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Diffusion in a time-dependent external field

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The problem of diffusion in a time-dependent (and generally inhomogeneous) external field is considered on the basis of a generalized master equation with two times, introduced by Trigger and co-authors [S. A. Trigger, G. J. F. van Heijst, and P. P. J. M. Schram, Physica A 347, 77 (2005); J. Phys.: Conf. Ser. 11, 37 (2005)]. We consider the case of the quasi-Fokker-Planck approximation, when the probability transition function for diffusion (PTD function) does not possess a long tail in coordinate space and can be expanded as a function of instantaneous displacements. The more complicated case of long tails in the PTD will be discussed separately. We also discuss diffusion on the basis of hydrodynamic and kinetic equations and show the validity of the phenomenological approach. A type of “collision” integral is introduced for the description of diffusion in a system of particles, which can transfer from a moving state to the rest state (with some waiting time distribution). The solution of the appropriate kinetic equation in the external field also confirms the phenomenological approach of the generalized master equation.

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I. INTRODUCTION

Models of continuous time random walks (CTRW) [1], for objects that may jump from one point to another in a generally inhomogeneous medium and which may stay in these points for some time before the next usually stochastic jump, are important for the solution of many physical, chemical, and biological problems. Recently these models have been applied also in economics and in social sciences (see, e.g., [2–4]). Usually the stochastic motion of the particles leads to a second moment of the density distribution that is linear in time \( \langle r^2(t) \rangle \sim t \). Such type of diffusion processes play a crucial role in plasmas, including dusty plasma [5], in nuclear physics [6], in neutral systems in various phases [7], and in many other problems. However, in many systems the deviation from the linear time dependence of the mean-square displacement have been experimentally observed, in particular, under essentially nonequilibrium conditions or for some disordered systems. The average square separation of a pair of particles passively moving in a turbulent flow grows, according to Richardson’s law, with the third power of time [8]. For diffusion typical for glasses and related complex systems [9] the observed time dependence is slower than linear. These two types of anomalous diffusion obviously are characterized as superdiffusion and subdiffusion.

The generalized master equation for the density evolution, which describes the various cases of normal and anomalous diffusion has been formulated in [10,11] by the introduction of the specific kernel function (PTD) \( W(r, r', \tau, t - \tau) \) depending on two times, which connects in a linear way the density distributions \( f \) of the stochastic objects (or particles) for the points \( r' \) at moment \( \tau \) and \( r \) at moment \( t \). The approach suggested in [10,11] clearly demonstrates the relation between the integral approach and the fractional differentiation method [12] and permits one to extend (in comparison with the fractional differentiation method) the class of sub- and superdiffusion processes, which can be successfully described. On this basis different examples of superdiffusive and subdiffusive processes were considered in [11] for the various kernels \( W \) and the mean-squared displacements have been calculated. The idea of the generalized master equation with two times [10,11] for diffusion in coordinate space has been recently used in [13] for the calculation of average displacements in the case of a time-dependent homogeneous external field. In [13] the jumps of the particles are assumed to be instantaneous, all particles are practically trapped and the electric field does not act on the waiting probability, which is independent of the external (electric) field. In these conditions the characteristic time scale of the external field has to be large (in comparison with the other time scales of the problem) and the probability of jumps is connected locally in time with the external field. As a result, in the diffusion equation the external field is placed outside of the integral on time.

It should be noted, however, that in the general case of the problem of diffusion in a time-dependent external field the force is placed under the integral over \( \tau \) [see the semiphenomenological consideration in [14] and Eqs. (15) and (16) below].

The general phenomenological approach to this problem has been formulated in [14].

This paper is motivated by the necessity to describe in more detail the influence of time-dependent and space-dependent external fields on the continuous-time random walks. The equation formulated in [10,11] is appropriate for this purpose and offers the opportunity for consideration of CTRW for both cases: long-tail space behavior of the PTD function, as well as for the fast decay of PTD function in coordinate space, when the Fokker-Planck-type expansion is applicable. For simplicity we consider in this paper only the last case.

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II. GENERALIZED MASTER EQUATION

Let us start from the generalized master equation with two times [10,11],

$$f(r,t) = f(r,t=0) + \int_0^t d\tau \int d\mathbf{r}' W(r,\mathbf{r}', \tau, t-\tau)f(\mathbf{r}', \tau)$$

$$- W(\mathbf{r}', r, \tau, t-\tau)f(r, \tau).$$

Equation (1) can be represented in an equivalent form, more similar to the structure of the Fokker-Planck equation, where the initial condition is absent,

$$\frac{\partial f(r,t)}{\partial t} = \int_0^t d\tau \int d\mathbf{r}' \{ W(\mathbf{r},\mathbf{r}', \tau, t-\tau)f(\mathbf{r}', \tau)$$

$$- W(\mathbf{r}', r, \tau, t-\tau)f(r, \tau) \}$$

or

$$\frac{\partial f(r,t)}{\partial t} = \int_0^t d\tau \int d\mathbf{r}' \{ P(\mathbf{r},\mathbf{r}', \tau, t-\tau)f(\mathbf{r}', \tau)$$

$$- P(\mathbf{r}', r, \tau, t-\tau)f(r, \tau) \},$$

where the PTD function $P(\mathbf{r},\mathbf{r}', \tau, t-\tau)$ is given by

$$P(\mathbf{r},\mathbf{r}', \tau, t-\tau) = 2W(\mathbf{r},\mathbf{r}', \tau, t-\tau)\delta(t-\tau)$$

$$+ \frac{\partial}{\partial \tau} W(\mathbf{r},\mathbf{r}', \tau, t-\tau)$$

(4)

Apparently, different—but equivalent—forms of the master equation exist with different kernels, although connected analytically. The form (3) is more similar to the form introduced in the papers [14–16], where memory effects have been considered in a very general form on the basis of a master equation with one time argument $t-\tau$, which describes the retardation (or memory) effects. It should be stressed, that in [16], in particular, the straightforward connection of the generalized master equation (GME) with the usual CTRW model has been established. In the framework of the specific multiplicative regime of the function $P(\mathbf{r},\mathbf{r}', \tau, t-\tau) = P(\mathbf{r},\mathbf{r}')\xi(t-\tau)$ the dependence of $P(\mathbf{r},\mathbf{r}')$ and $\xi(t-\tau)$ on the waiting time distribution and the jump length distribution is quite clear [see Eqs. (9) and (10) in [15]]. The same applies to the function $W$, which is connected with $P$ by Eq. (4). Similar problems for the kernel, depending on one time variable, have been discussed in [17]. In our further consideration we will derive the memory function as a function of the waiting time following the same line as in the papers [14–16] and we find the additional retardation function, which is the retardation of the mobility under the action of an external force (physically similar to dispersion of conductivity after Fourier transformation in time). A description of this retardation function depends on the specific model for the mobility and this will be considered in a separate paper. The argument $t-\tau$ describes the retardation (or memory) effects, which can be connected in the particular case of multiplicative PTD function $W(\mathbf{r},\mathbf{r}', \tau, t-\tau) = W(\mathbf{r},\mathbf{r}')\chi(t-\tau)$ with, for example, the probability for particles to stay during some time at a fixed position before moving to the next point. An equation with retardation, with the $W$ function depending only on one time argument $t-\tau$, has been suggested in [15] and applied in [16] to the case of the multiplicative representation of the PTD function. In general $W$ is not a multiplicative function in the sense mentioned above and, what is more important, is a function of two times $t$ and $t-\tau$ [10]. It should be mentioned that the closed form of the equation for the density distribution is an approximation. In some cases the exact solution for density distribution can be found (see, e.g., [16–19]), when a closed equation for the density distribution does not exist or gives a too rough approximate result. Nevertheless, in many practical situations Eqs. (1) or (3) are sufficiently exact and permit to describe various experimental data.

Let us consider the role of appearance of the two time arguments in the generalized master equation, Eq. (1), for the case of a time-dependent external force $\mathbf{F}(\mathbf{r},t)$. To simplify the consideration we can investigate the case of fast decay of the kernel $W(\mathbf{r},\mathbf{r}', \tau, t-\tau)=W(\mathbf{u},\mathbf{r}, \tau, t-\tau)$ as a function of $\mathbf{u}=\mathbf{r}-\mathbf{r}'$, when an expansion in the spirit of Fokker-Planck can be applied. In this case Eq. (1) takes the form [10,11]

$$f(\mathbf{r},t) = f(\mathbf{r},t=0) + \int_0^t d\tau \frac{\partial}{\partial \mathbf{r}_a} \left( A_a(\mathbf{r},\tau, t-\tau)f(\mathbf{r}, \tau) \right.$$

$$+ \frac{\partial}{\partial \mathbf{r}_b} \left[ B_{ab}(\mathbf{r},\tau, t-\tau)f(\mathbf{r}, \tau) \right] \right),$$

(5)

where the functions $A_a(\mathbf{r},\tau, t-\tau)$ and $B_{ab}(\mathbf{r},\tau, t-\tau)$ are the functionals of the PTD function (the indices are equal $\alpha, \beta = x, s$ in $s$-dimensional coordinate space),

$$A_a(\mathbf{r},\tau, t-\tau) = \int d^s u u_a W(\mathbf{u},\mathbf{r}, \tau, t-\tau)$$

(6)

and

$$B_{ab}(\mathbf{r},\tau, t-\tau) = \frac{1}{2} \int d^s u u_a u_b W(\mathbf{u},\mathbf{r}, \tau, t-\tau).$$

(7)

Equation (5) can be rewritten naturally in a form similar to Eq. (2), but now for the Fokker-Planck type approximation,

$$\frac{\partial f(\mathbf{r},t)}{\partial t} = \int_0^t d\tau \frac{\partial}{\partial \mathbf{r}_a} \left( A_a(\mathbf{r},\tau, t-\tau)f(\mathbf{r}, \tau) \right.$$

$$+ \frac{\partial}{\partial \mathbf{r}_b} \left[ B_{ab}(\mathbf{r},\tau, t-\tau)f(\mathbf{r}, \tau) \right] \right).$$

(8)

We suggest that the PTD function is independent of $f(\mathbf{r},t)$, therefore the problem is linear.

III. INFLUENCE OF THE EXTERNAL FIELDS

One of the main sources of inhomogeneity is an external field, which also provides the prescribed dependence of the PTD function on $\tau$. In other words we can suggest, in the particular case considered, that the dependence of $W(\mathbf{u},\mathbf{r}, \tau, t-\tau)$ on the arguments $\mathbf{r}$, $\tau$ is connected with a functional dependence on the external field.
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\[ W(u, r, \tau, t - \tau) = W(u, t - \tau; F(r, \tau)). \] (9)

If an external field is absent the PTD function is a function of the modulus \( u = u \), which implies that \( A \alpha = 0 \) and \( B = \delta_{\alpha \beta} \beta_0 (t - \tau) \) with

\[ B_0 (t - \tau) = \frac{1}{2 s} \int d^ru^2 W_0 (u, t - \tau). \] (10)

For relatively weak external fields the functional (9) can be linearized as

\[ W(u, t - \tau; F(r, \tau)) = W_0 (u, t - \tau) + W_1 (u, t - \tau) (u \cdot F(r, \tau)). \] (11)

The functions \( W_0 (u, t - \tau) \) and \( W_1 (u, t - \tau) \) are equal to \( W(u, t - \tau; F = 0) \) and the functional derivative \( \delta W(u, t - \tau; F(r, \tau)) / \delta u \cdot F(r, \tau) \) respectively. Then the functions \( A \alpha \) and \( B_{\alpha \beta} \) take the form

\[ A \alpha (r, \tau, t - \tau) = \frac{1}{2} F_{\alpha} (r, \tau) \int d^ru^2 W_1 (u, t - \tau) = F_{\alpha} (r, \tau) L(t - \tau), \] (12)

where \( L(t - \tau) \) is given by

\[ L(t - \tau) = \frac{1}{2} \int d^ru^2 W_1 (u, t - \tau). \] (13)

and

\[ B_{\alpha \beta} (r, \tau, t - \tau) = \delta_{\alpha \beta} \beta_0 (t - \tau). \] (14)

The generalized diffusion equation, Eq. (8), takes the form

\[ \frac{\partial f(r, t)}{\partial t} = \frac{d}{dt} \int_0^t \int d^r \tau [L(t - \tau) \nabla (F(r, \tau) f(r, \tau)) + B_0 (t - \tau) \Delta f(r, \tau)]. \] (15)

In general this equation contains two different functions \( B_0 \) and \( L \) depending on the argument \( t - \tau \). For the case of a time-independent inhomogeneous one-dimensional external field and in the particular case of the kernel dependence on time \( L(t - \tau) \sim (t - \tau)^{-\gamma} \) and \( B_0 (t - \tau) \sim (t - \tau)^{-\gamma - 1} \) \((0 < \gamma < 1)\) we arrive at the result, obtained in [20,21] for the fractional Fokker-Planck equation. This kind of time dependence for the kernel is typical for the subdiffusion processes.

The time-dependent mobility for the diffusion process (in the particular case of exponentially oscillating time-dependent external field and a time-independent diffusion coefficient) has been introduced in [22].

If the functional \( W(u, t - \tau; F(r, \tau)) \) is multiplicative, namely, \( W(u, t - \tau; F(r, \tau)) = W(u; F(r, \tau)) \chi(t - \tau) \), Eq. (15) can be simplified to

\[ \frac{\partial f(r, t)}{\partial t} = \frac{d}{dt} \int_0^t \int d^r \tau [D \Delta f(r, \tau) - b \nabla (F(r, \tau) f(r, \tau))]. \] (16)

Here \( b \) and \( D \) are constants, determined by the relations

\[ b = -\frac{1}{s} \int d^ru^2 \tilde{W}_1 (u) \] (17)

with \( \tilde{W}_1 (u) = \delta \tilde{W} (u; F(r, \tau)) / \delta (u \cdot F(r, \tau)) \) and

\[ D = \frac{1}{2s} \int d^ru^2 \tilde{W}_0 (u). \] (18)

As is easy to see for the external field \( F(r, \tau) \), which change slow in time [comparing with other characteristic time scales of the problem, e.g., with the time scale of the retardation function \( \chi(t - \tau) \) Eq. (16) coincides for the one-dimensional case with the diffusion equation in [13].

The physical meaning of the multiplicative structure of the functional \( W \) is that the independence of the time delay of the random walkers is independent of the external field. The dimensionless function \( \chi \) in this simple case is associated with the hopping-distribution function \( \psi (t) = \lambda \psi (\lambda t) \) introduced in the master equation by Scher and Montroll [15], with \( \lambda = 1 / \tau_0 \) \( (\tau_0 \) is the characteristic waiting time for the hopping distribution). Laplace transformations of these functions \( \chi \) and \( \psi \) relate them as follows:

\[ \chi (z) = \frac{\psi (z)}{1 - \psi (z)}. \] (19)

For an exponential hopping-time distribution \( \psi (t) = \lambda \exp (-\lambda t) \), where \( \lambda = 1 / \tau_0 \), we have \( \psi (z) = 1 / (1 + z) \), \( \chi (z) = 1 / z \), and \( \chi (t) = \chi (\lambda t) = 1 \). In this case Eq. (16) reduces to the usual diffusion equation in an external field with diffusion coefficient \( D \) and mobility \( b \),

\[ \frac{\partial f(r, t)}{\partial t} = D \Delta f(r, t) - b \nabla (F(r, t) f(r, t)). \] (20)

IV. HYDRODYNAMIC APPROACH

In order to better understand the situation on the basis of a nonphenomenological approach, let us consider the charged particles with an inhomogeneous density in the external electrical field in the hydrodynamic approximation. The equation for the density \( n(x, t) \) reads

\[ \frac{\partial}{\partial t} n(x, t) + \text{div} \mathbf{j}(x, t) = 0, \] (21)

where \( \mathbf{j}(x, t) = n(x, t) \mathbf{v}(x, t) \) and \( \mathbf{v}(x, t) \) is the hydrodynamic velocity. In the hydrodynamic approximation, when the charged particles (with charge \( e \) and mass \( m \)) move in the medium under the action of an external time-dependent electrical field \( \mathbf{E}(x, t) \), the equation of motion has (for constant temperature) the form

\[ \frac{\partial}{\partial t} [n(x, t) \mathbf{v}(x, t)] + \nabla \cdot [n(x, t) \mathbf{v}(x, t) \mathbf{v}(x, t)] = -\frac{T}{m} \nabla n(x, t) + \frac{e}{m} \mathbf{E}(x, t) n(x, t) - \nu n(x, t) \mathbf{v}(x, t). \] (22)
Here $\nu$ is the effective frequency of collisions with the particles of the thermostat. In the linear by $\nu$ approximation the solution of Eq. (23) gives the closed expression for the flux $j$ via the density $n(x,t)$. This solution for time-independent $\nu$ has the form

$$
\mathbf{j}(x,t) = \int_{-\infty}^{t} dt' \exp[-\nu(t-t')] \left[ \frac{e}{m}[n(x,t')\mathbf{E}(x,t')] - \frac{T}{m} \nabla n(x,t')] \right].
$$

(23)

Inserting this value of $\mathbf{j}(x,t)$ in Eq. (21) leads to the diffusion equation

$$
\frac{\partial n(x,t)}{\partial t} = -\int_{-\infty}^{t} dt' \{D(t-t')\Delta n(x,t') - e\mu(t-t') \nabla [n(x,t')\mathbf{E}(x,t')]\},
$$

(24)

where in the case considered the “effective diffusion function” and “effective mobility function” are given by $D(t) = T \exp(-\nu t)/m$ and $\mu(t) = \exp(-\nu t)/m$, respectively. If the functions $\mathbf{E}(x,t)$ and $n(x,t)$ change in time very slowly (the characteristic time for its change $\tau \approx 1/\nu$), Eq. (24) reduces to the standard form of the diffusion equation

$$
\frac{\partial n(x,t)}{\partial t} = D_0 \Delta n(x,t) - e\mu_0 \nabla [n(x,t)\mathbf{E}(x,t)].
$$

(25)

Here we introduced the notations $D_0 = T/m\nu$ for the diffusion coefficient and $\mu_0 = 1/m\nu$ for the mobility coefficient.

Equation (24) represents a particular case (in hydrodynamic approximation) of the general relations between the fluxes and acting thermodynamical and the external forces. Of course, the time integration in Eq. (24) can be considered in the normal hydrodynamical conditions as an excess of accuracy due to the inequality $\tau \approx 1/\nu$. For us, however, the most important result is the general structure of Eq. (24), which demonstrates that the time integral includes the electric field $\mathbf{E}(x,t)$. The structure of Eq. (24) confirms the result of our consideration on the basis of the generalized master equation for diffusion [14], where the time-dependent electric field is included in the time integration.

Since the equilibrium density in the external time-independent potential $\phi(x)$ has a form of the Boltzmann distribution $n(x) = \exp[-\phi(x)/T]$, the diffusion and mobility coefficients satisfy the Einstein relation $D_0 = \mu_0 T$. In the considered case the same statement is valid also for the effective diffusion and mobility functions $D(t)$ and $\mu(t)$, namely $D(t) = T\mu(t)$. The general structure of the diffusion equation (24) is similar to the phenomenological equation (16) (with the appropriate renormalization of the kernel, which eliminates the external derivative of the time integral).

V. KINETIC APPROACH

Let us start with the kinetic equation for the distribution function in an electric field

$$
\frac{\partial f(p,x,t)}{\partial t} + v \frac{\partial f(p,x,t)}{\partial x} + eE(x,t) \frac{\partial f(p,x,t)}{\partial p} = I_{sr}(p,x,t).
$$

(26)

Here $I_{sr}$ is some kind of “collision integral,” which can describe in general, as we show below, not only real collisions of particles, but also (for the appropriate problems, e.g., moving of the alive objects) the more complicated processes, as the displacements with some pauses, etc.

For simplicity we consider the one-dimensional case $s = 1$, but the generalization for the cases $s = 2,3$ is trivial. The distribution function $f(p,x,t)$ is normalized to the density $n(x,t)$,

$$
\int dp f(p,x,t) = n(x,t).
$$

(27)

For the case when the collision integral conserves the total number of particles, i.e.,

$$
\int dp I_{sr}(p,x,t) = 0,
$$

(28)

integration by $p$ leads to the continuity equation

$$
\frac{\partial n(x,t)}{\partial t} + \text{div } j(x,t) = 0.
$$

(29)

To calculate the flux $j(x,t)$ let us use the Fokker-Planck approximation for the collision integral $I_{sr}(p,x,t)$ and rewrite for this case Eq. (26) in the form

$$
\frac{\partial f(p,x,t)}{\partial t} + v \frac{\partial f(p,x,t)}{\partial x} + eE(x,t) \frac{\partial f(p,x,t)}{\partial p} = \frac{\partial}{\partial p} \left( \beta pf(p,x,t) + m^2 \tilde{D} \frac{\partial f(p,x,t)}{\partial p} \right).
$$

(30)

We suggest that the friction $\beta$ and the diffusion $\tilde{D}$ coefficients in velocity space are the constants, which satisfies the Einstein relation $\beta T = m \tilde{D}$. Integrating Eq. (30) by $p$ leads to the expression

$$
\frac{\partial j(x,t)}{\partial t} + \frac{\partial}{\partial x} \left[ \int dp v^2 f(p,x,t) \right] - \frac{e}{m} E(x,t)n(x,t) = - \beta j(x,t).
$$

(31)

If we assume that $f(p,x,t)$ has the quasiequilibrium form $f(p,x,t) = n(x,t)f_0(p)$, then we arrive at the following solution of Eq. (31) similar to Eq. (23),

$$
\mathbf{j}(x,t) = \int_{-\infty}^{t} dt' \exp[-\beta(t-t')] \left[ \frac{e}{m} n(x,t')\mathbf{E}(x,t') \right] - \langle v^2 \rangle \nabla n(x,t'),
$$

(32)

where for the Maxwellian distribution $f_0(p) = F_0(p)$ in the one-dimensional ($s = 1$) case $\langle v^2 \rangle = T/m$. In this case the diffusion equation is equivalent to Eq. (24) obtained in the hydrodynamic approach, but with the change $\nu \rightarrow \beta$ in the func-
turbation conductivity function in two parts: frequency-dependent conductivity of the particles. In the simple case considered the respective frequency-dependent conductivity $\sigma(\omega)$ is

$$\sigma(\omega) = \frac{i e^2 n_0}{m(\omega + i\nu)}. \quad (33)$$

Let us now consider the alternative case of the kinetic equation (26) when the collisions are negligible [$I_\nu = -\varepsilon f(p, x, t)$ with $\varepsilon \to 0$]. We also suppose that the electric field is weak and can be considered as a perturbation. To find the evolution of the density we split the distribution function in two parts: $f(p, x, t) = f_0(p, x, t) + f_1(p, x, t)$, where the perturbation $f_1$ is proportional to the electric field $E(x, t)$. The respective kinetic equations are

$$\frac{\partial f_0(p, x, t)}{\partial t} + v \frac{\partial f_0(p, x, t)}{\partial x} = 0, \quad f_0 = f_0(x - vt, p), \quad (34)$$

$$\frac{\partial f_1(p, x, t)}{\partial t} + v \frac{\partial f_1(p, x, t)}{\partial x} + \varepsilon E(x, t) \frac{\partial f_0(p, x, t)}{\partial p} = -\varepsilon f_1(p, x, t). \quad (35)$$

The continuity equations follow from Eqs. (34) and (35):

$$\frac{\partial n_0(x, t)}{\partial t} + \text{div} j_0(p, x, t) = 0, \quad (36)$$

where $j_0(x, t)$ describes the flux without the electrical field and

$$\frac{\partial n_1(x, t)}{\partial t} + \text{div} j_1(x, t) = 0, \quad (37)$$

where $j_1(x, t)$ describes the perturbation of the flux in the lowest order of the electric field.

The solution of Eq. (35) reads

$$f_1(p, x, t) = -e \int_{-\infty}^{t} dt' \exp[-\varepsilon(t-t')] \frac{\partial f_0(x - vt', p)}{\partial p} E[x - v(t-t'), t']. \quad (38)$$

Now we can calculate $j(x, t) = j_0(x, t) + j_1(x, t)$,

$$j_0(x, t) = \int dp v f_0(x - vt, p), \quad (39)$$

$$j_1(x, t) = \int dp v f_1(p, x, t)$$

$$= -e \int_{-\infty}^{t} dt' \exp[-\varepsilon(t-t')]$$

$$\times \int dp \frac{\partial f_0(x - vt', p)}{\partial p} E[x - v(t-t'), t']. \quad (40)$$

The latter equation can be rewritten as

$$j_1(x, t) = -e \int_{-\infty}^{t} dt' \exp[-\varepsilon(t-t')]$$

$$\times \int dp \frac{\partial f_0(x - vt', p)}{\partial p} \frac{\partial f_0(p)}{\partial p} E[x - v(t-t'), t'] \quad (41)$$

$$= \int_{-\infty}^{t} dt' \exp[-\varepsilon(t-t')]$$

$$\times \int dp \frac{\partial f_0(x - vt', p)}{\partial p} \delta E(x', t'). \quad (42)$$

In Eq. (42) the function $\pi(x, x', t, t')$ is equal to

$$\pi(x, x', t, t') = -e \int dp \frac{\partial f_0(x - vt, p)}{\partial p} \delta E(x - v(t-t')). \quad (43)$$

in which $f_0(x - vt, p)$ can also be written as $f_0(x' - vt', p)$. The function $\pi(x, x', t, t')$ takes into account the processes of space and time dispersion for the inhomogeneous and time-dependent distribution $f_0 = f_0(x - vt, p)$.

Let us choose the distribution function $f_0$ in the natural form $f_0(x - vt, p) = n_0(x - vt) f_0(p)$. Then finally we arrive at the expressions for the fluxes $j_0(x, t)$ and $j_1(x, t)$,

$$j_0(x, t) = \int dp v n_0(x - vt) f_0(p), \quad (44)$$

$$j_1(x, t) = -e \int_{-\infty}^{t} dt' \exp[-\varepsilon(t-t')]$$

$$\times \int dp \frac{\partial f_0(p)}{\partial p} n_0(x - vt) \delta E(x', t'). \quad (45)$$

The expression for $\pi(x, x', t, t')$ can be rewritten in the form

$$\pi(x, x', t, t') = -e \int dp \left( n_0(x - vt) \frac{\partial f_0(p)}{\partial p} \right)$$

$$- \frac{1}{m} f_0(p) \nabla_n n_0(x - vt) \delta E(x - x', t'). \quad (46)$$

Here and in what follows the operator $\nabla_n$ acts only on the function $n_0$ placed behind it. After integration by $v$ we find
\[\pi(x,x',t',t) = -em \frac{x-x'}{(t-t')^2} \left[ n_0([x-t-x]/(t-t')) \right] \]
\[\times \frac{\partial f_0(p)}{\partial p} \bigg|_{p = m(x-x')/(t-t')} \frac{1}{m} \nabla \]
\[\times n_0([x-t-x]/(t-t')) \left[f_0(p) \big|_{p = m(x-x')/(t-t')} \right]. \quad (47)\]

If \(E(x,t)\) is an oscillating function proportional to \(\sin(\omega t)\) or \(\cos(\omega t)\) or a function damping in time, the argument \(x-vt\) under the integral in Eq. (45) equals to \((x'-x)/t\). The expression of the particle density \(n_0(x-vt)\) (due to the presence of the \(\sigma\) function) in the limit of large \(t\) can be taken equal to \(x'\). In this case the function \(\pi\) can then in good approximation be written in the form

\[\pi(x,x',t,t') = -em \frac{x-x'}{(t-t')^2} \left[ n_0(x') \frac{\partial f_0(p)}{\partial p} \bigg|_{p = m(x-x')/(t-t')} \right] \]
\[\times \nabla n_0 \left[ x' \left( 1 + \frac{t'}{t} \right) - x\frac{t'}{t} \right]. \quad (48)\]

Therefore, the current \(j_1(x,t)\) for large \(t\) takes the form

\[j_1(x,t) = -e \int_{-\infty}^{t} dt' \exp[-e(t-t')] \int dx' \]
\[\times \int dx' \int dp \left[ n_0(x') \frac{\partial f_0(p)}{\partial p} \right] \]
\[+ \left[ \frac{1}{m} \nabla n_0(x') \right] f_0(p) \frac{1}{m} \nabla \delta(x-x' - v(t-t')) E(x',t'). \quad (49)\]

Then we arrive at the approximate expression of the “hydrodynamic” electrical flux in the collisionless case

\[j_1(x,t) = -e \int_{-\infty}^{t} dt' \exp[-e(t-t')] \int dx' \]
\[\times \left[ n_0(x') \mu'(x-x',t-t') + \frac{t'}{m} \nabla n_0(x') \nabla \right] \mu'(x-x',t-t') \quad (50)\]

where the generalized mobilities are given by

\[\mu'(x,t) = - \int dp \frac{\partial f_0(p)}{\partial p} \delta(x-vt) \quad (51)\]

and

\[\mu''(x,t) = - \int dp f_0(p) \delta(x-vt). \quad (52)\]

We can also introduce the mobility operator \(\bar{\mu}\)

\[j_1(x,t) = e \int_{-\infty}^{t} dt' \int dx' \exp[-e(t-t')] \]
\[\times E(x',t') \bar{\mu}(x,x',t,t') n_0(x'), \quad (53)\]

where \(\bar{\mu}(x,x',t,t')\) equals

\[\bar{\mu}(x,x',t,t') = - \int dp v \delta(x-x' - v(t-t')) \]
\[\times \left( \frac{\partial f_0(p)}{\partial p} + f_0(p) \frac{t'}{m} \nabla \right). \quad (54)\]

Therefore, Eq. (37) for the flux perturbation associated with the presence of the weak electrical field in the collisionless limit has the form

\[\frac{\partial n_1(x,t)}{\partial t} + e \nabla \int_{-\infty}^{t} dt' \int dx' \exp[-e(t-t')] \]
\[\times E(x',t') \bar{\mu}(x,x',t,t') n_0(x') = 0. \quad (55)\]

If the space dispersion is negligible \(\bar{\mu}(x,x',t,t') \sim \delta(x-x')\) and Eq. (55) transforms into

\[\frac{\partial n_1(x,t)}{\partial t} + \int_{-\infty}^{t} dt' \exp[-e(t-t')] \bar{\mu}(t,t') \]
\[\times \nabla \left[ E(x,t) n_0(x) \right] = 0. \quad (56)\]

Finally, for the case of slow changing in space of the density profile \(n_0(x)\), when the parameter \(v_0\) is \(L \ll 1\) \((\nu)\), \(\nu_0\) and \(L\) are the average velocity of the particles, the characteristic time scale for the electric field and the characteristic space scale for the density \(n_0(x)\), respectively the second term in brackets in Eq. (54) can be omitted and the operator \(\bar{\mu}\) modifies to the function \(\mu'\)

\[\bar{\mu}(x-x',t-t') \rightarrow \mu'(x-x',t-t') \quad (51)\]

\[\mu'(x-x',t-t') = - \int dp v \delta(x-x' - v(t-t')) \frac{\partial f_0(p)}{\partial p}. \quad (57)\]

Then the diffusion equation (55) simplifies to the form typical for the case with an electric field present,

\[\frac{\partial n_1(x,t)}{\partial t} + e \nabla \int_{-\infty}^{t} dt' \int dx' \exp[-e(t-t')] \mu'(x',t') \]
\[\times \mu'(x-x',t-t') n_0(x') = 0. \quad (58)\]

Evidently the function \(\mu'(x,t)\) is simply connected with the conductivity \(\sigma(x,t)\) (in the case considered with the collisionless conductivity) by the equality \(\sigma(x,t) = \nu_0\mu'(x,t)\).

This consideration provides the evident answer on how the time-dependent electrical field should be included in the diffusion equation and permits us to make the choice between the different forms of the diffusion equations considered earlier [14]. The structure of Eqs. (24), (32), and (58) confirms the result of the generalized diffusion equation, introduced in the papers [10,11] (on the example of some par-
VI. STOP-MOVE COLLISIONS

Now let us consider on the kinetic level the problem of transport for the particles, which can move in a time-dependent external electric field as the quasifree particles, but can be trapped and stay in the rest state during some time. The similar problem has been consider for the time-independent external field on the basis of the generalized Fokker-Planck equation in [23].

Let us introduce a “collision” integral I, that takes into account the specific “jumps” of the particles,

\[ I = - v f(p, x, t) + \int_{0}^{t} dt' \psi(t-t')f(p, x, t'). \]  

(59)

Therefore the kinetic equation reads

\[ \frac{\partial f(p, x, t)}{\partial t} + v \frac{\partial f(p, x, t)}{\partial x} + eE(x, t) \frac{\partial f(p, x, t)}{\partial p} = - v f(p, x, t) + \int_{0}^{t} dt' \psi(t-t')f(p, x, t'). \]  

(60)

This “stop-move” collision integral describes the moving particles, which may change from a “moving” state to the “rest” state and vice versa. We assume that the change from the “rest” state to “moving” state takes place with the recovering of the momentum distribution. The momentum distribution of the moving particles which leave the phase volume \( \{dx, dp\} \) at the moment \( t' \) at the point of the phase space \( x, p \) is equivalent to the momentum distribution of the particles, which arises from the “rest” state at the position \( x \) for \( t > t' \), with the delay time \( t - t' \). More complicated situations will be considered in a separate study. The function \( \psi(t) \) characterizes the probability for the particles to stay in a state of rest during a time span \( t - t' \).

Let us consider the conservation laws for the kinetic equation with such jumps. The continuity equation reads

\[ \frac{\partial n_{f}(x, t)}{\partial t} + \text{div} j(x, t) \]

\[ = \int dp I(p, x, t) \]

\[ = - v n_{f}(x, t) + \int_{0}^{t} dt' \psi(t-t')n_{f}(x, t'). \]  

(61)

We have distinguished between the “flying” particles and the particles at “rest” state. The function \( f(p, x, t) \) is the distribution of the “flying” particles \( (p \neq 0) \). We also introduce the density of the “rest” \( (p=0) \) particles \( n_{f}(x, t) \). We use the “stop-move collision” term for the process of transferring between the “flying” and the “rest” states.

The conservation of the total number of particles reads

\[ \int dx [n_{f}(x, t) + n_{f}(x, t)] = N, \]  

where \( N \) is the constant. There is also the evident equality

\[ \frac{\partial n_{f}(x, t)}{\partial t} = v m f(x, t) - v \int_{0}^{t} dt' \psi(t-t')n_{f}(x, t'). \]  

(63)

From Eqs. (60) and (63), it follows that

\[ \frac{\partial n_{f}(x, t)}{\partial t} + \frac{\partial n_{f}(x, t)}{\partial t} + \text{div} j(x, t) = 0. \]  

(64)

Equations for the numbers of “free” and “rest” particles are

\[ \frac{\partial n_{f}(x, t)}{\partial t} = - v n_{f}(x, t) + \int_{0}^{t} dt' \psi(t-t')n_{f}(x, t'), \]  

(65)

\[ \frac{\partial n_{f}(x, t)}{\partial t} = v n_{f}(x, t) - \int_{0}^{t} dt' \psi(t-t')n_{f}(x, t'). \]  

(66)

Integration of Eq. (64) by \( x \) leads to Eq. (62).

Now let us integrate the kinetic equation by \( p \) with the multiplier \( p \). The relevant equation of motion reads (dimension \( s=1 \))

\[ \frac{\partial j(x, t)}{\partial t} + \int dp v^{2} \frac{\partial f(p, x, t)}{\partial x} + \frac{eE(x, t)}{m} n_{f}(x, t) \]

\[ = - v j(x, t) + \int_{0}^{t} dt' \psi(t-t')j(x, t'). \]  

(67)

We will assume that the integral term with \( f(p, x, t) \) in Eq. (67) can be represented as \( d(t) \frac{\partial n_{f}(x, t)}{\partial x} \). This representation is exact for such a form of the distribution function \( f(p, x, t) = \tilde{f}(p, t)n_{f}(x, t) \), for example. The function \( d(t) \) in this case equals

\[ d(t) = \int dp v^{2} \tilde{f}(p, t). \]  

(68)

For the Maxwellian distribution \( d(t) \) is time independent \( d(t) = d = T/m \), where \( T \) is the temperature. In general \( d(t) = \langle v^{2} \rangle \) is the average velocity of the “flying” particles. Equation (67) represents the integrodifferential connection of \( j(x, t) \) and \( n_{f}(x, t) \),

\[ \frac{\partial j(x, t)}{\partial t} + d(t) \frac{\partial n_{f}(x, t)}{\partial x} = - \frac{eE(x, t)}{m} n_{f}(x, t) \]

\[ = - v j(x, t) + \int_{0}^{t} dt' \psi(t-t')j(x, t'). \]  

(69)

In order to solve this equation we use the adiabatic switched process for “hopping collisions” \((i_{0} = -\infty)\) and the Fourier-transform of Eq. (69) by time

\[ \{ - i \omega + v [1 - \psi(\omega)] \} j(x, \omega) = \varphi(x, \omega), \]  

(70)

where
\[ \psi(\omega) = \int_0^\infty d\tau \exp(i\omega\tau)\psi(\tau), \]  

\( (71) \)

and we denote

\[ \varphi(x,t) = -d(t)\frac{\partial n_j(x,t)}{\partial x} + \frac{eE(x,t)}{m}n_j(x,t). \]  

\( (72) \)

The solution for the flux is then

\[ j(x,t) = \int \frac{d\omega}{2\pi} \frac{\exp(-i\omega t)}{1 - \psi(\omega)} \varphi(x,\omega) \]  

\( (73) \)

or

\[ j(x,t) = \int dt' \int \frac{d\omega}{2\pi} \frac{\exp(-i\omega(t-t'))}{1 - \psi(\omega)} \varphi(x,\omega) \]  

\( (74) \)

The flux can be rewritten by introducing the function \( \chi(t-t') \),

\[ j(x,t) = \int dt' \chi(t-t') \left( d(t')\frac{\partial n_j(x,t')}{\partial x} - \frac{eE(x,t')}{m}n_j(x,t') \right). \]  

\( (75) \)

where

\[ \chi(t-t') = \int \frac{d\omega}{2\pi} \frac{\exp(-i\omega(t-t'))}{1 - \psi(\omega)}. \]  

\( (76) \)

Inserting this flux into the continuity equation we find the diffusion equation in the form

\[ \frac{\partial n_j(x,t)}{\partial t} = \int dt' \chi(t-t') \left( d(t')\Delta n_j(x,t') \right) - \frac{e}{m} \nabla \left[ E(x,t')n_j(x,t') \right], \]  

\( (77) \)

which, for time-independent \( d \), is the particular case of Eq. (24), based on the general master equation for diffusion, introduced in [1,2]. An essential feature of the diffusion process is the character of the influence of the time-dependent external field placed in Eq. (77) under the time integral. This equation coincides formally with the hydrodynamic equation (24) if \( \chi(t-t') \) is the retarded function \( \chi(t-t')=0 \) for \( t<t' \).

## VII. Conclusions

We show that the generalized master equation with two times, which has been introduced in [10,11], can describe the influence of inhomogeneous and time-dependent external fields on the diffusion processes. Linearization of the general master equation in the external field leads to essential simplifications. In this case the diffusion processes depend, in general, on two different functions of time, which describe retardation, or frequency-dependent mobility and diffusion, in particular, due to the finite time of occupation and transferring particles in space in the presence of the external field. Relations with simpler models are established. The rigorous consideration on the basis of the hydrodynamic approach and various kinetic equations confirms the results of the phenomenological approach of the generalized master equation. Of course, the kernel functions \( W \) or \( P \) can only be defined in a concrete way in the framework of particular physical models, e.g., on the basis of kinetic theory with specific collision integrals, describing the stochastic motion with retardation. We also introduced the stop-move collision integral, which describes the processes of diffusion with particles continuously changing from moving to resting and back. The appropriate kinetic equation is solved for a time-dependent external field, which also confirms the results of the diffusion master equation approach. This type of motion is very common in Nature and the introduced collision integral can easily be generalized to more complex processes of stop-move motion. The analysis presented in this paper opens up opportunities to consider a wide class of the problems of normal and anomalous transport in external fields on the basis of the generalized master equation with two times. The Einstein relations in general are not applicable to the case of the non-stationary external field, but in the particular cases can be valid for the time-dependent diffusion and mobility functions, as it was found above in the present paper.

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