with the interaction radius \( r_0 \)). It is quite obvious that this source does not reduce completely to the ordinary local gas density fluctuations. Being dependent on a random distribution of the particles’ encounters over values of the impact parameter, the actual rate of collisions of any given particle can randomly vary from one time interval to another. But, at the same time, a thermodynamic state of the gas is indifferent to these variations, since anyway they do not interfere with a local thermalization of the gas during time on order of the mean free path time \( \tau_0 \). Consequently, there are no relaxation mechanisms which would tend to establish some certain distribution (histogram) of the impact parameter values, and in this sense the relaxation time (or smoothing time) of this distribution is infinitely long. Such the reasonings show that fluctuations in the collision rate (and thus in the gas kinetic coefficients associated with this rate) are of a long-living “flicker” nature \[7, 11, 9, 10, 11\].

To deal with these fluctuations we must abandon \textit{a priori} molecular chaos, i.e. treat the pair DF, for particles which are encountering one another (in the sense explained above), as an autonomous statistical characteristics of gas evolution, which represents a local ensemble-average rate of encounters and thus rate of collisions proper. According to the BBGKY equations, the evolution of this DF is coupled with evolution of the higher-order DF for “clusters” of \( n > 2 \) relatively close encountering particles.
One might suggest that, taken together, they represent temporal statistics of impact parameters of particles’ encounters and thus statistics of the rate of collisions.

In Sec. 2 we will show that in the framework of the coarsened “collisional” (kinetic) description of the particles’ interaction the BBGKY hierarchy generates a separate system of evolution equations for just mentioned special DF of particles under mutual encounters. At that, the structure of these equations is such that in spatially inhomogeneous case it forbids Boltzmann’s molecular chaos. The only possibility in general is a weakened version of the molecular chaos hypothesis (examined in Sec. 3) which incorporates the inter-particle statistical correlations 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 by the example of self-diffusion, these equations predict flicker (1/f) fluctuations in the transport coefficients of a gas. This result, discussed in Sec. 5, supports the fundamental conception of 1/f noise which was first proposed in [7, 8].

2. Collisional approximation

Since the BBGKY hierarchy can not be solved rigorously, we naturally appeal to the idea, which was suggested by Bogolyubov in [1], about possibility of asymptotic separation of “collisional” and “kinetic” space-time scales in the low-density limit ($\lambda_0 = \text{const.}$, $\mu \equiv r_0/\lambda_0 \sim \rho r_0^3 \to 0$, where $\rho$ is mean gas density). In other words, following [1], let us assume that at a sufficiently late stage of the gas evolution all many-particle DF $F_n$ possess, along with $F_1$, only slow time dependence characterized by “kinetic” time scales $\tau_0 = \lambda_0/v_0$ ($v_0 = \sqrt{T/m}$ is thermal velocity). In order to implement this idea into practice we have to specify the approximate asymptotic form in which we are seeking a solution of the BBGKY equations. For this purpose, Bogolyubov in [1] introduced the assumption that all of the DF $F_n$ are local, in respect to time, functionals of the one-particle DF $F_1$. That assumption makes a use
of the molecular chaos hypothesis unavoidable, although the BBGKY equations by themselves in no way impose this hypothesis. The “slowness” of \( F_n \), however, gives a longer list of possibilities. We will accordingly discuss a less rigid formulation of the separation of scales.

To consider DF for closely spaced particles, it is natural to express the inter-particle 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, \( q^{(n)} = (1/n) \sum_{j=1}^{n} q_j \), in units of \( \lambda_0 \). Putting the particle velocities in dimensionless form by dividing by thermal velocity scale \( v_0 \), and putting the time in dimensionless form by the mean free time \( \tau_0 \) (in accordance with the presumed slowness of changes of DF), we can write the following expression for the volume-normalized DF:

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

(2.1)

The separation of scales presupposes that in a certain asymptotic sense the “reduced” DF of close-lying particles, \( \tilde{F}_n \), do not depend on the gas density \( \rho \), i.e. do not contain the gas parameter \( \mu = \rho r_0^3 \) as a special independent argument. Let us examine the consequences of this - still preliminary - suggestion by substituting (2.1) into the BBGKY equations.

To exhibit the scale \( r_0 \) explicitly, it is convenient to specify the inter-particle interaction force to be \( (T/r_0) f(q_{ij}/r_0) \). At that, we can always choose \( r_0 \) and \( \lambda_0 \) in such a way that the relation \( \lambda_0 = 1/\rho r_0^2 \) holds. Let us introduce the designations \( z_n = q^{(n)}/\lambda_0 \) and \( x_{ij} = q_{ij}/r_0 \), while retaining the old notations \( t \) and \( v_j \) for new dimensionless time \( t/\tau_0 \) and velocities \( v_j/v_0 \). The BBGKY equations can then be easy put in the following form:

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

(2.2)

where operator \( L'_n \) (which acts on the functional dependence on \( x_{ij} \) and \( v_j \) only) is the Liouville operator of the relative motion and interaction of \( n \) particles, which
results from the complete $n$-particle Liouville operator by eliminating the center-of-mass motion, and

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

is the center-of-mass velocity.

It is seen from equations (2.2) that formally strict independence of $\tilde{F}_n$ on $\mu$ would imply a supplement to the equations in the form of the requirement

$$L'_n \tilde{F}_n = 0,$$  \hspace{1cm} (2.3)

which just excludes contributions of “fast” relative interactive motion of particles. The physical meaning of this requirement is easy understandable. It asserts that different dynamical states, which realize in the course of an encounter of $n$ particles on the same phase trajectory in $n$-particle phase space, have the same probability in the statistical ensemble under consideration. In other words, different dynamic stages of the same collision (in particular, in- and out-states) are represented by the statistical ensemble with equal weights.

In essence, this statistical property is obligatory attribute of such a gas evolution which allows coarsened description in terms of collisions (when details of geometry and time history of the interaction process are replaced by indication of only input and output of a momentary “collision”). Therefore we can expect that exact solution of the BBGKY hierarchy asymptotically satisfies the requirement (2.3), and thus (2.3) should be thought of as more adequate basis of the collisional approximation than that proposed in [1] (indeed, the alternative to (2.3) would be unfitness of the concept of collision at all, which would contradict the elementary physical logics).

At the same time, undoubtedly, the equality (2.3) never holds in literal rigorous sense, at least because the presupposed scale separation concerns only not too long inter-particle distances, at any case $|q_{ij}| \ll \lambda_0$ ($|x_{ij}| \ll \mu^{-1}$). We will thus move on to a more correct treatment of the separation. For this purpose it is quite sufficient
to understand (2.3) as the condition that the quantity \( \mu^{-1} L'_n \tilde{F}_n \) (or \( L'_n F_n \) in the original dimensional form) is small in comparison with the other terms of the \( n \)-th BBGKY equation. Furthermore, it is sufficient if (2.3) holds only on the average over some region in the space \( q_{ij} \) with a linear size \( a \) much larger than \( r_0 \) but much smaller than \( \lambda_0 \). A natural (and unambiguous in order of magnitude) choice for \( a \) if the average distance between neighboring particles: \( a = \rho^{-1/3} \) (in the 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 \( \lambda_0 \). Then one can neglect the vanishingly small (\( \lesssim a/\lambda_0 \sim \mu^{2/3} \)) difference between the centers of mass of the configurations on the left and right sides of (2.2), and replace the chain of variables \( z_n \) by the single common variable \( z \): the coordinate of a physically small collision volume. The belonging to the same such volume will be taken below as the criterion of closeness of particles.

Let us denote the mentioned averaging operation by the overline, and the result of the averaging of \( \tilde{F}_n \) by \( \overline{A_n} = \overline{\tilde{F}_n} \). By virtue of this definition of DF \( A_n \), any of \( A_n = A_n(t, z, v_1, ..., v_n) \) depend only on \( t, z \) and the velocities \( v_j \) and characterizes a local mean (ensemble-average) density of the number of \( n \)-particle encounters. At that, according to the aforesaid, now instead of (2.2) we have

\[
\overline{\mu^{-1} L'_n \tilde{F}_n} = 0 , \tag{2.4}
\]

(or \( \overline{L'_n F_n} \) in the dimensional form). Due to this equality the equations (2.2) turn into

\[
\left( \frac{\partial}{\partial t} + u_n \nabla \right) A_n = \overline{J_n} , \tag{2.5}
\]

where \( \nabla = \partial/\partial z \), and (as in (2.4)) the limit \( \mu \to 0 \) is taken in mind.
It is thus clear that in general inhomogeneous case, when $\nabla A_n \neq 0$, a solution of equations (2.5) can not be written as the product of one-particle DF:

$$A_n(t, z, v_1, ..., v_n) \neq \prod_{j=1}^{n} A_1(t, z, v_j) ,$$

since the inertial terms $u_n \nabla A_n$ constantly generate statistical correlations between close-lying particles, due to their joint drift (together with their collision volume) relative to the inhomogeneity. As the consequence, the circumstance that particles belong to the same encounter or collision event already establishes statistical correlations between them. At that, of course, from the probabilistic point of view, there is no principal difference between encounters and collisions proper.

We thus arrive at the conclusion that in non-homogeneous situations the collisional approximation - by virtue of its very nature - contradicts the hypothesis of molecular chaos, since in the language of collisions the relative motion of colliding particles becomes an inner constituent part of the collision as a whole and therefore automatically excluded from the equations for DF what characterize number density of collisions. As a result, even in the hydrodynamic stage, the evolution of gas is described by the infinite system of equations (2.5).

But, on the other hand, the collisional character of gas evolution does not prevent factorization of the $n$-particle DF $F_n(t, q_1, ..., q_n, v_1, ..., v_n)$ if the particles are sufficiently far apart from each other, i.e. are not close in the above-defined sense. Indeed, if in the limit $r_0/\lambda_0 \to 0$ ($\lambda_0 = \text{const}$) one keeps the inter-particle distances $q_{ij}$ fixed in units of $\lambda_0$, instead of $r_0$, then the BBGKY equations reduce to such the equations for $F_n$ which have the factored solution $F_n = \prod_j F_1(t, q_j, v_j)$. However, in the (right side of) equation for $F_1$ we see the pair DF taken at quite different type of limit, when $q_{12}$ is fixed in units of $r_0$, i.e. $F_2|_{q_2=q_1}$, which leads to the hierarchy (2.5)\footnote{Notice that our reasonings nowhere appeal to details of the interaction potential (presuming only that it is short-range enough). Therefore nothing prevents us to extend our conclusions to the limit of the hard-sphere interaction. Moreover, there is no alternative, since only ansatz like (2.3) ensures that probabilities are conserved during collisions.}. 

\begin{align*}
{2 \text{ Notice that our reasonings nowhere appeal to details of the interaction potential (presuming only that it is short-range enough). Therefore nothing prevents us to extend our conclusions to the limit of the hard-sphere interaction. Moreover, there is no alternative, since only ansatz like (2.3) ensures that probabilities are conserved during collisions.}}
\end{align*}
The switch to the common spatial variable $z$ in (2.5), of course, presumes that $|q^{(n)} - q^{(n+1)}| \ll l$ and $na^3 \ll l^3$, where $l$ is characteristic scale of the non-homogeneity and $na^3$ is characteristic volume of a cluster of $n$ close particles. In the limit under consideration, both these requirements are satisfied by an infinite margin if $l \gtrsim \lambda_0$ (since then $na^3/l^3 \sim n\mu^2 \to 0$) and thus do not restrict the number of DF $A_n$ which are “tied” to a given coordinate $z$.

3. WEAKENED MOLECULAR CHAOS

The requirements (2.4) are main tools of construction of a collisional approximation: due to them the right sides of (2.2) and (2.5) can be reduced to the collisional form. In particular, with $n = 2$, Eq. (2.4) becomes

$$
\frac{\mu^{-1}L'_n \tilde{F}_n}{a^{-3} \mu^{-1}} = \frac{L'_n \tilde{F}_n dq_{21}}{|x_{21}| < a} = \int_{|x_{21}| < a/r_0} L'_n \tilde{F}_n dx_{21} = 0
$$

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

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

With the help of this equality the right side $\mathcal{J}_1 = J_1$ in the first of equations (2.2) and (2.5) transforms to integral

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

over an infinitely remote surface $|x_{21}| = \infty$ (with $ds$ being its normal vector), so that $\mathcal{J}_1$ is determined by the particle flow into the “collision volume” $|x_{21}| < \infty$ from the surrounding gas.

Depending on the sign of the scalar product $(v_2 - v_1) \cdot ds$, the DF $\tilde{F}_2$ represents either in- or out-state of particle 2 with respect to particle 1. Let us denote by $A_2^{in}$ the values of $\lim_{\mu \to 0} \tilde{F}_2$ on that part of the boundary surface $|q_{21}| \approx a$ which corresponds to in-states. The boundary values for the out-states can then be expressed in terms of the $A_2^{in}$ with the help of the two-particle scattering matrix. After that, $\mathcal{J}_1$ acquires
the standard form of the collision integral:

\[
\left( \frac{\partial}{\partial t} + u_1 \nabla \right) A_1 = \int dv_2 \tilde{S}_{12} A^{in}_2 .
\]

Here and below \( \tilde{S}_{ij} \) is the ordinary “Boltzmann collision operator” for the collision of particles \( i \) and \( j \). The action of this operator is defined by [1, 2, 3]

\[
\tilde{S}_{ij} \psi(v_i,v_j) = |v_i - v_j| \int d^2b \left[ \psi(v'_i,v'_j) - \psi(v_i,v_j) \right],
\]

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

Analogously, we can use (2.4) with \( n > 2 \) to perform similar transformations of the integrals \( J_n \). In the limit \( \mu \to 0 \) the functions \( A_n \) are determined by the average of \( \tilde{F}_n \) over an infinite (3(n-1)-dimensional) region of dimensionless inter-particle distances. Therefore the result of this averaging represents only such (pre- or post-collisional) configurations of \( n \) particles where none of them are just now in a collision. Correspondingly, only two-particle collisions (between some of \( n \) lefthanded particles in (2.5) and “external” righthanded \((n+1)\)-st particle from the rest of the gas) contribute to \( J_n \). We thus find what could have predicted earlier:

\[
\left( \frac{\partial}{\partial t} + u_n \nabla \right) A_n = \sum_{j=1}^{n} \int dv_{n+1} \tilde{S}_{jn+1} A^{in}_{n+1} , \tag{3.1}
\]

where \( A^{in}_{n+1} \) is the boundary DF (similar to \( A^{in}_2 \)) representing configurations with the external particle which always is in infinitely remote \( in \)-state in respect to other \( n \) particles. To underline the particular role of the external particle, we will distinguish its velocity among other arguments of \( A^{in}_{n+1} \) and write \( A^{in}_{n+1} = A^{in}_{n+1}(t, z, v_1, ..., v_n|v_{n+1}) \).

In order to transform (3.1) into a closed system of equations, we have to relate the right-side boundary DF \( A^{in}_{n+1} \) to the left-side functions. In this step - after transition to the collision integrals - we need to invoke the concept of molecular chaos. Concretely, let us assume that the external \((n+1)\)-st particle, due to its just noted specificity, has
no velocity correlations with the other particles:

\[ A_{n+1}^{in}(t, z, v_1, ..., v_n | v_{n+1}) = A_1(t, z, v_{n+1}) A'_{n}(t, z, v_1, ..., v_n) . \]

However, this velocity factorization does not mean absolute statistical independence, 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 DF corresponding to the condition that a collision with an additional particle takes place).

In the “pure” form the correlation of particles in the configuration space is described by the DF integrated over all velocities. Since in all the configurations under consideration the particles are infinitely close together from the standpoint of the scale \( \lambda_0 \), the degree of their spatial correlations in all these configurations should be the same. This statement is expressed by the equality

\[
\int A_{n+1}^{in} dv_1 ... dv_{n+1} = \int A_{n+1} dv_1 ... dv_{n+1} .
\]

In essence, it claims the conservation of the number of particles in the collision processes (notice that \( A_{n+1} \) is indirect characteristics of intermediate stages of encounters and collisions). This equality makes it possible to relate \( A_{n+1}^{in} \) to \( A_{n+1} \) and thus \( A'_{n} \) to \( A_{n+1} \). It is easy to see that unambiguously simplest form of the relationships is

\[
A'_{n}(t, z, v_1, ..., v_n) = \int A_{n+1}(t, z, v_1, ..., v_n, v_{n+1}) dv_{n+1} \left( \int A_1(t, z, v_1) dv_1 \right)^{-1}
\]

or, equivalently,

\[
A_{n+1}^{in}(t, z, v_1, ..., v_n | v_{n+1}) = \frac{A_1(t, z, v_{n+1})}{\int A_1(t, z, v) dv} \int A_{n+1}(t, z, v_1, ..., v_n, v) dv . \tag{3.2}
\]

This relationship does not touch on the correlations between members of the left-side \( n \)-particle cluster.

Expression (3.2) is a weakened version of the hypothesis of molecular chaos. It incorporates the spatial statistical correlations of colliding particles, i.e. it asserts that only their velocities and momenta are statistically independent, but not their coordinates (thus, all the \( n+1 \) particles may be mutually dependent in the configuration space).
Along with (3.2), Eqs. 2.5 form a closed - we wish to stress this closure - hierarchy of kinetic equations. In the limit of spatially homogeneous gas, this hierarchy permits the completely factored solution, \( A_n(t, v_1, \ldots, v_n) = \prod_{j=1}^{n} A_1(t, v_j) \), and becomes equivalent to the Boltzmann equation

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

Moreover, this equation follows already from the first of of formulas (3.2) when we note that the conditions of inter-consistent normalization of the set of DF,

\[
\Omega^{-1} \int \int F_{n+1} dq_{n+1} dv_{n+1} = F_n
\]

(with \( \Omega \) being total, infinite, volume of the system), can be reduced in the homogeneous limit to the local form \( \int F_{n+1} dv_{n+1} = F_n \) \((F_0 = 1)\). This implies \( \int A_{n+1} dv_{n+1} = A_n \), and from (3.2) with \( n = 1 \) we have \( A_2^n(t, v_1 | v_2) = A_1(t, v_1)A_1(t, v_2) \).

In general non-homogeneous case, such relations no longer hold, since the exact global form of the conditions of mutual consistency of DF cannot be replaced by a spatially local form. The evolution of one-particle DF is determined by the entire infinite chain of equations (2.5) and (3.2), and becomes definitely non-Markovian, in contrast with evolution in the Boltzmann model. Clearly, this then leads to a low-frequency temporal dispersion of the spatially non-local 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. Of course, it would be wrong to think about the spatial non-homogeneity as a cause of these fluctuations (they take place also in homogenous and equilibrium states). In fact, the non-homogeneity gives only the means by which they manifest themselves in the one-time DF \( F_n \), due to dependencies of \( F_n \) in non-homogeneous non-equilibrium states on the kinetic coefficients. Next, let us consider a simplest non-homogeneous problem concerning self-diffusion of gas particles.
4. 1/F NOISE OF SELF-DIFFUSION

To analyze self-diffusion we need to eliminate from the kinetic equations the hydrodynamic modes associated with the five integrals of motion of the system as whole. This can be done easily by taking the known formal approach (see e.g. [2]): replacing the probability distribution of the external particle in the collision integral by the equilibrium one-particle DF. In our notation, replacing (3.2) by

\[ A_{n+1}(t, z, v_1, ..., v_n | v_{n+1}) = A_0(t, v_{n+1}) \int A_{n+1}(t, z, v_1, ..., v_n, v) dv, \]  

(4.1)

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

Physically, this replacement describes a situation in which the gas is in equilibrium state in the macroscopic thermodynamical sense. There is only a small perturbation of the statistical equilibrium with regard to a single marked “test” particle and its immediate surroundings. The statistical state of the surroundings will be described by the set of DF which stand on the left sides of (2.5) and (3.1). The rest of the gas serves as the thermostat. Clearly, if the one-particle DF is assigned to the test particle, then the higher-order DF represent clusters consisting of the test particle and \( n - 1 \) other particles from its surroundings. Thus we assign the index 1 to our test particle.

Further, we also will make use of the Green-Kubo theorem, according to which (see e.g. [6]) the generalized diffusion coefficient \( \hat{D}(\tau, \nabla) \), which figures in the general non-local form of the self-diffusion equation (see e.g. [12]),

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

(4.2)

- with \( \nabla = \partial/\partial R \) and \( W(t, R) \) denoting probability density distribution of coordinate of the diffusing particle, - can be related to the linear response of DF of the test particle to an infinitely weak (potential) force \( f_{ex}(q_1) \) applied to it (we take in mind, as usually, that the force is “switched on” at some time moment, e.g. \( t = 0 \), before which the gas was in all respects at the equilibrium). Namely, it is a straightforward matter to prove
that the following relation holds (see Appendix A):

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

(4.3)

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

\[ D(p, \nabla) = \int_0^\infty d\tau \tilde{D}(\tau, \nabla). \]

To find the response we have to add terms \( m^{-1} f_{ex}(q_1) \partial F_n / \partial v_1 \) to the left sides of the BBGKY equations. In the kinetic equations (3.1), i.e. in the framework of the collisional approximation under the low-density limit (and in the dimensionless notation), these terms look as \( f_{ex}(z) \partial A_n / \partial v_1 \). The replacement of \( q_1 \) by \( z \) in the argument of \( f_{ex} \) presupposes that a change of \( f_{ex} \) over length scales \( \lesssim a \) is negligibly small and that the external force has no substantial effect on the dynamics of collisions.

These assumptions are well legitimate in the limits \( a f_{ex} / T \to 0 \) and \( \mu \to 0 \) if, in addition, characteristic spatial scale (wave length) of the force, \( k \), is not too small: \( |k|^{-1} \gtrsim \lambda_0 \).

After the relations (4.1) are substituted into Eqs (3.1) the Boltzmann collision integral on the right sides transforms into a generalized Fokker-Planck operator \( \Lambda \) (or the “Boltzmann-Lorentz operator” [2]) defined by

\[ \Lambda_j \psi(v_j) = \int dv_{n+1} \tilde{S}_{j, n+1} \psi(v_j) A_0(v_{n+1}) . \]

As the result, we come to the equations (in the dimensionless form)

\[ \left( \frac{\partial}{\partial t} + \left[ \frac{1}{n} \sum_{j=1}^{n} v_j \right] \frac{\partial}{\partial z} + f_{ex}(z) \frac{\partial}{\partial v_1} \right) A_n = \sum_{j=1}^{n} \Lambda_j \int A_{n+1} dv_{n+1} \]  

(4.4)

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 directly from evolution of an non-equilibrium state in absence of external forces. This approach, however, is less convenient since it requires special consideration of initial stage of the evolution before its kinetic stage.
Next, consider the mentioned linear response, setting on \( A_n = A_0^n + \phi_n \) (\( \phi \to 0 \)), taking the Fourier transform in \( z \) and the Laplace transform in \( t \), and denoting Fourier transforms of \( \phi_n \) by \( \tilde{\phi}_n \). Then Eqs.4.4 yield
\[
\left(p + \frac{ik}{n} \sum_{j=1}^{n} v_j \right) \tilde{\phi}_n = \sum_{j=1}^{n} \Lambda_j \int \tilde{\phi}_{n+1} d\nu_{n+1} + v_1 \tilde{f}_{ex} p^{-1} A_0^n .
\] (4.5)

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 of the force inhomogeneity:
\[
D(p, ik) = D_0(p) + (ik)^2 D_1(p) + \ldots .
\]

Second, we choose the simplified model form of the operator \( \Lambda \), namely, the Einstein-Fokker-Planck (EFP) operator:
\[
\Lambda_j = \gamma \left( \frac{\partial}{\partial v_j} v_j + \frac{\partial^2}{\partial v_j^2} \right) .
\]

Here we have used that \( \Lambda_j A_0(v_j) = 0 \).

In reality, such the operator could not arise from a short-range interaction potential (since it corresponds to scattering through only small angles). This circumstance, however, should not corrupt the qualitative side of our results, because all that is required of \( \Lambda \) is that it ensures relaxation of velocities to thermal equilibrium. This choice is convenient in that all the eigenfunctions of \( \Lambda \) turn to product of \( A_0 \) and polynomials.

We may recall that the operator \( \Lambda \) corresponding to the Maxwell interaction potential has the same property [2] (therefore the following calculations can be generalized to this case). But the EFP operator has a further advantage: it makes it possible to exploit the separation of variables and thus to work with only projections of vector variables onto the force’s wave vector \( k \), i.e. to deal with formally one-dimensional problem (notice that if \( f_{ex} \) is a potential force then vector \( \tilde{f}_{ex} \parallel k \)).
Our next step is expansion of the response in the wave vector of the force-induced inhomogeneity:

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

Using formula (4.3) to relate this series to the above expansion of the diffusion coefficient, we find

$$D_0 = \int v_1 C^{(0)}_1 dv_1, \quad D_1 + D_0^2/p = \int v_1 C^{(2)}_1 dv_1 \equiv \delta_1.$$  

Inserting the same series into (4.5), we come to equations

$$p C^{(0)}_n = \sum_{j=1}^{n} \Lambda_j \int C^{(0)}_{n+1} dv_{n+1} + v_1 A^0_n,$$

$$p C^{(N)}_n = \sum_{j=1}^{n} \Lambda_j \int C^{(N)}_{n+1} dv_{n+1} - C^{(N-1)}_n \frac{1}{n} \sum_{j=1}^{n} v_j.$$  

The equations from the first row can be solved easily with our choice of $\Lambda$ and yield

$$C^{(0)}_n = \frac{v_1 A^0_n}{p + \gamma}, \quad D_0(p) = \frac{1}{p + \gamma}. \quad (4.6)$$  

The solution of the second row of equations for $C^{(1)}_n$ should be sought in the form

$$C^{(1)}_n = \left( \alpha_n v_1 \sum_{j=1}^{n} v_j + \beta_n \right) A^0_n D_n,$$

where $\alpha_n$ and $\beta_n$ 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

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

Now consider the functions

$$\delta_n = \int v_1 C^{(2)}_n dv_1 ... dv_n,$$

the first of which determines $D_1$ (see above). Multiplying the chain of equations for $C^{(2)}_n$ by $v_1$ and integrating over all velocities, we find, after some algebra,

$$p \delta_n = -\gamma \delta_{n+1} - n^{-1} [ (n+2) \alpha_n + \beta_n ] D_0.$$
Substituting the expressions found above for $\alpha_n$ and $\beta_n$ into this equation, we find $\delta_1$ and thus $D_1$ in the form of the repeating sum:

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

where $X \equiv \gamma/p$. Then, with the help of the identity

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

we can transform the series over $n$ to the easy summable form:

$$D_1 + \frac{D_0^2}{p} = \frac{D_0}{p^2X} \int_0^X \sum_{n=1}^{\infty} \frac{(-y)^{n-1}}{n^2} + \frac{n+1}{n} \sum_{j=n}^{\infty} (-2y)^{j-n} \, dy = \frac{D_0}{p\gamma} \int_0^{\gamma/p} \left\{ \frac{\ln (1+y)}{y} + \frac{1}{1+2y} \left[ \frac{\ln (1+y)}{y} + \frac{1}{1+y} \right] \right\} . \quad (4.7)$$

We have gone into the details of the calculations to demonstrate the characteristic $p$ dependence of the response which is rather general and holds under another choice of the operator $\Lambda$. Let us consider this dependence at $|p| \ll \gamma$ and thus examine the behavior of the diffusion coefficient at low frequencies. From (4.6) and (4.7) at $p/\gamma \to 0$ we have $D_0 = 1/\gamma$ and

$$D(p,ik) \approx D_0 \left[ 1 + (ik)^2 \frac{D_0}{2p} \left( \ln \frac{\gamma}{p} + c \right) + ... \right] , \quad (4.8)$$

where $c$ is a numerical constant. In the dimensional notation, evidently, we must write $D_0 = v_0^2 \tau_0 / \gamma = (T/m) \tau_m$ and replace $\gamma$ by $\gamma/\tau_0 \equiv 1/\tau_m$ in the logarithm, with $\tau_m$ being the momentum relaxation time.

Further, we turn to direct statistical characteristics of random diffusive (“Brownian”) displacement of the test particle as described by the diffusion equation (4.2). Knowing the first $N$ terms of the expansion of the diffusion coefficient in $ik$, we can find theoretically the first $N+2$ of the statistical moments of the displacement,

$$M_n(t) = \int R^n W(t,R) dR .$$
From (4.2) we have, particularly,
\[ \int_0^\infty M_2(t) e^{-pt} dt = \frac{2D_0(p)}{p} , \quad \int_0^\infty M_4(t) e^{-pt} dt = \frac{24}{p^2} \left[ D_1(p) + \frac{D_0^2(p)}{p} \right]. \]
Now, combining these formulas with (4.7) and (4.8) and performing the inverse Laplace transform for \( t \gg \tau_m \), we obtain
\[ M_2(t) \approx 2D_0 t , \quad M_4(t) \approx 3M_2^2(t) + 6D_0^2 t^2 \left[ \ln^2 \frac{t}{\tau_m} + c' \ln \frac{t}{\tau_m} + c'' \right], \quad (4.9) \]
where \( D_0 = T\tau_m/m \), and \( c' \) and \( c'' \) are numerical constants.

Let us compare this result with that which would follow from the canonic approximation based on the molecular chaos hypothesis and the Boltzmann-Lorentz equation. At that, in place of our infinite system of equations (4.5) we would have the single closed equation,
\[ (p + ikv_1) \tilde{\phi}_1 = \Lambda_1 \tilde{\phi}_1 + v_1 \tilde{f}_ex p^{-1} A_0(v_1), \]
which at arbitrary choice of the operator \( \Lambda \) implies
\[ M_2(t) \approx 2D_0 t , \quad M_4(t) \approx 3M_2^2(t) + c_0 \lambda_0^2 D_0 t , \quad (4.10) \]
with \( c_0 \) being a numerical constant (\( c_0 = 0 \) when \( \Lambda \) is of the EFP type) and the same diffusivity \( D_0 \) as above (by its sense, \( D_0 = \lim_{t \to \infty} M_2(t)/2t \)).

The second term in the expressions for \( M_4(t) \) in (4.9) and (4.10) is the fourth-order cumulant (semi-invariant) of the test particle displacement, \( \kappa_4(t) \equiv M_4(t) - 3M_2^2(t) \).
As is known, it is a measure of "non-Gaussianity" of the displacement. In particular, it shows how substantially a (more or less random) value of diffusivity \( \tilde{D} \) measured from a concrete realization of the Brownian motion can differ from the diffusivity \( D_0 \) characterizing the average over statistical ensemble of realizations. The "Boltzmann" asymptotic (4.10), that is \( \kappa_4(t) \propto t^\nu \) with \( \nu > 1 \), means that random wandering of the test particle can be exhaustively described by the single statistical parameter \( D_0 \).

This is not the case, however, if \( \kappa_4(t) \propto t^\nu \) with \( \nu > 1 \). Such kind of the asymptotic means that it is no longer possible to pack an arbitrary typical realization within the
framework of a single parameter $D_0$. It is not difficult to make sure that such the asymptotic is statistically equivalent to the existence if flicker fluctuations of diffusivity with low-frequency power spectrum $\propto \omega^{-(\nu-1)}$.

In the theory under consideration, in contrast with the Boltzmann theory, we are just in such the situation, since, according to (4.9), $\kappa_4(t) \propto t^2 \ln^2(t/\tau_m)$. It can be described, on a coarse enough time scale (when relatively small terms proportional to $t$ in $\kappa_4(t)$ can be neglected), as a Gaussian random walk with a random diffusivity $\tilde{D} = \tilde{D}(t)$. Treating $\tilde{D}$ as global characteristics of the entire time interval $(0,t)$ under observation, we come to a “doubly random” walk whose path probability density distribution and statistical moments can be written as follow,

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

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

where the angle brackets mean average in respect to $\tilde{D}$ with $\langle \tilde{D} \rangle = D_0$. The corresponding interpretation of the asymptotic (4.9) in terms of power spectrum, $S_D(\omega)$, of the diffusivity fluctuations at $\omega \tau_m \ll 1$ yields (see Appendix B)

$$D_0^{-2} S_D(\omega) \approx \pi \omega \ln \frac{1}{\omega \tau_m}.$$  \hspace{1cm} (4.11)

Thus, the random diffusivity, or the “rate of diffusion”, of the test particle (and hence of any particle) is a random process with a $1/f$ spectrum. Let us discuss this result.

A measurement of spectrum of the diffusivity fluctuations is nothing but a measurement of the equilibrium average value of definite fourth-order polynomial functional of the particle velocity. An experiment of this type is not merely thinkable but really

\footnote{The approach suggested twenty years ago in the present paper [Sov. Phys. JETP 67 (12), 2469 (1988)] later was simplified and improved in [Yu. E. Kuzovlev, “On statistics and 1/f noise of Brownian motion in Boltzmann-Grad gas and finite gas on torus. I. Infinite gas”, arXiv: cond-mat/0609515]. There the asymptotic

$$W(t, R) \approx \int_0^\infty \exp \left[ -R^2/4t\tilde{D} \right] \frac{d\tilde{D}}{4\pi t \tilde{D}^{1/2}} \frac{\Gamma(5/2)}{(4\pi D_0 t)^{1/2} (1 + R^2/4D_0)^{5/2}}$$

was found, with $w(x) = x^{-3} \exp(-1/x)$ representing effective probability density distribution of the relative rate of diffusion $x = \tilde{D}/D_0$.}
has been carried out by Voss and Clarke (see references in [7, 8]). However, it is vastly simpler to imagine measurements of usual quadratic functionals of the drift velocity of gas particle (under influence of an external force) and thus spectra of fluctuations in particle’s mobility. Natural reasonings prompt that these fluctuations should be (at least at low frequencies) a statistical copy of the fluctuations in diffusivity. In the Appendix C we prove that this is indeed the case for the system under our consideration (the “extension of the Einstein relation to fluctuations” takes place).

From the standpoint of a principal experimental test of the theory, it would be interesting to extend it to multi-component gases, in particular, weakly ionized gas. It can be shown that diffusivity fluctuations of some component of a mixture represent a generalized flicker noise with power spectrum $\omega^{-\alpha}$, where the exponent takes a value from interval $1 \leq \alpha < 2$, depending on ratios of masses and momentum relaxation times of the components. Hence, the same principal mechanism of diffusivity fluctuations may produces a variety of flicker-type spectra. This can be illustrated also be spectrum $\omega^{-1} \ln^{-2} (1/\omega \tau_0)$ found in the earlier phenomenological theory (see [7, 9, 11, 14]).

The spectrum (4.11), as well as the asymptotic (4.9), give clear evidences that the diffusivity and mobility fluctuations behave like statistically non-stationary and non-ergodic random processes. This statement means that in measurements of the diffusivity or mobility on a concrete particular realization of the particle’s random walk the variance (in the sense of the ensemble average) of the result does not decrease, or even increases instead, when increasing length of the observation. The probabilistic aspects of such a behavior were studied in [9, 11]. Here, it is necessary to emphasize that such the statistical non-stationarity has no relation to a thermodynamical non-stationarity, since formulas (4.8) and (4.9) concern thermodynamically equilibrium gas. The matter is that the non-stationarity manifests itself only in dependencies on duration of observation of a test particle, but not on time moment when the observation starts. Thus, the diffusivity and mobility, as well as kinetic and transport coefficients in general,
can undergo a non-stationary low-frequency fluctuations even in thermodynamically stationary and equilibrium systems. This principal possibility should be taken in mind when interpreting experiments.

5. Conclusion

The 1/f self-diffusion noise found above is the property of an infinitely low-density gas. Hence, the mechanism of this noise by its very nature is indifferent to the gas density and is not related to any dynamic many-particle correlations (e.g. through repeated collisions). It can be related only to fluctuations in the rate and efficiency of collisions of a given gas particle with the rest of gas because of randomness of geometrical factors of their encounters. The corresponding noise is just the 1/f noise if the system constantly forgets a total number of previous collisions of the particle and their past rates \[9, 10, 11\]. More rigorously, the loss of memory is implied by the property of mixing of phase trajectories of the system in its full phase space. For a gas this property was proved already in \[4\]. Notice that in fact in \[4\] it was shown also that generally just the mixing of phase trajectories causes their non-ergodic behavior, so that time-average rate of collisions (or some other events) along a particular trajectory is not obligated to coincide with the ensemble-average rate, regardless of duration of the time averaging. The essential paradoxical point is that although such the random behavior results from the loss of memory, it can be described in the statistical language only by means of infinitely long-living correlations.

In the derivation of kinetic equations (like the Boltzmann equation), however, always an assumption is made (like the molecular chaos) in order to replace actual random rate of collisions, or other elementary kinetic events, by some ensemble-average value.\[4\]

\[4\] This real mission of the molecular chaos hypothesis (Boltzmann’s “Stosszahlansatz”) still is not realized even by important physicists. The common naive opinion is that it claims independence of particles’ velocities. But in fact it introduces also a priori predetermined rate of collisions (although neither the underlying mechanics nor the statistical ensemble if initial conditions to this mechanics do present such a quantity). In contrast to it, the “weakened molecular chaos” ansatz, as expressed
This decisive assumption is thus introduced already into the “zero-order” theory of infinitely low-density gas. Of course, taking into account finite gas density effects (see e.g. [3]) results in appearance of characteristic long-scale hydrodynamic fluctuations which contribute to both velocity and diffusivity of any particle and thus to inter-particle correlations. But, in spite if these complications, the above pointed out mechanism of the 1/f fluctuations anyway remains lost.

In the present work, our goal was just a correct exposure and reconstruction of the loss, at least in the low-density limit, at that accenting principal role of spatial non-homogeneity of gas. Notice that the generalization of the genuine Boltzmann equation to inhomogeneous situations by means of automatic adding of the drift term already has attracted critical comments more than once in the past (see e.g. [5]). The hierarchy of kinetic equations found in Sec.3 is nothing but the correct (compatible with the concept of collision) formulation of the Boltzmann equation for inhomogeneous case.

At last, let us note a relation of our theory to the formally exact generalized non-Markovian kinetic equation for one-particle distribution function obtained in [6] by the method of projection operators. In [6] it was shown that analyticity of the kernel of this equation in respect to the Laplace transform variable ($p$ in our notation) means its coincidence in the low-density limit with the Boltzmann equation. Hence the latter is invalid if the kernel is nonanalytic. The asymptotic (4.5) indicates just such the case. Thus, our specific theory agrees with the abstract theory of [6].

---

5 This fact prompts that, analogously, the kinetic theory of electron-phonon systems in solids (in particular, the theory of polarons) loses 1/f fluctuations in the phonon relaxation rates and electron mobilities at very beginning of the theory, when it attracts the hypothesis of “random phases” or another ansatz to throw out statistical inter-(quasi-)particle correlations. About that, see e.g. [8], the article [Yu. Kuzovlev, “Relaxation and 1/f noise in phonon systems”, JETP 84 (6), 1138 (1997)] and preprint [Yu. E. Kuzovlev, “Kinetic theory beyond conventional approximations and 1/f noise”, arXiv: cond-mat/9903350]. Thus, in essence, the present paper (along with [7, 11]) shows the way to rather general explanation of the 1/f-noise phenomenon.
I wish to thank A. I. Lomtev, G. N. Bochkov, and Yu. M. Ivanchenko and participants of his seminar for useful discussions.

Appendix A.

The switching on at time \( t = 0 \) a potential force field \( f_{ex}(r) = -\partial U(r)/\partial r \) acting onto the test particle is described by the Hamiltonian

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

where \( \theta(t) \) is the Heaviside step function, \( H_0 \) is Hamiltonian of the unperturbed gas, and \( Q_k \equiv e^{ikq_1} \) and \( X_k(t) \equiv -[ik\tilde{f}_{ex}(k)]k^{-2}\Omega^{-1}\theta(t) \) in couples play roles of generalized variables and conjugated external forces. Let us consider the “flows”

\[
I_k \equiv \frac{\partial Q_k}{\partial t} = ikv_1 e^{ikq_1},
\]

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

\[
\langle I_k(t) \rangle = \frac{1}{T} \sum_{k'} \int_{-\infty}^{t} \langle I_k(t), I_k(t') \rangle_0 X_{k'}(t') dt',
\]

where \( \langle ... \rangle_0 \) means the average over equilibrium statistical ensemble of phase trajectories of the system corresponding to the Gibbs canonic statistical ensemble of initial states of these trajectories, and \( \langle ... \rangle \) means the non-equilibrium average. In our case, in view of the homogeneity and isotropy of the equilibrium gas, the above relation takes the form

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

The distribution of probability density of the test particle displacement, or path, in equilibrium gas can be determined by the expression

\[
W(t - t_0, R) = \langle \delta(q_1(t) - q_1(t_0) - R) \rangle.
\]
Let us apply to it the differentiation operation \( \frac{\partial^2}{\partial t^2} \) and then make the Fourier transform in respect to \( R \) (at \( t_0 = 0 \)) and the Laplace transform in respect to \( t \). Using \( \langle v_1 \rangle_0 = 0 \), we find
\[
p [p \tilde{W}(p,ik) - 1] = -k \int_0^\infty dt e^{-pt} \langle v_1(t) \exp \{-ik [q_1(t) - q_1(0)]\} v_1(0) \rangle_0 k ,
\]
where \( \tilde{W}(p,ik) \) is the transform of \( \tilde{W}(t,R) \). For it from (4.2) we have the identity
\[
p\tilde{W}(p,ik) - 1 = -k D(p,ik) \tilde{W}(p,ik) ,
\]
which, as combined with (A.2), yields
\[
\frac{D(p,ik)}{p + D(p,ik) k^2} = \frac{1}{p} \int_0^\infty dt e^{-pt} \langle v_1(t) \exp \{-ik [q_1(t) - q_1(0)]\} v_1(0) \rangle_0 .
\]
At last, performing in (A.1) the Laplace transform and comparing the result with (A.3), we come to the formula (4.3).

Appendix B.

The asymptotic of the fourth-order cumulant \( \kappa_4(t) \) expressed by (4.9) indicates non-stationary character of the fluctuations in diffusivity (observed on a particular random walk of the test particle). In other words, this asymptotic indicates the absence of a certain time-average value of the diffusivity. Therefore, \( \tilde{D}(t) \) should be treated as a non-stationary random process (in the sense of the probability theory). Since at \( t \ll \tau_m \) we have \( M_{2n}(t) \propto t^{2n} \), this process begins from zero value: \( \tilde{D}(0) = 0 \). The power spectrum of a random process of this sort is characterized, as is known, by so-called structural function:
\[
\langle [\tilde{D}(t) - \tilde{D}(0)]^2 \rangle = 2 \int_0^\infty [1 - \cos \omega t] S_D(\omega) \frac{d\omega}{2\pi} .
\]
At \( t \gg \tau_m \), after differentiation in respect to \( t \), this expression and formulas of Sec.4 together yield:
\[
\int_0^\infty \omega S_D(\omega) \sin \omega t \frac{d\omega}{\pi} = \frac{d}{dt} \frac{M_4(t)}{12 t^2} \approx \frac{D_0^2}{t} \ln \frac{t}{\tau_m} .
\]
The spectrum (4.11) follows immediately.
APPENDIX C.

Let at time $t = 0$ a constant force $f$ begins to act upon the test particle ("constant" means that $f$ is independent on $t$ and $q_1$), and $W(t, R; f)$ denotes resulting probability distribution of the particle’s displacement, $R(t) = q_1(t) - q_1(0)$. According to the generalized fluctuation-dissipation relations (see e.g. [13] and corresponding use of these relations in [8]), we can write

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

(C.1)

It is not difficult to transform this exact equality into

$$W(t, R; f) - W(t, -R; f) = \tanh\left(\frac{fR}{2T}\right) \left[ W(t, R; f) + W(t, -R; f) \right] \, .$$

(C.2)

Multiplying this by $R$ and integrating over $R$, we find such a consequence of (C.1):

$$\langle R(t) \rangle = \left\langle R(t) \tanh\frac{fR(t)}{2T} \right\rangle \, .$$

(C.3)

Now, consider the third derivative of this equality with respect to $f$ at $f = 0$:

$$\left[ \frac{\partial^3 \langle R(t) \rangle}{\partial f^3} \right]_{f=0} = \frac{3}{2T} \left[ \frac{\partial^2 \langle R^2(t) \rangle}{\partial f^2} \right]_{f=0} - \frac{\langle R^4(t) \rangle_0}{4T^3} \, ,$$

(C.4)

and apply this general relation to our problem. The average displacement

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

under the influence of the constant force $f_{ex} = f = \text{const}$ is determined by the homogeneous solution to equations (4.4). 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 (C.4) increases linearly with the time. However, the last term in (C.4), which contains the fourth-order statistical moment of equilibrium displacement, $\langle R^4(t) \rangle_0 = M_4(t)$,

---

6 Besides [13], the generalized fluctuation-dissipation relations were investigated e.g. in the works [G. N. Bochkov and Yu. E. Kuzovlev, “Fluctuation-dissipation relations for nonequilibrium processes in open systems”, Sov. Phys. JETP 49, 543 (1979); “Fluctuation-dissipation theory of nonlinear viscosity”, Sov. Phys. JETP 52, No.12 (1980); “Nonlinear fluctuation-dissipation relations and stochastic models in nonequilibrium thermodynamics. I. Generalized fluctuation-dissipation theorem”, Physica A 106, 443-480 (1981)].
due to (4.9) increases far more rapidly. Hence, this term is compensated (exactly at $t/\tau_m \to \infty$) by the first right-hand term of (C.4). As the result, from (C.3) and (C.4) we obtain

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

$$\langle R^2(t) \rangle = M_2(t) + \frac{f^2}{12T^2} M_4(t) \approx 2D_0 t + \frac{f^2 t^2}{T^2} \langle \tilde{D}^2(t) \rangle . \quad \text{(C.5)}$$

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 (C.5) shows that the Einstein relation between the diffusivity and the mobility holds not only in the ordinary sense (for the ensemble-average values) but also for their fluctuations. Correspondingly, the spectrum (4.11) simultaneously refers to the relative fluctuations in mobility. A similar relation, concerning the spectral density of equilibrium electric voltage noise and electrical conductivity, has been confirmed experimentally in the famous Voss-Clarke experiment (see e.g. [8]).
REFERENCES

[1] N. N. Bogolyubov. Problems of dynamical theory in statistical physics. North-Holland, 1962.
[2] P. Resibois and M. de Leener. Classical kinetic theory of fluids. Wiley, New-York, 1977.
[3] E. M. Lifshitz and L. P. Pitaevski. Physical kinetics. Pergamon, 1981.
[4] N. S. Krylov. Works on the foundations of statistical physics. Princeton, 1979 [Russian original: USSR Academy of Sciences Publ., Moscow-Leningrad, 1950].
[5] M. Kac. Probability and related topics in physical sciences. Intersci. Publ., London, N.-Y., 1957.
[6] R. Balesku. Equilibrium and nonequilibrium statistical mechanics. Wiley, New York, 1975.
[7] Yu. E. Kuzovlev and G. N. Bochkov, “On origin and statistical characteristics of 1/f-noise”, Izv. Vyssh. Uchebn. Zaved. Radiofizika, 26, No. 3, 310 (1983) [“Production and statistical properties of 1/f-noise”, Radiophysics and Quantum Electronics 26, No.3, 228 (1983)]; Preprint No.157, NIRFI (Scientific-Research Radiophysics Institute), Gorkii (Nijni-Novgorod), USSR, 1982.
[8] G. N. Bochkov and Yu. E. Kuzovlev, Sov. Phys. Uspekhi 26, 829 (1983).
[9] G. N. Bochkov and Yu. E. Kuzovlev, “On the theory of 1/f noise”, Preprint No.195, NIRFI (Scientific-Research Radiophysics Institute), Gorkii (Nijni-Novgorod), USSR, 1985.
[10] G. N. Bochkov and Yu. E. Kuzovlev, in Proceedings of the 4-th All-Union Conference on fluctuation phenomena in physical systems, p.110, Izd. IFP AN LitS SR, 1986.
[11] G. N. Bochkov and Yu. E. Kuzovlev, “Some probability characteristics of 1/f-noise”, Radiophysics and Quantum Electronics 27, No.9, p. 811 (1984).
[12] D. N. Zubarev, in Scientific and technological progress. Current problems in mathematics, Vol. 15, Izd. VINITI, Moscow, 1980.
[13] G. N. Bochkov and Yu. E. Kuzovlev, “On general theory of thermal fluctuations in nonlinear systems”, Sov. Phys. JETP 45, 125 (1977).
[14] The model of [7] is based to some extent on the restrictive assumption of asymptotic “decay of correlations” which predetermines integrability of the spectrum $S_D(\omega)$ (i.e. stationarity of the underlying random process). Physically, this restriction is not obligatory [9].

Translated by Dave Parsons and me

DONETSK INSTITUTE FOR PHYSICS AND TECHNOLOGY OF NASU, ul. R. LUXEMBURG 72, DONETSK 83114, UKRAINE
E-mail address: kuzovlev@kinetic.ac.donetsk.ua