STOCHASTIC THEORY OF DIFFUSION

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Markov and non-Markov forms of the diffusion equations are obtained, and they are analyzed in translationally invariant systems. The relationships between the diffusion flux and the thermodynamic force are discussed. The inertial effects in Brownian particle diffusion and stochastic models related to the hyperbolic diffusion equation are examined.

One of the problems of the theory of high-speed processes is the analysis of the general structure of the transport equations and the investigation of the space—time variance of the nonequilibrium kinetic coefficients [1-5]. Since in the majority of cases the approximate calculation of kinetic coefficients is related to the approximation of the real transport process by a stochastic model, it is interesting to describe high-speed transport processes directly in the terminology of stochastic representations.

The phenomenon of diffusion of nonmutually interacting particles and of self-diffusion in classical systems is analyzed in this paper on the basis of a model description for which the particle velocity $\mathbf{u}(t)$ is approximated by some random process, whose statistical properties qualitatively reflect reality. The classical example of such an approximation is Brownian motion theory, in which $\mathbf{u}(t)$ is considered as a Gaussian process. As is known, this theory describes well the situation for which a change in particle velocity because of interaction with the surrounding medium is sufficiently small. In the more general case of strong changes in the velocity (linear Boltzmann systems) a jump process can be used to approximate $\mathbf{u}(t)$, as has been shown by Tolubinskii [6, 7].

The motion of individual particles in diverse physical systems can be described, on the average, in the terminology of the probability $P(t, \mathbf{r}; t_0, \mathbf{r}_0)$ of a particle going from the point $\mathbf{r}_0$ where it is at the time t_0, to the point $\mathbf{r}$ at the time t. In the hydrodynamic limit P satisfies the known parabolic diffusion equation (the approximation of a random diffusion process [8]). The situation is considerably more complicated for small times and high space gradients because of the influence of the detailed structure of the particle velocity fluctuations on its motion in coordinate space in this case. These fluctuations depend on the nature of the forces acting on the particle and can differ substantially in different physical systems.

The discussion of the possible forms of the equations describing diffusion for small times is indeed the subject of this paper.

Derivation of the Fundamental Equations

The stochastic equation describing particle motion in coordinate space is

$$\frac{d\mathbf{r}(t)}{dt} = \mathbf{u}(t, \mathbf{r}(t)). \tag{1}$$

We assume here that the random field $\mathbf{u}$ is defined by its correlation functions. For each trajectory $\mathbf{u}(t, \mathbf{r})$, a probability density "not averaged" in $\mathbf{r}$-space $\mu(t, \mathbf{r})$ can be introduced. Thus, if it is assumed that the particle is at the point $\mathbf{r}_0$ at $t = 0$, and $\mathbf{r}_u(t)$ denotes the solution of (1) for a specific function $\mathbf{u}(t, \mathbf{r})$ with $\mathbf{r}_u(0) = \mathbf{r}_0$, then

$$\mu(t, \mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_u(t)). \tag{2}$$

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The desired probability density P(t, **r**) is found by averaging (2) over all possible realizations **u**(t, **r**)

$$P(t, \mathbf{r}) = \langle \delta(\mathbf{r} - \mathbf{r}_u(t)) \rangle \equiv M\mu(t, \mathbf{r}), \tag{3}$$

where M is the mathematical expectation operation. The continuity equation

$$\frac{\partial \mu}{\partial t} = -\vec{\nabla}(\mathbf{V} + \mathbf{v})\mu, \tag{4}$$

follows from the definition of $\mu(t, \mathbf{r})$, where $\mathbf{V} = \langle \mathbf{u}(t, \mathbf{r}) \rangle$, $\mathbf{v} = \mathbf{u} - \mathbf{V}$.

Since the operators M and (I — M) are orthogonal projections, we obtain in the customary projection scheme [9]

$$\frac{\partial P(t, \mathbf{r})}{\partial t} + \vec{\nabla}\cdot\mathbf{V}P(t, \mathbf{r}) = \vec{\nabla}\cdot\int_0^t dt' \langle \mathbf{v}(t) U(t, t') \vec{\nabla}\cdot\mathbf{v}(t') \rangle P(t', \mathbf{r}), \tag{5}$$

where

$$U(t, t') = T\exp\left\{-\vec{\nabla}\cdot\int_{t'}^{t} [\mathbf{V}(t_1) + (I - M)\mathbf{v}(t_1)]\, dt_1\right\}. \tag{6}$$

Within the framework of the stochastic approach assumed here, the equation obtained is exact and valid in all physical situations in which the particle velocity can be approximated by an arbitrary random process. Here (5) has an integrodifferential of "non-Markov" form. This is a result of the finiteness of the velocity correlation time, which results in the process **r**(t) not being a Markov process.

However, a differential "Markov" form of the exact diffusion equation is possible. The effects of remembering the process **r**(t) are hence reflected in the time dependence of the differential equation operator. Let us introduce the evolution operator S(t, t') of (4):

$$S(t, t') = T\exp\left\{-\vec{\nabla}\cdot\int_{t'}^{t} [\mathbf{V}(t_1) + \mathbf{v}(t_1)]\, dt_1\right\}. \tag{7}$$

It follows from the definition of S(t, t') that

$$\mu(t') = S^{-1}(t, t')\mu(t) \tag{8}$$

from which by taking account of the identity

$$P(t') = MS^{-1}(t, t')[P(t) + (I - M)\mu(t)] \tag{9}$$

we obtain, analogously to [10],

$$\frac{\partial P(t, \mathbf{r})}{\partial t} + \vec{\nabla}\cdot\mathbf{V}P(t, \mathbf{r}) = G(t)P(t, \mathbf{r}), \tag{10}$$

where

$$G(t) = \langle \vec{\nabla}\mathbf{v}(t)[I + X(t)]^{-1}X(t) \rangle, \tag{11}$$

$$X(t) = \int_0^t U(t, t')\vec{\nabla}\mathbf{v}(t') MS^{-1}(t, t')\, dt'. \tag{12}$$

Analysis of the Diffusion Equations in Translationally Invariant Systems

Let **v**(t) be independent of **r** and **V** = const. This case can be realized in particle motion under the effect of a constant force field in a homogeneous thermodynamically equilibrium medium, say, when the perturbation it exerts on the spatial distribution of medium particles is negligible.

Let us examine the general structure of the diffusion equations which take account of the influence of equilibrium particle-velocity fluctuations on its motion in coordinate space by assuming the initial velocity distribution to be equilibrium. Since the transformation $P'(t, \mathbf{r}) = \exp(\vec{\nabla}\mathbf{V}t)P(t, \mathbf{r})$ permits elimination of the convective term in (5) and (10) in this case, we shall henceforth seek it by considering such a transformation carried out.

1. An expression for the diffusion flux **j**(t, **r**) in the form of a convolution of the thermodynamic

force with the operator kernel* follows from (12):

$$\mathbf{j}(t,\ \mathbf{r}) = -\int_0^t dt' \langle \mathbf{v}U(0,\ t')\,\mathbf{v}(t')\rangle \cdot \vec{\nabla} P(t-t',\ \mathbf{r}). \tag{13}$$

Expanding U in a series in **V** and introducing the notation

$$\mathbf{d}_n(t') = \int_0^{t'} dt_1 \ldots \int_0^{t_{n-3}} dt_{n-2} \langle \mathbf{v}(t')(I-M)\,\mathbf{v}(t_1)\ldots(I-M)\,\mathbf{v}(t_{n-2})\,\mathbf{v}\rangle, \tag{14}$$

we represent (13) as

$$\mathbf{j}(t,\ \mathbf{r}) = \sum_{n=2}^{\infty}(-1)^{n-1}\int_0^t \mathbf{d}_n(t') : \vec{\nabla}^{n-1} P(t-t',\ \mathbf{r})\,dt', \tag{15}$$

where the product of the vectors is understood to be a tensor, and the colon defines the convolution operation; (15) yields a dependence of the diffusion flux on the power of the density gradient which is not local in time. The expression (13) can also be represented as

$$\mathbf{j}(t,\ \mathbf{r}) = -\int_0^t dt' \int dr' \mathbf{D}(t',\ \mathbf{r}') \cdot \vec{\nabla} P(t-t',\ \mathbf{r}-\mathbf{r}'), \tag{16}$$

where

$$\mathbf{D}(t,\ \mathbf{r}) = \langle \mathbf{v}U(0,\ t)\,\mathbf{v}(t)\rangle\,\delta(\mathbf{r}); \tag{17}$$

and (16) is analogous to the main relationship in the thermodynamics of irreversible processes [12]

$$\mathbf{j}(\omega,\ \mathbf{k}) = -\mathbf{D}^{(0)}(\omega,\ \mathbf{k}) \cdot i\mathbf{k}P(\omega,\ \mathbf{k}), \tag{18}$$

in which, however,

$$\mathbf{D}^{(0)}(\omega,\ \mathbf{k}) = \langle \mathbf{jj}(t,\ r)\rangle_{\omega,k} \tag{19}$$

is a diffusion coefficient possessing a space — time variance, independent of the thermodynamic force (ikP). The relationship (18) holds in the first order of the thermodynamic force. In this case it follows from the exact expression (16) in the first order in M upon the expansion of U in (13).

An analysis of the "Markov" form of the diffusion equation (10) results in a different expansion of the diffusion flux in a power series in the density gradient from (15). Expanding (11) in a power series in $\underline{\nabla}$ and introducing the notation

$$\mathbf{D}_n(t) = \int_0^t dt_1 \ldots \int_0^{t_{n-2}} dt_{n-1} \langle \mathbf{v}(t)\ldots\mathbf{v}(t_{n-1})\rangle^c, \tag{20}$$

where $\langle \mathbf{v}(t_1)\ldots\mathbf{v}(t_n)\rangle^c$ are the semi-invariants of the velocity correlation functions, we obtain

$$\mathbf{j}(t,\ \mathbf{r}) = \sum_{n=2}^{\infty}(-1)^{n-1}\mathbf{D}_n(t) : \vec{\nabla}^{n-1} P(t,\ \mathbf{r}). \tag{21}$$

It must be noted that this result can also be obtained by a more direct means by expanding S(t, t') in semi-invariants of the correlation functions **v**(t) analogously to [13-15]. However, the derivation of (10) establishes a direct connection between the differential and integrodifferential forms of the diffusion equations.

However, (21), in contrast to (15), is a local form of the dependence of the flux on the powers of the density gradients. Taking (21) into account, the "Markov" form of the diffusion equation becomes

$$\frac{\partial P(t,\ \mathbf{r})}{\partial t} = \sum_{n=2}^{\infty}(-1)^n \mathbf{D}_n(t) : \vec{\nabla}^n P(t,\ \mathbf{r}). \tag{22}$$

Hence (15) and (21) can represent the basis for an approximate analysis of fast diffusion processes at small gradients. However, it must be kept in mind that these expansions are not equivalent. Thus, it will be shown below that by conserving the first terms in (15) and (21), we shall arrive at distinct diffusion situations.

2. The coefficients $\mathbf{D}_n$ and $\mathbf{d}_n$ with odd n are zero in the absence of external fields in an isotropic

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*An expression analogous to (13) has been obtained in [5, 11] in the case of particle diffusion in a linear Boltzmann system by the direct application of the projection operators method to the kinetic equation.

medium. In this case, (5) and (10) describe the free relaxation of arbitrary spatially inhomogeneous density distributions.

Let us consider the approximation associated with the possibility of describing such relaxation by a parabolic diffusion equation and the possibility of thereby approximating the motion in coordinate space by a Markov random process. When the initial distribution $P(0, \mathbf{r})$ possesses a bounded Fourier spectrum ($P(0, \mathbf{k}) = 0$ for $k > k_{max}$) it is convenient to go over to the Fourier representation and to write $P(t, \mathbf{k})$ as

$$P(t, \mathbf{k}) = \langle \exp\left[i\mathbf{k} \cdot \int_0^t \mathbf{v}(t')\, dt'\right] \rangle P(0, \mathbf{k}). \tag{23}$$

An expression similar to (23) has been studied in [16], where it is shown that for $t \gg \tau_V$, $T_k^{-1} = (1/3)k^2 \langle v^2\rangle \tau_V \ll \tau_V^{-1}$

$$P(t, \mathbf{k}) = P(0, \mathbf{k}) \exp(-t/T_k). \tag{24}$$

Hence, P satisfies the parabolic diffusion equation

$$\frac{\partial P(t, \mathbf{r})}{\partial t} = D\Delta P(t, \mathbf{r}), \tag{25}$$

where $D = (1/\langle v^2\rangle)$ is the diffusion coefficient, and $\tau_V = (1/\langle v^2\rangle) \int_0^\infty \langle \mathbf{v}\cdot\mathbf{v}(t)\rangle dt$. Therefore, the parabolic equation (25) is applicable to the description of the relaxation of slightly inhomogeneous density perturbations $k_{max}^2 \ll 3/\langle v^2\rangle \tau_V$ at the time of large times and velocity correlations τ_V.

To investigate the domain of applicability of (25) in the more general case of strongly localized perturbations [when $P(t, \mathbf{r})$ contains a Fourier component and with large k], let us examine the approximation associated with the derivation of (25) from the exact equation (22) for $P(0, \mathbf{r}) = \delta(\mathbf{r})$. Let us represent the formal solution of (22) as

$$P(t, \mathbf{r}) = \exp\left[\sum_{n=2}^{\infty} \int_0^t dt' \mathbf{D}_{2n}(t') : \vec{\nabla}^{2n}\right] P^{(0)}(t, \mathbf{r}), \tag{26}$$

where

$$P^{(0)}(t, \mathbf{r}) = \exp\left[\int_0^t dt' \mathbf{D}_2(t') : \vec{\nabla}^2\right] \delta(\mathbf{r}) \tag{27}$$

which is a solution of (25) for $t \gg \tau_V$. Expanding the exponential operator in (26) in a power series in the gradients, taking account of their effect on $P^{(0)}$ for $t \gg \tau_V$, and estimating the generator terms by assuming that $D_{2n}(\infty) \lessgtr (\langle v^2\rangle/3)^n \tau_V^{2n-1}$ [14, 16], we obtain $P(t, \mathbf{r}) \simeq P^{(0)}(t, \mathbf{r})$ for $t \gg \tau_V$ and $\mathbf{r}^2 \ll Dt$. These conditions indeed establish the domain of applicability of (25) in the case of localized density perturbations. However, it must be noted that the estimates presented for $\mathbf{D}_{2n}(\infty)$ are not valid when $\mathbf{v}(t)$ can be approximated in the asymptotic by a δ-correlated process of the pulse noise type which results in a generalized Poisson process $\mathbf{r}(t)$.*

Let us consider a quantity characterizing the perturbation-propagation velocity

$$c(t) = \frac{d}{dt} \sqrt{\langle r^2(t) \rangle}.$$

It is known that $c(t) \to \infty$ follows from (25) as $t \to 0$. From the exact equations $\langle r^2(t)\rangle = 2\delta : \int_0^t D_2(t')dt' \to \langle v^2\rangle t^2$ as $t \to 0$ and, therefore $c(t) \to \sqrt{\langle v^2\rangle}$.

3. Keeping only the first member in the expansion (21) of the diffusion flux, we obtain

$$\frac{\partial P(t, \mathbf{r})}{\partial t} = \mathbf{D}_2(t) : \vec{\nabla}^2 P(t, \mathbf{r}). \tag{28}$$

This approximation corresponds to the approximation of the particle velocity by a Gaussian random process for which $D_n(t) = 0$ for $n > 2$ according to (20). Such an approximation is possible for the description of Brownian motion.

The generalized Langevin equation [17]

*For example, a jump self-diffusion mechanism.

$$\frac{d\mathbf{v}(t)}{dt} = -\int_0^t \vec{\varphi}(t-t')\cdot\mathbf{v}(t')\,dt' + \mathbf{F}(t) \tag{29}$$

can be used to examine the diffusion of Brownian particles in a fluid subjected to hydrodynamic fluctuations. The expression for the attentuation matrix follows from the fluctuation—dissipation relationship

$$\langle \mathbf{F}(t)\mathbf{F}(t')\rangle = \langle \mathbf{vv}\rangle\cdot\vec{\varphi}(t-t'). \tag{30}$$

If $\mathbf{F}(t)$ is assumed a Gaussian process, then it follows from (29) that $\mathbf{v}(t)$ is also a random Gaussian process, and (28) is valid in this case. Let us present the result of calculation $\mathbf{D}_2(t)$ for an isotropic model by setting $\langle \mathbf{F}(t)\mathbf{F}(t')\rangle = (\langle v^2\rangle/3)\vec{\delta}\varphi_0 \exp(-t/\tau_c)$, i.e., by considering the process $\mathbf{F}(t)$ a Markov process

$$\mathbf{D}_2(t) = \delta\,\frac{\langle v^2\rangle}{3}\cdot\frac{e^{-\gamma t}}{\gamma^2-\varkappa^2}\left[2\gamma e^{\gamma t} - 2\gamma\,\mathrm{ch}\,\varkappa t - \frac{\varkappa^2+\gamma^2}{\varkappa}\,\mathrm{sh}\,\varkappa t\right], \tag{31}$$

where $\gamma = 1/2\tau_c$, $\varkappa = \sqrt{\gamma^2 - \varphi_0}$. For $\tau_c \to 0$, $\varphi_0 \to \infty$, $\tau_c\varphi_0 = \tau_v$ = const, which corresponds to approximating $\mathbf{F}(t)$ by a δ-correlated process, the known expression obtained in the investigation of the influence of inertial effects on Brownian diffusion [18, 19]

$$\mathbf{D}_2(t) = \vec{\delta}\,\frac{\langle v^2\rangle}{3}\,\tau_v\left(1 - e^{-t/\tau_v}\right) \tag{32}$$

follows from (31). For $t > \tau_v$ $\mathbf{D}_2(t) = \vec{\delta}\tau_v(\langle v^2\rangle/3)$ and (28) goes over into the Kramers — Smoluchowsky equation. Therefore, the conditions for applicability of the asymptotic diffusion equation in the Brownian motion case do not constrain the analysis to small volumes of coordinate space. Let us note that all the coefficients $\mathbf{d}_n$ in the "non-Markov" representation of (28) are not zero.

4. Now, let us examine the opposite physical situation which results in $\mathbf{d}_n = 0$ for $n > 2$ in a "non-Markov" form of the diffusion equation. In the one-dimensional case this situation is realized by approximating $\mathbf{v}(t)$ by a Markov random process with two states, $-v$ and v. We see by direct substitution that only the first member is hence retained in (15), and

$$j(t,\ x) = -v^2\int_0^t e^{-t'/\tau_v}\,\frac{\partial P(t-t',\ x)}{\partial x}\,dt'. \tag{33}$$

In this case the equation for $P(t,\ x)$ is a hyperbolic diffusion equation. The three-dimensional model resulting in the generalization of (33) is related to a Markov jump process $\mathbf{v}(t)$ whose distribution satisfies a linear equation of Boltzmann type with a transition probability density per unit time of the form

$$W(v,\ v') = \frac{1}{\tau_v v^2}\,\delta(\mathbf{v}-\mathbf{v}')\,\frac{1}{8}\sum_i \delta(\mathbf{n}-\mathbf{n}_i), \tag{34}$$

where $\mathbf{n}$ is the unit vector in the direction $\mathbf{v}$, $\mathbf{n}_i$ — are the eight directions from the center of a cube to its vertices. This model describes particle motion with a constant velocity and anisotropic dissipation with equal probability in the eight directions $\mathbf{n}_i$. Using the Markov property of this process, the particle-velocity correlation functions and the coefficients $\mathbf{d}_n(t)$ can be calculated. The diffusion equation hence obtained is not invariant relative to rotations of the coordinate system, which is a result of anisotropy of the dissipation. In a coordinate system whose axes are parallel to the edges of the cube related to the directions $\mathbf{n}_i$, $\mathbf{d}_2(t) = \delta(v^2/3)e^{-t/\tau_v}$, $\mathbf{d}_n(t) = 0$ for $n > 2$. Hence, in this coordinate system the three-dimensional equation

$$\tau_v\,\frac{\partial^2 P}{\partial t^2} + \frac{\partial P}{\partial t} = \frac{v^2}{3}\,\tau_v \Delta P \tag{35}$$

is valid. Under appropriate initial conditions, (35) describes free particle motion at the velocity $v/\sqrt{3}$ along each of the three isolated space directions at the times $t \ll \tau_v$. Hence, $P(x_i) = (^1/_2)[\delta(x_i - vt/\sqrt{3}) + \delta(x_i + vt/\sqrt{3})]$. At the same time, spherically symmetrical solutions of the wave equation do not describe free motion, and, therefore, (35) cannot be related to the model of motion with a constant velocity for $t < \tau_v$ and in the presence of spherical symmetry. The stochastic model of motion with a constant velocity, which admits of the spherically symmetric distribution $\mathbf{r}(t)$, is described by a single-velocity transport equation with isotropic scattering [20] and results in the following form of the coefficient $d_n(t)$:

$$d_{2n}(t) = \frac{v^{2n}}{(2n-2)!} t^{2n-2} e^{-t/\tau} \Pi \mathbf{n} [(- \Pi \mathbf{n}]^{2n-2} n, \quad d_{2n+1} = 0,$$

where $\Pi f(\mathbf{n}) = (1/4\pi) \int d\Omega f(\mathbf{n})$. Taking account of just $d_2(t)$ results in an equation of type (35) invariant relative to rotations; however, there is no foundation for neglecting the remaining coefficients for $t \lessapprox \tau_V$ in this case.

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