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Non-Markovian Brownian Motion in a Viscoelastic Fluid

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A theory of non-Markovian translational Brownian motion in a Maxwell fluid is developed. A universal kinetic equation for the joint probability distribution of position, velocity, and acceleration of a Brownian particle is derived directly from the extended dynamic equations for the system. Unlike the extended Fokker–Planck equation which corresponds to Mori–Kubo generalized Langevin equation and provides only with calculations of one-time moments, the universal kinetic equation obtained gives complete statistical description of the process. In particular, an exact generalized Fokker–Planck equation in the velocity space valid for any time instant is derived for the free non-Markovian Brownian motion. It shows that both the "master telegraph" and the respective kinetic equations, obtained in the molecular theory of Brownian motion, are type of approximations. The long and short time behavior of velocity and force correlations for a free Brownian particle is investigated in the general case of a nonequilibrium initial value problem. A corresponding diffusion equation in the coordinate space, and the generalized Einstein relation between the diffusion coefficient and the mobility are derived. © *1996 American Institute of Physics.* [S0021-9606(96)50115-0]

I. INTRODUCTION

Statistical description of Brownian motion belongs to the most fundamental problems in physics with a wide variety of applications. The Brownian motion of small particles suspended in a viscous fluid has been studied since 1905. In pioneering papers by Einstein,[1] Smoluchovski,[2] and Langevin[3] this motion has been treated as a Gaussian Markovian random process. The classical model of Brownian motion uses the simple Stokes formula for the hydrodynamic force acting on the spherical particle in a viscous incompressible fluid. This familiar Stoke's law was derived originally for the steady motion of a sphere. In 1851 Stokes[4] calculated the frequency-dependent friction coefficient for a sphere oscillating in a viscous quiescent fluid. The corresponding expression for motion with arbitrary changing velocity was found by Boussinesq in 1903. Thus the Brownian motion of a particle in a viscous, inertial fluid has to be considered as a non-Markovian random process because the frictional resistance of a particle depends on its history. The non-Markovian theory of Brownian motion in viscous fluid with due account for the hydrodynamic aftereffect described by Stokes–Boussinesq's formula was proposed by Vladimirsky and Terletsky[5] in 1945 and developed later by several authors.[6–9]

If the liquid surrounding moving particle is viscoelastic, as all the liquids are in fact,[6] the stochastic motion of a Brownian particle is non-Markovian, even if the inertia of the liquid is negligible.[10–14] The interpretation of the Brownian motion as a non-Markovian stochastic process is corroborated by the molecular theory which considers the motion of a heavy particle in a medium consisting of light particles.[15–18] Several statistical approaches to the study of non-Markovian random processes have been developed. They are summarized in reviews.[19–21]

This work analyzes the Brownian motion in a viscoelastic liquid with one relaxation time. The analysis is based on increasing the dimension of space of dynamical variables. In doing this, we introduce an additional variable representing the Markovian random force, which is considered as the solution of an additional stochastic equation with a delta-correlated random force. Thus the problem of Brownian motion in the simplest viscoelastic liquid can be reduced to the statistical description of an extended dynamical system subjected to a delta-correlated random force. The model of Brownian motion studied here is more realistic than the classical one, since it gives a finite variance of the acceleration (force) of a Brownian particle.

II. BROWNIAN DYNAMICS WITH MARKOVIAN RANDOM FORCE

The motion of an elastically bound Brownian particle in a quiescent viscoelastic liquid with a single relaxation time τ is described by the stochastic equations of motion

$$\frac{d}{dt} r_i = u_i ,$$

$$m \frac{du_i}{dt} = F_i - \alpha r_i + \Phi_i \tag{2.1}$$

with the relaxed friction

$$\tau \frac{dF_i}{dt} + F_i = -\zeta u_i . \tag{2.2}$$

Here **r** and **u** are the radius vector and velocity of the Brovnian particle of mass m;$\zeta = 6\pi a \eta$ is the friction coeffi-

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cient; a is the radius of the particle; η and τ are the viscosity coefficient and relaxation time of the fluid, respectively.

A systematic viscoelastic drag F_i and a random force Φ_i, along with an external quasielastic force $-\alpha r_i$, act on the particle. This description of the Brownian motion is valid only for time intervals that are not too short. In this case, the force exerted by the surrounding medium on the particle can be divided into systematic and random parts.

The solution of the hydrodynamic problem of inertialess translational motion of a spherical particle in a viscoelastic fluid with a single relaxation time[12,14] leads to the simple expression (2.2) for the viscoelastic friction force **F**. In the particular case of a viscous Newtonian fluid ($\tau=0$) it reduces to the well known Stokes' law

$$F_i^0=-\zeta u_i\,.$$

Equation (2.2) is easily solved to yield the following expression for the drag on the sphere in the Maxwell fluid in terms of the initial force F_i^0,

$$F_i(t)=F_i^0 e^{-(t-t_0)/\tau}-\int_{t_0}^{t} B(t-s)u_i(t)ds. \tag{2.3}$$

Here the friction kernel $B(t)$ is given by

$$B(t)=\frac{\zeta}{\tau}\,e^{-t/\tau}. \tag{2.4}$$

In the case of the zero initial condition, $F_i^0=0$, Eq. (2.3) is simplified to

$$F_i(t)=-\int_{t_0}^{t} B(t-s)u_i(t)ds. \tag{2.5}$$

For $t\gg t_0$, the drag on the sphere is

$$F_i(t)=-\int_{-\infty}^{t} B(t-s)u_i(t)ds. \tag{2.6}$$

Equations (2.3), (2.5), and (2.6) lead to different Langevin equations with memory. We will use here the universal relaxation Eq. (2.2).

The random force $\Phi_i(t)$ maintains the thermal motion of the particle. At any time, the average value of this force vanishes,

$$\langle \Phi_i(t)\rangle=0.$$

The random force $\Phi_i(t)$ being affected by a large number of equally strong independent impulses changes direction rapidly. Therefore one can assume that it satisfies the conditions of the central limit theorem and has the Gaussian distribution. According to the Callen–Welton fluctuation-dissipation theorem[22] the spectral density of the random force is determined by the relation

$$K_{ik}(\omega)=T(Z_{ik}[\omega]+Z_{ki}[-\omega]). \tag{2.7}$$

Here $K_{ik}(\omega)$ are the Fourier components of the correlation function $\langle \Phi_i(t)\Phi_k(0)\rangle$; $Z_{ik}[\omega]$ is the impedance matrix of the system and T is the temperature in energy units. We use the following notations for the two-side and one-side Fourier transforms:

$$x(\omega)=\int_{-\infty}^{\infty} x(t)e^{i\omega t}dt,\quad x[\omega]=\int_{0}^{\infty} x(t)e^{i\omega t}dt.$$

The impedance matrix of the system under study has the form

$$Z_{ik}[\omega]=(B[\omega]-\alpha/i\omega-i\omega m)\,\delta_{ik}\,. \tag{2.8}$$

Here $B[\omega]$ is the complex friction coefficient of a Brownian particle in a Maxwellian fluid,

$$B[\omega]=\frac{\zeta}{1-i\omega\tau}.$$

Substituting Eq. (2.8) into Eq. (2.7) yields the fluctuation-dissipation relation for the non-Markovian stochastic equations of motion (2.1),

$$K_{ik}(\omega)=2T\,\frac{\zeta}{1+(\omega\tau)^2}\,\delta_{ik}\,.$$

Since the resulting spectral density depends on the frequency ω, the random force $\Phi_i(t)$ is not delta-correlated. The corresponding correlation function has the form

$$\langle \Phi_i(t)\Phi_k(0)\rangle=T\,\frac{\zeta}{\tau}\,e^{-|t|/\tau}\delta_{ik}\,. \tag{2.9}$$

Thus the random force $\Phi_i(t)$ acting on a Brownian particle in a viscoelastic Maxwellian fluid is correlated exponentially. Its statistical properties do not depend on the quantity α characterizing the external force. In the limit $\tau\to 0$, the random force $\Phi_i(t)$ is represented by the Gaussian white noise, and Eq. (2.5) reduces to the familiar Einstein relation,

$$\langle \Phi_i(t)\Phi_k(0)\rangle=2T\zeta\,\delta(t)\,\delta_{ik}\,.$$

Note that Eq. (2.9) also follows from the fluctuation-dissipation theorem for non-Markovian Langevin equation with memory, obtained by Mori[22] and Kubo[23] from different approaches.

The Markovian random force $\Phi_i(t)$ can then be regarded as the solution of the first order stochastic differential equation[12,13]

$$\tau\,\frac{d}{dt}\,\Phi_i(t)+\Phi_i(t)=\xi_i(t) \tag{2.10}$$

with a delta-correlated random force $\xi(t)$,

$$\langle \xi_i(t)\xi_k(0)\rangle=2T\zeta\,\delta(t)\,\delta_{ik}\,, \tag{2.11}$$

and initial condition referred to $-\infty$. Equation (2.10) is a result of the solution for an inverse problem of the classical theory of Brownian motion—to obtain the white noise $\xi_i(t)$ from a random function with given statistical characteristics (2.9).

Equations (2.10) and (2.11) with arbitrary initial condition may be considered as a most general form of fluctuation-dissipation theorem for non-Markovian Langevin Eq. (2.1). The well known fluctuation-dissipation relation (2.9) is the special case for the initial condition referred to

$-\infty$. According to Eq. (2.10), the starting random force $\Phi_i(t)$ is related to white noise $\xi_i(t)$ by the following integral relation:

$$\Phi_t(t)=\Phi_i^0 e^{-(t-t_0)/\tau}+\frac{1}{\zeta}\int_{t_0}^{t} B(s)\xi_i(s)ds,$$

where Φ_i^0 is the initial random force. It has a memory over the time equal to the relaxation time of the Maxwell fluid.

Using the relaxation equations for systematic (2.2) and random force (2.10), we can rewrite the set (2.1) of stochastic equations into an equivalent one with a delta-correlated random force,

$$\frac{dr_i}{dt}=u_i,\quad \frac{du_i}{dt}=\dot{u}_i,$$
$$m\tau\frac{d}{dt}\dot{u}_i+m\dot{u}_i=-(\zeta+\alpha\tau)u_i-\alpha r_i+\xi_i. \tag{2.12}$$

Thus in the resulting equation of motion (2.12) the set of independent variables includes the first-order acceleration $\dot{\mathbf{u}}$. This defines a multidimensional Markovian process $\{\mathbf{r},\mathbf{u},\dot{\mathbf{u}}\}$. It should be noted however that not every random process can be reduced to a Markovian one, even in the most general sense. For instance, this is impossible when significant residual effects are associated with inertia of the liquid or in the case of a viscoelastic fluid with a continuous spectrum of relaxation times.

III. KINETIC DESCRIPTION

The statistical characteristics of the Brownian motion under study can be found directly from the linear stochastic equations (2.12). In many cases, however, the differential equation for the distribution function of the solution of Eqs. (2.12) gives a more convenient probabilistic description. For this reason, it is desirable to establish a precise correspondence between Eq. (2.12) and the equation for the distribution function, analogous to the Fokker–Planck equation. In the derivation we follow the method of Klyatskin–Tatarskii.[25] This method allows us to derive kinetic equations for various distribution functions directly from the stochastic equations of motion.

We define the distribution function for the solution of the system of Eqs. (2.12) as follows:

$$f(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},\mathbf{t})=\langle\delta[\mathbf{r}-\mathbf{r}(\mathbf{t})]\delta[\mathbf{u}-\mathbf{u}(\mathbf{t})]\delta[\dot{\mathbf{u}}-\dot{\mathbf{u}}(\mathbf{t})]\rangle. \tag{3.1}$$

Here $\mathbf{r}(t)$, $\mathbf{u}(t)$, and $\dot{\mathbf{u}}(t)$ are the solution of Eqs. (2.12) corresponding to a certain realization of the random force $\xi_i(t)$ and the averaging is performed over the set of all realizations.

Taking the time derivative of Eq. (3.1) and using Eqs. (2.12), we obtain

$$\frac{\partial f}{\partial t}+u_e\frac{\partial f}{\partial r_e}+\dot{u}_e\frac{\partial f}{\partial u_e}-\frac{\alpha r_e+(\zeta+\alpha\tau)u_e}{m\tau}\frac{\partial f}{\partial\dot{u}_e}$$
$$=\frac{1}{\tau}\frac{\partial}{\partial\dot{u}_e}(\dot{u}_e f)-\frac{1}{m\tau}\frac{\partial}{\partial\dot{u}_e}\langle\xi_e(t)R[\xi]\rangle. \tag{3.2}$$

Here $R[\xi]=\delta[\mathbf{r}-\mathbf{r}(t)]\delta[\mathbf{u}-\mathbf{u}(t)]\delta[\dot{\mathbf{u}}-\dot{\mathbf{u}}(\mathbf{t})]$ is a nonlinear functional of the Gaussian stochastic process $\xi(t)$ with zero average. To close Eq. (3.2) we need to express the average value $\langle\xi_e R[\xi]\rangle$ in terms of f. It is done by employing the Furutsu–Novikov formula[26,27] which in our case has the form

$$\langle\xi_e(t)R[\xi]\rangle=\int\langle\xi_e(t)\xi_n(s)\rangle\left\langle\frac{\delta R[\xi]}{\delta\xi_n(s)}\right\rangle ds. \tag{3.3}$$

Using the formulas,

$$\frac{\delta r_i(t)}{\delta\xi_j(t)}=0,\quad \frac{\delta u_i(t)}{\delta\xi_j(t)}=0,\quad \frac{\delta\dot{u}_i(t)}{\delta\xi_j(t)}=\frac{1}{m\tau}\delta_{ij}$$

which follow immediately from Eqs. (2.12), we can obtain the explicit expression for the functional derivative $\delta R[\xi]/\delta\xi_e(s)$,

$$\frac{\delta R[\xi]}{\delta\xi_e(t)}=-\frac{1}{m\tau}\frac{\partial R[\xi]}{\partial\dot{u}_e}.$$

As a result we find a closed kinetic equation for the one-time distribution function,

$$\frac{\partial}{\partial t}f(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},t)+u_e\frac{\partial f}{\partial r_e}+\dot{u}_e\frac{\partial f}{\partial u_e}-\alpha\frac{r_e+\tau_\alpha u_e}{m\tau}\frac{\partial f}{\partial\dot{u}_e}$$
$$=\frac{\partial}{\partial\dot{u}_e}\left(\frac{\dot{u}_e}{\tau}+D_{\dot{u}}\frac{\partial}{\partial\dot{u}_e}\right)f. \tag{3.4}$$

The diffusion coefficient in the acceleration space is determined in the form

$$D_{\dot{u}}=\frac{T}{m}\frac{1}{\tau_m\tau^2},$$

where the following notations for the relaxation times

$$\tau_m=m/\zeta,\quad \tau_\alpha=\tau+\tau^B,\quad \tau^B=\zeta/\alpha$$

are introduced.

The distribution function $f(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},t)$ of position, velocity, and acceleration can be found from Eq. (3.4) for a given initial distribution $f_0=f(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},t_0)$. Further on, one can obtain the phase-space distribution function

$$f(\mathbf{r},\mathbf{u},t)=\int f(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},t)d\dot{\mathbf{u}}.$$

This distribution cannot be established from the classical Fokker–Planck equation, since the process $\{\mathbf{r}(t),\mathbf{u}(t)\}$ is not Markovian.

For free Brownian motion in a Maxwellian fluid ($\alpha=0$) the kinetic equation

$$\frac{\partial}{\partial t} f(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},t)+u_e \frac{\partial f}{\partial r_e}+\dot{u}_e \frac{\partial f}{\partial u_e}-\frac{u_e}{\tau\tau_m}\frac{\partial f}{\partial \dot{u}_e} = \frac{\partial}{\partial \dot{u}_e}\left(\frac{\dot{u}_e}{\tau}+D_{\dot{u}}\frac{\partial}{\partial \dot{u}_e}\right) f \tag{3.5}$$

follows from Eq. (3.4).

Using Eq. (3.4) we can determine one-time statistical characteristics of the multidimensional Markovian process $\{\mathbf{r}(t),\mathbf{u}(t),\dot{\mathbf{u}}(t)\}$. Since the solution of the system (2.12) is a linear functional of a Gaussian random force the joint distribution of the probabilities of $\mathbf{r}(t)$, $\mathbf{u}(t)$, and $\dot{\mathbf{u}}(t)$ is also Gaussian and it is sufficient to calculate only the first and second moments of this distribution. For the average values, the following system of linear equations holds:

$$\frac{d}{dt}\langle r_i\rangle=\langle u_i\rangle,\ \frac{d}{dt}\langle u_i\rangle=\langle \dot{u}_i\rangle, \qquad \tau\frac{d}{dt}\langle \dot{u}_i\rangle+\langle \dot{u}_i\rangle=-\frac{\alpha}{m}(\langle r_i\rangle+\tau_\alpha\langle u_i\rangle). \tag{3.6}$$

The stationary solution of this system has the form

$$\langle r_i\rangle=0,\ \langle u_i\rangle=0,\ \langle \dot{u}_i\rangle=0.$$

The evolution of the second one-time moments,

$$x_{ik}(t)=\langle r_i(t)r_k(t)\rangle,\ y_{ik}(t)=\langle r_i(t)u_k(t)\rangle,$$
$$z_{ik}(t)=\langle u_i(t)u_k(t)\rangle,\ n_{ik}(t)=\langle r_i(t)\dot{u}_k(t)\rangle,$$
$$m_{ik}(t)=\langle u_i(t)\dot{u}_k(t)\rangle,\ e_{ik}(t)=\langle \dot{u}_i(t)\dot{u}_k(t)\rangle,$$

is described by the set of equations

$$\begin{aligned}
&\frac{d}{dt}x_{ik}=y_{ik}+y_{ki},\ \frac{d}{dt}y_{ik}=z_{ik}+n_{ik},\ \frac{d}{dt}z_{ik}=m_{ik}+m_{ki},\\
&\tau\frac{d}{dt}n_{ik}+n_{ik}=\tau m_{ik}-\frac{\alpha}{m}(x_{ik}+\tau_\alpha y_{ik}),\\
&\tau\frac{d}{dt}m_{ik}+m_{ik}=\tau e_{ik}-\frac{\alpha}{m}(y_{ki}+\tau_\alpha z_{ik}),\\
&\tau\frac{d}{dt}e_{ik}+2e_{ik}=2\frac{T}{m\tau\tau_m}\delta_{ik}-\frac{2\alpha}{m}[n_{(ik)}+\tau_\alpha m_{(ik)}].
\end{aligned} \tag{3.7}$$

The stationary solution of the system (3.7) has the form

$$\langle r_i u_k\rangle=0,\ \langle u_i\dot{u}_k\rangle=0,$$
$$\langle u_i u_k\rangle=\frac{T}{m}\delta_{ik},\ \langle r_i\dot{u}_k\rangle=-\frac{T}{m}\delta_{ik},$$
$$\langle \dot{u}_i\dot{u}_k\rangle=\frac{T}{m}\left(\frac{\alpha}{m}+\frac{1}{\tau\tau_m}\right)\delta_{ik}. \tag{3.8}$$

Equations (3.8) exactly correspond to the law of equipartition of energy over the degrees of freedom. Thus as $t\to\infty$, the Brownian particle comes into thermodynamic equilibrium with the surrounding viscoelastic medium and is characterized by the correlation matrix

$$\begin{vmatrix} \langle r_i r_k\rangle & \langle r_i u_k\rangle & \langle r_i\dot{u}_k\rangle\\ \langle u_i r_k\rangle & \langle u_i u_k\rangle & \langle u_i\dot{u}_k\rangle\\ \langle \dot{u}_i r_k\rangle & \langle \dot{u}_i u_k\rangle & \langle \dot{u}_i\dot{u}_k\rangle \end{vmatrix}=\begin{vmatrix} \frac{T}{\alpha} & 0 & -\frac{T}{m}\\ 0 & \frac{T}{m} & 0\\ -\frac{T}{m} & 0 & \frac{\alpha T\tau_\alpha}{\tau m^2}\end{vmatrix}\delta_{ik}.$$

Therefore the multidimensional stochastic process under study has the stationary distribution

$$f_s(\mathbf{r},\mathbf{u},\dot{\mathbf{u}}) =C\exp\left[-\frac{m\mathbf{u}^2+m\tau\tau_m\dot{\mathbf{u}}^2+2\alpha\tau\tau_m\mathbf{r}\dot{\mathbf{u}}+\alpha(1+\tau/\tau^B)\mathbf{r}^2}{2T}\right]. \tag{3.9}$$

Here C is a constant determined by the normalization condition $\int f d\mathbf{r} d\mathbf{u} d\dot{\mathbf{u}}=1$. Equation (3.9) represents a generalization of the well known Maxwell Boltzmann distribution. A new feature of the distribution (3.9) is statistical dependence of coordinates and accelerations. It is easy to verify that this distribution is the stationary solution of Eq. (3.4). The equilibrium distribution (3.9) depends on the individual properties of the Brownian particle and on the external parameters ζ and τ, characterizing the viscoelastic properties of the surrounding medium. Integrating it over accelerations results in the Maxwell Boltzmann distribution

$$f_s(\mathbf{r},\mathbf{u})\propto\exp\left(-\frac{m\mathbf{u}^2+\alpha\mathbf{r}^2}{2T}\right).$$

Therefore the stationary distribution functions in the phase-space for the Brownian motion in viscous and viscoelastic liquids are identical.

IV. ONE-TIME STATISTICAL CHARACTERISTICS

In order to determine how a Brownian particle attains the stationary state, starting from arbitrary initial condition, let us now turn our attention to the analysis of one-time correlations. As mentioned, the asymptotic state of Brownian particle at $t\to\infty$ may be interpreted as a thermal equilibrium with the surrounding fluid at temperature T. We now will study the particular form of Eqs. (2.12),

$$m\tau\frac{d^2u_i}{dt^2}+m\frac{du_i}{dt}+\zeta u_i=\xi_i(t), \tag{4.1}$$

describing the free Brownian motion in a Maxwell fluid, i.e., in the absence of an external force field. The statistical properties of a Gaussian delta-correlated random force $\xi_i(t)$ is defined by Eq. (2.11). According to Eq. (4.1), the velocity of Brownian particle $\mathbf{u}$ is a non-Markovian stochastic process, wich can be considered as a "projection" of the Markovian process $\{\mathbf{u}(t),\dot{\mathbf{u}}(t)\}$. It is interesting that Eq. (4.1) is mathematically equivalent to the second-order stochastic differential equation in position space, that describes Brownian motion of a simple harmonic oscillator in viscous fluid.[28] From the non-Markovian stochastic differential Eq. (4.1) with a delta-correlated random force in the right-hand side one can derive the following evolution equations for the average values:

$$\frac{d\langle u_i\rangle}{dt}=\langle \dot u_i\rangle,$$
$$\tau\tau_m \frac{d}{dt}\langle \dot u_i\rangle+\tau_m\langle \dot u_i\rangle+\langle u_i\rangle=0 \tag{4.2}$$

with initial condition

$$y_i^0=\langle u_i^0\rangle,\quad z_i^0=\langle \dot u_i^0\rangle$$

and the second-order moments

$$\frac{dz_{ik}}{dt}=m_{ik}+m_{ki},$$
$$\tau\tau_m \frac{d^2 z_{ik}}{dt^2}+\tau_m\frac{dz_{ik}}{dt}=2\tau\tau_m e_{ik}-2z_{ik}, \tag{4.3}$$
$$\tau\frac{de_{ik}}{dt}+2e_{ik}=2\frac{T}{m\tau\tau_m}\delta_{ik}-\frac{1}{\tau_m}\frac{dz_{ik}}{dt}.$$

The derivation Eqs. (4.3) is based on the Furutsu–Novikov formula (3.3). The averages appearing in the moment equations by using one are easily determined

$$\langle \xi_i(t)u_k(t)\rangle=0,\ \langle \xi_i(t)\dot u_k(t)\rangle=\frac{T}{\tau\tau_m}\delta_{ik}.$$

We consider the nonequilibrium initial value problem with the initial second-order moments

$$z_{ik}^0=\langle u_i^0u_k^0\rangle,\quad m_{ik}^0=\langle u_i^0\dot u_k^0\rangle,\quad e_{ik}^0=\langle \dot u_i^0\dot u_k^0\rangle.$$

The initial velocity u_i^0 and the initial acceleration $\dot u_i^0$ of Brownian particle are assumed to be Gaussian distributed.

One of the main problems in the theory of Brownian motion is the calculation of velocity moment functions. From Eqs. (4.2) and (4.3) it is a simple matter to obtain the closed equations for the average velocity $y_i(t)=\langle u_i\rangle$ and one-time velocity $z_{ik}(t)$ and acceleration $e_{ik}(t)$ correlations,

$$\tau\tau_m\frac{d^2y_i}{dt^2}+\tau_m\frac{dy_i}{dt}+y_i=0,$$
$$\tau_m\tau^2\frac{d^3z_{ik}}{dt^3}+3\tau\tau_m\frac{d^2z_{ik}}{dt^2}+2(2\tau+\tau_m)\frac{dz_{ik}}{dt}+4z_{ik}=4\frac{T}{m}\delta_{ik},$$
$$\tau_m\tau^2\frac{d^3e_{ik}}{dt^3}+3\tau\tau_m\frac{d^2e_{ik}}{dt^2}+2(2\tau+\tau_m)\frac{de_{ik}}{dt}+4e_{ik}=4\frac{T}{m\tau\tau_m}\delta_{ik}. \tag{4.4}$$

Solving Eqs. (4.2) and (4.3), we find the expressions for the one-time moments,

$$y_i\equiv\langle u_i\rangle=\chi(t)y_i^0-\tau^+\tau^-\dot\chi(t)z_i^0,$$
$$z_i\equiv\langle \dot u_i\rangle=\dot\chi(t)y_i^0-\tau^+\tau^-\ddot\chi(t)z_i^0,$$
$$z_{ik}\equiv\langle u_i(t)u_k(t)\rangle=\frac{T}{m}\delta_{ik}+(z_{ik}^0-z_{ik}^e)\varphi(t)-m_{(ik)}^0\tau^+\tau^-\dot\varphi(t)+(e_{ik}^0-e_{ik}^e)(\tau^+\tau^-)^2\dot\chi^2(t),$$
$$e_{ik}\equiv\langle \dot u_i(t)\dot u_k(t)\rangle=\frac{T}{m\tau\tau_m}\delta_{ik}+(z_{ik}^0-z_{ik}^e)\beta(t)-m_{(ik)}^0\tau^+\tau^-\dot\beta(t)+(e_{ik}^0-e_{ik}^e)(\tau^+\tau^-)^2\ddot\chi^2(t),$$
$$m_{ik}\equiv\langle u_i(t)\dot u_k(t)\rangle=\tfrac{1}{2}[(z_{ik}^0-z_{ik}^e)\dot\varphi(t)-m_{ik}^0\tau^+\tau^-\ddot\varphi(t)+(e_{ik}^0-e_{ik}^e)(\tau^+\tau^-)^2\dot\beta(t)], \tag{4.5}$$

where $\varphi(t)=\chi^2(t)$ and $\beta(t)=\dot\chi^2(t)$. Here we have defined the relaxation times $\tau^\pm$ by

$$\tau^\pm=\tfrac{1}{2}[\tau_m\pm\sqrt{\tau_m^2-4\tau\tau_m}]. \tag{4.6}$$

The function

$$\chi(t)=\frac{1}{\tau^+-\tau^-}(\tau^+e^{-t/\tau^+}-\tau^-e^{-t/\tau^-}) \tag{4.7}$$

may be interpreted as the response function, associated with system (4.1), to the external force $\xi_i(t)$. Another useful way of expression of $\chi(t)$ is

$$\chi(t)=e^{-t/2\tau}\left(\mathrm{Cosh}\frac{\gamma t}{2}+\frac{\alpha}{\gamma}\mathrm{Sinh}\frac{\gamma t}{2}\right), \tag{4.7a}$$

where $\gamma=1/\tau^- - 1/\tau^+$. The convenience of formula (4.7a) is that it gives for the moments (4.5) finite and real expressions even in aperiodic ($\gamma=0$) and underdamped ($\gamma=i\gamma_1$) cases.

Equation (4.5) shows that the short-time behavior of the stochastic process $\{\mathbf{u},\dot{\mathbf{u}}\}$ depends on an initial condition. However, after the transient time, which is determined by the relaxation time of viscoelastic fluid, the solution asymptotically approaches a unique, equilibrium state determined by the statistical characteristics

$$z_{ik}^e=\frac{T}{m}\delta_{ik},\quad m_{ik}^e=0,\quad e_{ik}^e=\frac{T}{m\tau\tau_m}\delta_{ik}. \tag{4.8}$$

If the initial condition is determined by the accelerations equilibrium distribution and $z_{ik}^0=u_0^2\delta_{ik}$, we obtain

$$\langle u_i(t)u_k(t)\rangle=\left[\frac{T}{m}+\left(u_0^2-\frac{T}{m}\right)\chi^2(t)\right]\delta_{ik}. \tag{4.9}$$

Equation (4.9) shows how the equipartition value is reached. This result is similar to that obtained originally in the classic papers[28] for the Brownian motion in viscous fluid, where, however, a different (nonexponential) function $\chi(t)$ was found.

For the one-time cumulants,

$$\langle u_i(t), u_k(t)\rangle = \langle (u_i - \langle u_i\rangle)(u_k - \langle u_k\rangle)\rangle,$$

$$\langle u_i(t), \dot{u}_k(t)\rangle = \langle (u_i - \langle u_i\rangle)(\dot{u}_k - \langle \dot{u}_k\rangle)\rangle,$$

$$\langle \dot{u}_i(t), \dot{u}_k(t)\rangle = \langle (\dot{u}_i - \langle \dot{u}_i\rangle)(\dot{u}_k - \langle \dot{u}_k\rangle)\rangle,$$

we have the simple expressions

$$\langle u_i(t), u_k(t)\rangle = \frac{T}{m}[1 - \chi^2(t) - \tau^+\tau^-\dot{\chi}^2(t)]\delta_{ik},$$

$$\langle \dot{u}_i(t), \dot{u}_k(t)\rangle = \frac{T}{m\tau\tau_m}[1 - \tau^+\tau^-\dot{\chi}^2(t) - (\tau^+\tau^-)^2\ddot{\chi}^2(t)]\delta_{ik},$$

$$\langle u_i(t), \dot{u}_k(t)\rangle = \frac{T}{\zeta}\dot{\chi}^2(t)\delta_{ik}. \tag{4.10}$$

Analysis of Eqs. (4.5) and (4.10) shows that the force and the velocity of Brownian particle suspended in a Maxwell fluid are correlated over long time intervals. In this case, velocity and acceleration of Brownian particle are characterized in general by the nonexponential one-time correlations. The steady state is reached after a long time. The physical origin of the slow approach of correlations to the equilibrium values lies in the viscoelasticity of the surrounding fluid.

We now consider the asymptotic behavior of the expression (4.5) for the one-time correlations of velocities, $z_{ik}(t)$, and accelerations, $e_{ik}(t)$, at $t\to\infty$, i.e., when approaching to the equilibrium. Depending on the value of root in Eq. (4.6), there are two cases.

(1) $\tau_m > 4\tau$. The most interesting situation here is when $\tau \ll \tau_m$. In this case, the viscous behavior of the liquid is dominant over the viscoelastic one, and except for the equilibrium value of e_{ik}^e, where the relaxation parameter τ is essential, one can expect that all the transitional phenomena will depend mostly on the viscosity of liquid and the mass of Brownian particle. Brief calculations using Eq. (4.5), yield the following asymptotic result:

$$z_{ik}(t) \approx z_\infty[\delta_{ik} - (\delta_{ik} - z_{ik}^0/z_\infty)\exp(-t/\tau_m)],$$

$$e_{ik}(t) \approx e_\infty[\delta_{ik} - (\tau/\tau_m)(\delta_{ik} - z_{ik}^0/z_\infty)\exp(-t/\tau_m)].$$

$$[t\to\infty,\ z_\infty = T/m,\ e_\infty = z_\infty/(\tau\tau_m)]. \tag{4.11}$$

Since $\tau \ll \tau_m$, the correlations of accelerations reach the equilibrium much faster than that of velocities.

(2) $\tau_m < 4\tau$. In this case, approaching to the equilibrium is accompanied by oscillations, both the correlations $z_{ik}(t)$ and $e_{ik}(t)$ reach the equilibrium almost synchronously, and the relaxation properties of liquid are very essential. This is the case of a behavior appropriate for polymer solutions and melts.

V. KINETIC EQUATION IN VELOCITY SPACE

In this section we derive the equation for the velocity probability density of free Brownian motion in the Maxwell fluid, starting directly from the non-Markovian Langevin Eqs. (4.1). The derivation follows the functional method similar to that proposed by Klyatskin–Tatarskii.

The distribution function $f(\mathbf{u},t)$ of a Brownian particle in a velocity space may be defined by

$$f(\mathbf{u},t) = \langle \delta(\mathbf{u} - \mathbf{u}(t))\rangle, \tag{5.1}$$

where $\mathbf{u}(t)$ is a solution of Eq. (4.1) for a given realization of random force $\xi_i(t)$ with initial condition specified at $t=0$. The velocity of Brownian particle $\mathbf{u}(t)$ depends on time t and initial velocity u_0, and is a linear functional of the noise $\xi_i(t)$. The averaging is done over the set of all realizations $\{\xi(t)\}$ and over the distribution of initial velocities.

Equation (5.1) yields

$$\frac{\partial f(\mathbf{u},t)}{\partial t} = -\frac{\partial}{\partial u_e}\langle \dot{u}_e(t)\delta(\mathbf{u} - \mathbf{u}(t))\rangle. \tag{5.2}$$

We now take the time derivative of Eq. (5.2) to obtain

$$\frac{\partial^2 f(\mathbf{u},t)}{\partial t^2} = -\frac{\partial}{\partial u_e}\langle \ddot{u}_e(t)\delta(\mathbf{u} - \mathbf{u}(t))\rangle + \frac{\partial^2}{\partial u_e \partial u_n}\langle \dot{u}_e(t)\dot{u}_n(t)\delta(\mathbf{u} - \mathbf{u}(t))\rangle. \tag{5.3}$$

Taking into account the initial stochastic Eq. (4.1), we find from Eqs. (5.2) and (5.3) the following equation for the distribution function:

$$\frac{\partial^2 f}{\partial t^2} + \frac{1}{\tau}\frac{\partial f}{\partial t} = \frac{1}{\tau\tau_m}\frac{\partial}{\partial u_e}(u_e f) - \frac{1}{m\tau}\frac{\partial}{\partial u_e}\langle \xi_e(t)\delta(\mathbf{u} - \mathbf{u}(t))\rangle + \frac{\partial^2}{\partial u_e \partial u_n}\langle \dot{u}_e(t)\dot{u}_n(t)\delta(\mathbf{u} - \mathbf{u}(t))\rangle. \tag{5.4}$$

To calculate the averages in Eq. (5.4) we use the Furutsu–Novikov formula (3.3) and a similar formula for the mean of the product of two nonlinear functionals $P[\xi]$ and $R[\xi]$ of a Gaussian stochastic process $\xi(t)$ with a zero mean value[11]

$$\langle P[\xi]R[\xi]\rangle = \langle P[\xi]\rangle\langle R[\xi]\rangle + \int\int \left\langle \frac{\delta P[\xi]}{\delta \xi_e(t_1)}\right\rangle \times \left\langle \frac{\delta P[\xi]}{\delta \xi_n(t_2)}\right\rangle \langle \xi_e(t_1)\xi_n(t_2)\rangle dt_1 dt_2. \tag{5.5}$$

Equation (5.5) was derived by employing a functional Taylor-series expansions of $P[\xi]$ and $R[\xi]$ and using then the statistical properties of $\xi(t)$.

As a result we get for the velocity distribution function the closed kinetic equation

$$\tau\tau_m\frac{\partial^2 f}{\partial t^2} + \tau_m\frac{\partial f}{\partial t} = \frac{\partial}{\partial u_e}\left[u_e + \tau\tau_m\langle \dot{u}_e(t)\dot{u}_n(t)\rangle\frac{\partial}{\partial u_n}\right]f(\mathbf{u},t). \tag{5.6}$$

Here $\langle u_e(t)\dot{u}_n(t)\rangle$ is the one-time acceleration correlations defined in Eq. (4.5). The generalized Fokker Planck equation in velocity space (5.6) for the non-Markovian Brownian motion in a Maxwell fluid is important result of this paper. Equation (5.6) can be also expressed as follows:

$$\tau^+\tau^- \frac{\partial^2 f}{\partial t^2}+(\tau^+ + \tau^-)\frac{\partial f}{\partial t} = \frac{\partial}{\partial u_s}\left[u_s + D_{sn}(t)\frac{\partial}{\partial u_n}\right] f(\mathbf{u},t). \tag{5.7}$$

Here

$$D_{sn}(t)=\frac{T}{m}\delta_{sn}+\tau^+\tau^-[(z^0_{sn}-z^e_{sn})\beta(t) - m^0_{(sn)}\tau^+\tau^-\dot{\beta}(t)+(e^0_{sn}-e^e_{sn})(\tau^+\tau^-)^2\ddot{\chi}^2(t)].$$

This equation is valid for any time and any value of the parameters of the system, given in terms of the response function $\chi(t)$. The kinetic coefficients $D_{sn}(t)$ have different forms depending on the statistical properties of the initial velocity and initial acceleration of Brownian particle. This is in agreement with the physical fact that the evolution of non-Markovian processes depends significantly on initial conditions. If the Brownian motion starts from zero initial values of velocity and acceleration, the equation for the velocity distribution function (5.7) still holds but

$$D_{sn}(t)=\frac{T}{m}[1-\tau^+\tau^-\dot{\chi}^2(t)-(\tau^+\tau^-)^2\ddot{\chi}^2(t)]\delta_{sn}. \tag{5.8}$$

In the case of a Brownian motion in a viscous fluid, when $\tau^+=m/\zeta$ and $\tau^-=0$, Eqs. (5.7) and (5.8) are reduced to the known classical Fokker–Planck equation in velocity space.

The generalized Fokker–Planck Eq. (5.7) can be represented as a retarted equation

$$m\frac{\partial f(\mathbf{u},t)}{\partial t}=\int_0^t ds B(t-s)\frac{\partial}{\partial u_e}\left[u_e+D_{en}(s)\frac{\partial}{\partial u_n}\right] f(\mathbf{u},s) \tag{5.9}$$

with the same memory kernel (2.4) as in the starting Langevin equation with exponential memory.

For a long time interval, when the equilibrium acceleration distribution has already reached the asymptota Eq. (4.11), we have $\langle \dot{u}_e(t)\dot{u}_n(t)\rangle=(T/m\tau\tau_m)\delta_{en}$. In this particular case, the equation for the velocity distribution function (5.6) takes the form of the telegraph equation,

$$\tau\frac{\partial^2 f}{\partial t^2}+\frac{\partial f}{\partial t}=\frac{\zeta}{m}\frac{\partial}{\partial u_e}\left[u_e+\frac{T}{m}\frac{\partial}{\partial u_e}\right] f(\mathbf{u},t) \tag{5.10}$$

with constant coefficients. The master telegraph equation analogous to Eq. (5.10) has been also derived in the papers[29,30] for non-Markovian processes associated with nonequilibrium phenomena.

Note that the telegraph Eq. (5.10) coincides with that derived in the molecular theory of Brownian motion[15,18]

$$\frac{\partial f(\mathbf{u},t)}{\partial t}=\frac{1}{m}\int_0^t ds B(t-s)\frac{\partial}{\partial u_e}\left(u_e+\frac{T}{m}\frac{\partial}{\partial u_e}\right) f(\mathbf{u},s) \tag{5.11}$$

if the memory kernel $B(t)$ is the exponential function (2.4). In this case, Eq. (5.11) can be rewritten as a differential Eq. (5.10).

VI. THE DYNAMICS OF TWO-TIME DISTRIBUTION FUNCTION

We now study the time correlations of the random process $\mathbf{a}=\{\mathbf{r}(t),\mathbf{u}(t),\dot{\mathbf{u}}(t)\}$, determined by the system of stochastic Eqs. (2.12). All statistical characteristics of the Markovian Gaussian process $\mathbf{a}(t)$ can be determined with the help of the two-time distribution function

$$f_2(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},t;\mathbf{r}',\mathbf{u}',\dot{\mathbf{u}}',t')=\langle\delta[\mathbf{a}-\mathbf{a}(t)]\delta[\mathbf{a}'-\mathbf{a}'(t')]\rangle. \tag{6.1}$$

If f_2 is known, it is possible to establish any n-time distribution function. Therefore f_2 completely characterizes the process under study.

Differentiating the expression (6.1) with respect to time and using the dynamic Eqs. (2.12), the causality condition and the Furutsu–Novikov formula, we obtain the following equation for f_2:

$$\frac{\partial}{\partial t} f_2(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},t;\mathbf{r}',\mathbf{u}',\dot{\mathbf{u}}',t')+u_e\frac{\partial f_2}{\partial r_e}+\dot{u}_e\frac{\partial f_2}{\partial u_e} -\alpha\frac{r_e+\tau_\alpha u_e}{m\tau}\frac{\partial f_2}{\partial \dot{u}_e}=\frac{\partial}{\partial \dot{u}_e}\left(\frac{\dot{u}_e}{\tau}+D_{\dot{u}}\frac{\partial}{\partial \dot{u}_e}\right) f_2. \tag{6.2}$$

In contrast to the initial system of stochastic equations, Eq. (6.2) represent the stochastic information in a much more compact form.

With the help of the kinetic Eq. (6.2), one can find a set of equations for the two-time correlations. For definiteness, let $t>t'$. Then Eq. (6.2) yields

$$\frac{d}{dt}\langle r_i(t)r_k(t')\rangle=\langle u_i(t)r_k(t')\rangle,$$

$$\frac{d}{dt}\langle r_i(t)u_k(t')\rangle=\langle u_i(t)u_k(t')\rangle,$$

$$\frac{d}{dt}\langle u_i(t)u_k(t')\rangle=\langle \dot{u}_i(t)u_k(t')\rangle,$$

$$m\tau\frac{d}{dt}\langle \dot{u}_i(t)r_k(t')\rangle+m\langle \dot{u}_i(t)r_k(t')\rangle =-\alpha[\langle r_i(t)r_k(t')\rangle+\tau_\alpha\langle u_i(t)r_k(t')\rangle],$$

$$m\tau\frac{d}{dt}\langle \dot{u}_i(t)u_k(t')\rangle+m\langle \dot{u}_i(t)u_k(t')\rangle =-\alpha[\langle r_i(t)u_k(t')\rangle+\tau_\alpha\langle u_i(t)u_k(t')\rangle]. \tag{6.3}$$

The initial conditions for this system are expressed in terms of the one-time correlations (3.7). The final state of the system under study is a stationary stochastic process which is determined by the two-time distribution function $f_{2s}(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},\mathbf{r}',\mathbf{u}',\dot{\mathbf{u}}';s)$. Here $s=t-t'$. Note that in this case, the one-time distribution function (3.9) is completely time independent. As follows from Eq. (6.2), the stationary two-time distribution satisfies the equation

$$\frac{\partial}{\partial t} f_{2s}(\mathbf{r},\mathbf{u},\dot{\mathbf{u}},\mathbf{r}',\mathbf{u}',\dot{\mathbf{u}}',s)+u_e \frac{\partial f_{2s}}{\partial r_e}+\dot{u}_e \frac{\partial f_{2s}}{\partial u_e} -\alpha \frac{r_e+\tau_\alpha u_e}{m\tau} \frac{\partial f_{2s}}{\partial \dot{u}_e}=\frac{\partial}{\partial \dot{u}_e}\left(\frac{\dot{u}_e}{\tau}+D_{\dot{u}} \frac{\partial}{\partial \dot{u}_e}\right) f_{2s}. \tag{6.4}$$

We now turn our attention to determining the stationary probabilistic characteristics of the Brownian motion under study, which do not depend on the time instant of measurement. In this case we can find from Eq. (6.3) the equilibrium correlation functions for the velocity and acceleration of a free Brownian particle moving in a Maxwell fluid

$$\langle u_i(t)u_k(0)\rangle=\frac{T}{m}\frac{1}{\tau^+-\tau^-}\left[\tau^+ \exp\left(-\frac{|t|}{\tau^+}\right)-\tau^- \times\exp\left(-\frac{|t|}{\tau^-}\right)\right]\delta_{ik},$$

$$\langle \dot{u}_i(t)\dot{u}_k(0)\rangle=\frac{T}{m}\frac{1}{\tau^+-\tau^-}\left[\frac{1}{\tau^-}\exp\left(-\frac{|t|}{\tau^-}\right)-\frac{1}{\tau^+}\exp\left(-\frac{|t|}{\tau^+}\right)\right]\delta_{ik}. \tag{6.5}$$

The velocity correlation function $\phi_{ik}(t)=\langle u_i(t)u_k(0)\rangle$ obeys the equation

$$\tau^+\tau^- \frac{d^2}{dt^2}\phi_{ik}(t)+(\tau^++\tau^-)\frac{d}{dt}\phi_{ik}(t)+\phi_{ik}(t)=0. \tag{6.6}$$

It may be of interest to note that the Gray's statistical model[31] of transport process in a monatomic liquid, where no assumption of the Brownian motion type was made about the statistical features of the molecular motion, resulted in a similar second-order equation for the velocity correlation function of a liquid molecules. From Eq. (6.6) one can derive the relation between the velocity correlation function and the friction kernel $B(t)$ defined by Eq. (2.4),

$$m\frac{d}{dt}\phi_{ik}(t)=-\int_0^t B(t-s)\phi_{ik}(s)ds. \tag{6.7}$$

This result may be interpreted as the equation of motion for the velocity correlation function. Note also that using a projection operator technique, Zwanzig[32] derived an equation describing the time evolution of the autocorrelation function of a dynamical variable in terms of a well-defined memory function. The form of equation obtained from this approach formalism is identical to Eq. (6.7). The equation for the distribution function of a Brownian particle in velocity space (5.12) derived in the molecular theory of Brownian motion[15,18] leads to Eq. (6.7), too.

From the practical viewpoint, it is important to know the mean square displacement of the Brownian particle $\langle(\Delta r_i)^2\rangle$, where $\Delta r_i=r_i(t)-r_i(0)$, in a given direction i over the time interval t. In this case we have

$$\langle(\Delta r_i)^2\rangle=\frac{2T}{m}\left\{(\tau^++\tau^-)|t| +\frac{(\tau^+)^3}{\tau^+-\tau^-}\left[\exp\left(-\frac{|t|}{\tau^+}\right)-1\right] -\frac{(\tau^-)^3}{\tau^+-\tau^-}\left[\exp\left(-\frac{|t|}{\tau^-}\right)-1\right]\right\}. \tag{6.8}$$

At long times when $t\gg\tau^+$, the mean-square displacement of a free Brownian particle in a viscoelastic Maxwell fluid is a linear function of time and is determined by the Einstein's formula,

$$\langle(\Delta r_i)^2\rangle=2Dt.$$

Here

$$D=\frac{T}{m}(\tau^++\tau^-)=\frac{T}{\zeta}$$

is the diffusion coefficient. Therefore over long time intervals the Brownian particle "forgets" its past and the process becomes inertialess.

In the particular case $\tau^-=0$ and $\tau^+=\tau_m$, corresponding to a viscous liquid surrounding the Brownian particle, Eqs. (6.5) and (6.8) are reduced to the classical results[28]

$$\langle u_i(t)u_k(0)\rangle=\frac{T}{m}\exp\left(-\frac{|t|}{\tau_m}\right)\delta_{ik},$$

$$\langle(\Delta r_i)^2\rangle=\frac{2T}{\zeta}\left\{|t|+\tau_m\left[\exp\left(-\frac{|t|}{\tau_m}\right)-1\right]\right\}. \tag{6.9}$$

According to Eq. (6.9), the exponential correlation of the velocity differs from zero only within a time interval of order $\tau_m=m/\zeta$. In addition, it differs qualitatively from generally nonexponential correlation (6.5) for the non-Markovian Brownian motion in a Maxwell fluid.

VII. THE DIFFUSION APPROXIMATION

Excluding from the analysis any processes occurring over short time intervals, we can neglect the inertia of Brownian particle. According to Eqs. (2.1) and (2.6) the equation of motion of an inertialess Brownian particle in a Maxwell fluid has the form

$$-\int_{-\infty}^t B(t-s)\dot{r}_i(s)ds-\alpha r_i(t)+f_i(t)=0. \tag{7.1}$$

The friction kernel

$$B(t)=\frac{\zeta}{\tau}e^{-t/\tau}$$

characterizes the viscoelastic resistance, to which a spherical particle moving in a resting Maxwell fluid is subjected. It is related to the complex viscosity of the fluid $\eta[\omega]$ by

$$B[\omega]=6\pi a\,\eta[\omega],\quad \eta[\omega]=\eta/(1-i\omega\tau).$$

We analyze the random process defined by Eq. (7.1) by the method of spectral analysis. Using the Fourier expansion for the random functions $\mathbf{r}(t)$ and $\mathbf{f}(t)$ we obtain from Eq. (7.1) an equation relating the Fourier components of the coordinates $r_i(\omega)$ and the generalized random force $\xi_i^r(\omega)=(1-i\omega\tau)f_i(\omega)$ of the Brownian particle,

$$r_i(\omega)=\chi[\omega]\xi_i^r(\omega). \tag{7.2}$$

The generalized susceptibility, determined in the form

$$\chi[\omega]=1/[\alpha-i\omega(\zeta+\alpha\tau)] \tag{7.3}$$

satisfies all requirements of a spectral characteristic for the one-side Fourier transform. However, more general expression $\chi^*[\omega]=1/(\alpha-i\omega B[\omega])$ in the relation $r_i(\omega)=\chi^*[\omega]f_i(\omega)$ cannot be used as the generalized susceptibility, since it does not approach zero as $\omega\rightarrow\infty$.

The statistical properties of the generalized random force $\xi_i^r(t)$ can be determined with the help of the Callen–Welton fluctuation-dissipation theorem. The formulation of the theorem given by Landau and Lifshitz,[33]

$$K_{ik}^{\xi^r}(\omega)=\frac{iT}{\omega}\,(\chi^{-1}[\omega]-\chi^{-1}[-\omega])\,\delta_{ik}, \tag{7.4}$$

is now widely used. Substituting the specific expression (7.3) for $\chi[\omega]$ we find from Eq. (7.4) the correlation function of the random force $\xi_i^r(t)$,

$$\langle\xi_i^r(t)\xi_i^r(s)\rangle=2T(\zeta+\alpha\tau)\,\delta(t-s)\,\delta_{ik}.$$

Hence the residual random force $f_i(t)$ in the inertialess dynamical Eq. (7.1), is exponentially correlated

$$\langle f_i(t)f_k(s)\rangle=T\,\frac{\zeta+\alpha\tau}{\tau}\,\exp\left(-\frac{|t-s|}{\tau}\right)\delta_{ik}. \tag{7.5}$$

In much the same way as in the previous section it is possible to derive the corresponding equation for the distribution function $W(\mathbf{r},t)$ from the non-Markovian inertialess Langevin Eq. (7.1). In doing so we obtain

$$\frac{\partial W(\mathbf{r},t)}{\partial t}=\frac{1}{\tau_\alpha}\,\frac{\partial(r_eW)}{\partial r_e}+D_r\,\frac{\partial^2W}{\partial r_e^2}. \tag{7.6}$$

The generalized Smoluchowski Eq. (7.6) describes the diffusion of an elastically bound Brownian particle in a viscoelastic fluid with one relaxation time. Here the diffusion coefficient is expressed as follows:

$$D_r=\frac{T}{\zeta+\alpha\tau}. \tag{7.7}$$

This result is a generalization of the well-known Einstein relation between the diffusion coefficient and the mobility. According to Eq. (29) the mobility of a Brownian particle in a relaxing fluid $b=1/(\zeta+\alpha\tau)$ depends on the external field. In the particular case $\tau=0$, Eq. (7.6) reduces to the well-known Smoluchowski equation for a Markovian Brownian oscillator. If there are no external forces, i.e., $\alpha=0$, then the generalized and classical diffusion equations are identical. In the case $\alpha\neq0$ only their stationary solutions coincide.

The mean square displacement of an elastically bound Brownian particle in a quiescent Maxwell fluid in a direction i is determined by the expression

$$\langle(\Delta r_i)^2\rangle=\frac{2T}{\alpha}\left[1-\exp\left(-\frac{t}{\tau_\alpha}\right)\right]. \tag{7.8}$$

Equation (7.8) is reduced to well known equation for the Brownian motion of simple harmonic oscillator in viscous fluid when $\tau=0$. It demonstrates that the mean-square displacement increases much more slowly in a viscoelastic fluid than in a viscous fluid. This is caused by the fact that the mobilities of a Brownian particle in these fluids are different.

VIII. CONCLUDING REMARKS

The theory of Brownian motion developed here is phenomenological as opposed to the molecular theory of Brownian motion.[15–18] The later provides a more detailed explanation of the effect of the fluid properties on motion of Brownian particle. Averaging microscopic equations of motion has resulted in a generalized Fokker–Planck equation with retarded kernel (5.11). However in general, the equation obtained in molecular approach[15–18] is only an approximation which can exactly define only the first-order one-time moments.[34,35] For instance, in the case of the exponential memory kernel, Eq. (5.11) yields only a second-order differential equation for the one-time velocity correlations of Brownian particle. This is in contradiction to our exact result defined by the third-order differential Eq. (4.4).

The present work was originally motivated by an attempt to find an exact equation for the velocity distribution function corresponding to a non-Markovian Langevin Eq. (4.1). As a simple check for the obtained Eq. (5.6), we can mention that the second-order evolution equation for the averaged velocity and the third-order equation for the one-time correlations of velocity of Brownian particle can be obtained using Eq. (5.6) exactly in the forms of Eqs. (4.4).

An important conclusion can be made about the comparison of the statistical properties of the random forces of the inertialess Eq. (7.1) and exact Eq. (2.1) stochastic equations of motion. In a transition from Eq. (2.1) to Eq. (7.1), along with the limit $m\rightarrow0$, it is also necessary to change the statistical characteristics of the random force. According to Eq. (7.5), they depend on parameter α in coordinate space, which characterizes the external forces. Thus the statistical properties of the random forces in coordinate space in the absence of external forces are different from those in the presence of external forces. If this is neglected, one can obtain incorrect results for the equilibrium correlations of the coordinates of the Brownian particle, corresponding to the direct limit $m\rightarrow0$ in the expression for the equilibrium distribution function Eq. (3.9). However, the more systematic transition from the stationary distribution function $f_s(\mathbf{r},\mathbf{u},\dot{\mathbf{u}})$ to the distribution function $W_s(\mathbf{r})$ should be made by integrating the distribution Eq. (3.9) over the velocities and accelerations. The interesting feature of the Brownian motion model studied here is that, in contrast with classical theory of Brownian motion, these two transitions to the distribution function $W_s(\mathbf{r})$ are not equivalent.

Finally, it should be mentioned that the stochastic equation in velocity space Eq. (4.1) for free Brownian motion in the Maxwell fluid is mathematically equivalent to the non-Markovian differential equation in position space, describing the Brownian motion of a harmonic oscillator in viscous fluid.[28] In Sec. V we derive the Eq. (5.7) for the distribution function of the solution of second-order stochastic differential Eq. (4.1) with the arbitrary initial conditions. It is possible to associate Eq. (5.7) with the validity of the solution for an old problem of the derivation of exact equation for the distribution function in position space for the Brownian motion in viscous fluid and external periodic potential[36,37] for any time instant. An approximate answer to this problem is given by the Smoluchowski diffusion equation[2] valid only for long times and high frictions. This aspect will be treated in more detail elsewhere.

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