Vol. A52 (1977) ACTA PHYSICA POLONICA No 3

ON THE THEORY OF TIME-DEPENDENT CORRELATIONS IN MANY BODY SYSTEMS*

BY A. R. ALTENBERGER

Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw**

(Received March 3, 1977)

Theory of time-dependent displacements of mechanical quantities in the many body systems is presented. Validity of the gaussian approximation of the displacements distribution is considered. As an example, kinetic equations for the distribution functions of momentum and position displacements of brownian particles moving in equilibrium fluid are derived.

1. Introduction

When we consider time evolution of an arbitrary physical quantity we are frequently interested in the determination of the probability distribution of the time dependent displacements of this quantity from its initial value. Although in stationary systems any function of the phase space variables has a constant and time independent average, the actual observed values of this function can be significantly different from the mean. Since there is no reason to expect any preference for the displacements leading towards the mean value, one tends to believe that the displacements can be described by the gaussian distribution. This problem was discussed mainly in connection with the theory of brownian motion and was stated in fundamental papers of Einstein [1] and Smoluchowski [2]. More recently it became important for the so called hydrodynamic description of the Van Hove self time-correlation function [3–6]. It is the aim of the present note to show under what circumstances the gaussian distribution can be considered as a proper description of the real time-dependent displacements.

In the next section, the general formulation of the problem is presented. Section 3 is devoted to the problem of multidimensional random processes and in Section 4 we present some illustrative examples of the general formalism. In the last section a discussion of the results is given.

---

* This work was partly supported by the Polish Academy of Sciences, Research Project 03.10.

** Address: Instytut Chemii Fizycznej PAN, Kasprzaka 44/52, 01-224 Warszawa, Poland.

2. General theory

Within the framework of classical mechanics the time evolution of an arbitrary mechanical quantity $Y(\Gamma, t)$ can be described by the Poisson–Liouville equation

$$dY(\Gamma, t)/dt = \partial Y/\partial t + L(\Gamma)Y(\Gamma, t) \tag{2.1}$$

where by $\Gamma = (\{q_i\}, \{p_i\})$ we denote a whole set of coordinates and momentums of all the particles of the system and $L(\Gamma)$ is the Liouville operator which is defined by

$$L(\Gamma) = \sum_i \{dq_i/dt\partial/\partial q_i + dp_i/dt\partial/\partial p_i\}, \tag{2.2}$$

$$dq_i/dt = \partial H/\partial p_i, \tag{2.3}$$

$$dp_i/dt = -\partial H/\partial q_i, \tag{2.4}$$

H is the Hamiltonian of the system. If function $Y(\Gamma, t)$ does not depend explicitly on time (e.g. when $\partial Y/\partial t = 0$) the time evolution of this function is caused only by the canonical transformation of the phase space variables $\Gamma_{t=0} \rightarrow \Gamma_t(\Gamma)$ and $Y(\Gamma, t) = Y(\Gamma_t, 0)$. The phase set Γ_t at time t is a function of the initial set Γ and if the later is known precisely, the initial and future values of the function $Y(\Gamma, t)$ are determined. Usually such complete information is not available and we have to assume that only the initial distribution $\varrho(\Gamma)$ of the phase space variables is known.

Thus equation (2.1) describes the time evolution of a stochastic process with random initial parameters. When dealing with the many body systems we also face a serious problem stemming from the fact that only in exceptional cases analytical solution of the equations of motion (2.3) and (2.4) is possible. Usually it is necessary to make some approximations with respect to the dynamics of the system and validity of these approximations determines the range of validity of the theory.

We restrict ourselves to problems in which $Y(\Gamma, t)$ is not an explicit function of time. It is always possible to divide the Liouville operator into two parts

$$L = L_0 + \lambda\delta L \tag{2.5}$$

defined in such a way that

$$L_0 Y(\Gamma, t = 0) = 0, \tag{2.6}$$

and

$$\lambda\delta L = L - L_0. \tag{2.7}$$

The ordering parameter λ $(0 \leqslant \lambda \leqslant 1)$ is introduced only for convenience and can be set equal to one at the end of the calculations. Evolution equation can be now expressed in the form

$$dY/dt = (L_0 + \lambda\delta L)\, Y, \tag{2.8}$$

and it is clear that if $\lambda = 0$ then the function Y is a constant of motion.

We define now the time-dependent displacement of $Y(\Gamma, t)$ by

$$X(\Gamma, t) = Y(\Gamma, t) - Y(\Gamma, 0). \tag{2.9}$$

This function fulfils the following evolution equation

$$dX/dt = (L_0+\lambda\delta L)X+\lambda\delta L\ Y(\Gamma,0) = (L_0+\lambda\delta L)X(\Gamma,t)+\dot{Y}(\Gamma,0), \tag{2.10}$$

where

$$\dot{Y}(\Gamma,0) = LY(\Gamma,0). \tag{2.11}$$

Equation (2.10) can be formally solved in the form of infinite series and we obtain

$$X(\Gamma,t) = \int_0^t dt_0\{1+\sum_{n\geq 1}\lambda^n\int_0^{t_0} dt_1 \ldots \int_0^{t_{n-1}} dt_n\delta L(t_n)\delta L(t_{n-1})\ldots\delta L(t_1)\}\lambda\delta L(t_0)Y(\Gamma,0), \tag{2.12}$$

where $\delta L(t)$ is the operator defined by

$$\delta L(t) = \exp(tL_0)\,\delta L\exp(-tL_0). \tag{2.13}$$

Probability density of finding displacement $X(\Gamma,t) = x$ at time t is given by the expression

$$f(x,t) = \int d\Gamma\,\varrho(\Gamma)\,\delta[X(\Gamma,t)-x] = \langle\delta[X(\Gamma,t)-x]\rangle, \tag{2.14}$$

where by a pointed bracket we denote an averaging over a square integrable initial distribution $\varrho(\Gamma)$ of the phase space variables.

We can now define the characteristic function $\hat{f}(k,t)$ which is related to the distribution (2.14) by

$$\hat{f}(k,t) = \int_{-\infty}^{\infty} dxe^{ikx}f(x,t) = \langle e^{ikX(\Gamma,t)}\rangle. \tag{2.15}$$

It can be easily proved that the characteristic function fulfils the following equation of evolution

$$\partial_t\hat{f}(k,t) = ik\,\hat{u}(k,t)\hat{f}(k,t)-k^2\hat{D}(k,t)\hat{f}(k,t), \tag{2.16}$$

or an equivalent relation

$$\hat{f}(k,t) = \exp[ik\int_0^t dt'\hat{u}(k,t')]\exp[-k^2\int_0^t dt'\hat{D}(k,t')]$$

$$= [\cos k\int_0^t dt'\hat{u}(k,t')+i\sin k\int_0^t dt'\hat{u}(k,t')]\exp[-k^2\int_0^t dt'\hat{D}(k,t')], \tag{2.17}$$

if $\hat{u}(k,t)$ is defined as the Fourier transform of the drift coefficient given by

$$k\cdot\hat{u}(k,t) = \operatorname{Im}\partial\ln\hat{f}(k,t)/\partial t, \tag{2.18}$$

and $\hat{D}(k,t)$ as the Fourier transform of the diffusion coefficient defined by

$$k^2\hat{D}(k,t) = -\operatorname{Re}\partial\ln f(k,t)/\partial t. \tag{2.19}$$

From the definitions (2.18) and (2.19) it follows immediately that the transport coefficients can be expressed in terms of averages by

$$\hat{u}(k,t) = \{\langle\dot{X}(t)\cos kX(t)\rangle\langle\cos kX(t)\rangle+\langle\dot{X}(t)\sin kX(t)\rangle$$
$$\langle\sin kX(t)\rangle\}\{\langle\sin kX(t)\rangle^2+\langle\cos kX(t)\rangle^2\}^{-1}, \tag{2.20}$$

and

$$\hat{D}(k,t) = \left\{ \left\langle \dot{X}(t)X(t)\frac{\sin kX(t)}{kX(t)} \right\rangle \langle \cos kX(t)\rangle \right.$$

$$\left. -\langle \dot{X}(t)\cos kX(t)\rangle \left\langle X(t)\frac{\sin kX(t)}{kX(t)} \right\rangle \right\} \{\langle \sin kX(t)\rangle^2 + \langle \cos kX(t)\rangle^2\}^{-1}, \quad (2.21)$$

where

$$\dot{X}(t) = dX(\Gamma, t)/dt. \quad (2.22)$$

It should be noted that the formulas (2.20) and (2.21) are exact and follow from the assumed form of the evolution equation (2.16).

From the general properties of characteristic functions we have

$$\int_0^t dt'\hat{D}(k,t') \geqslant 0, \quad (2.23)$$

$$\hat{u}(k,t) = \hat{u}(-k,t), \quad (2.24)$$

$$\hat{D}(k,t) = \hat{D}(-k,t). \quad (2.25)$$

There are also limiting conditions

$$\hat{u}_0(t) = \lim_{k\to 0} \hat{u}(k,t) = \langle \dot{X}(t)\rangle, \quad (2.26)$$

$$\hat{D}_0(t) = \lim_{k\to 0} \hat{D}(k,t) = \langle \dot{X}(t)X(t)\rangle - \langle \dot{X}(t)\rangle \langle X(t)\rangle$$

$$= 1/2d/dt\{\langle X(t)X(t)\rangle - \langle X(t)\rangle^2\} = \int_0^t dt'\{\langle \dot{X}(t)\dot{X}(t')\rangle - \langle \dot{X}(t)\rangle \langle \dot{X}(t')\rangle\}. \quad (2.27)$$

It follows from equation (2.16) that the displacement distribution function fulfils the generalized diffusion equation of the form

$$\partial_t f(x,t) + \nabla_x \int_{-\infty}^{\infty} dx'u(x-x',t)f(x',t) = \nabla_x^2 \int_{-\infty}^{\infty} dx'D(x-x',t)f(x',t), \quad (2.28)$$

where the local drift and diffusion coefficients are related to their Fourier transforms through the following expressions

$$\hat{u}(k,t) = \int_{-\infty}^{\infty} dx \cos kx\, u(x,t), \quad (2.29)$$

$$\hat{D}(k,t) = \int_{-\infty}^{\infty} dx \cos kx D(x,t). \quad (2.30)$$

If the local diffusion coefficients is a positively defined function ($D(x,t) > 0$ for any x and t) then $\hat{D}(k,t) \leqslant \hat{D}_0(t)$. Besides if $D(x,t)$ and $u(x,t)$ are integrable functions of x (e. g. $|\hat{D}_0(t)| < \infty$ and $|\hat{u}_0(t)| < \infty$) then

$$\lim_{k\to\pm\infty} \hat{D}(k,t) = 0, \quad (2.31)$$

$$\lim_{k\to\pm\infty} \hat{u}(k, t) = 0, \tag{2.32}$$

on the basis of the Riemann–Lebesque theorem.

We have also two important moment relations. The first connects an average displacement with the drift coefficient

$$m_x(t) = \langle X(t)\rangle = \int_0^t dt'\hat{u}_0(t') \tag{2.33}$$

and the second one — the diffusion coefficient with the dispersion of the random process $X(t)$

$$\sigma_x^2(t) = 2\int_0^t dt'\hat{D}_0(t') = \langle X(t)X(t)\rangle - \langle X(t)\rangle^2. \tag{2.34}$$

The last expression generalizes the well known Einstein relation for the average square displacement of a brownian particle and can be considered as a special case of the fluctuation-dissipation theorem.

It is also instructive to determine the short time behaviour of the transport coefficients. By expansion in the Maclaurin series we obtain

$$\hat{u}(k, t) = \langle \dot{X}(\Gamma, 0)\rangle + t\langle \ddot{X}(\Gamma, 0)\rangle \tag{2.35}$$

$$\lim_{t\to 0} \hat{u}(k, t) = \langle \dot{X}(\Gamma, 0)\rangle \tag{2.36}$$

and

$$\hat{D}(k, t) = t[\langle \dot{X}(\Gamma, 0)\dot{X}(\Gamma, 0)\rangle - \langle \dot{X}(\Gamma, 0)\rangle^2] \tag{2.37}$$

$$\lim_{t\to 0} \hat{D}(k, t) = 0. \tag{2.38}$$

From these expressions it follows that the short time forms of the transport coefficients are independent of the wave vector.

So far we did not make any approximation and equation (2.17) is entirely equivalent to the initial definition of the characteristic function (2.15). Calculation of the local transport coefficients $\hat{u}(k, t)$ and $\hat{D}(k, t)$ is at least as much troublesome as the calculation of the initial expression. The form of the evolution equation (2.16) can be greatly simplified if we use instead of the local transport coefficients their long wave limits (2.26) and (2.27). This means the use of preaveraged transport coefficients in place of those which are valid for a specified values of the displacement variable. Such a procedure known as a "hydrodynamic" approximation was suggested by several authors in various contexts. However, one should remember that this cannot be considered as a first step of any systematic procedure based on the expansion of the drift and diffusion coefficients in a power series with respect to the wave vector. Although several authors suggested this kind of generalization of the usual diffusion equation introducing higher order transport coefficients (so called Burnett and super Burnett coefficients) this proposition seems to be unacceptable in view of the Marcinkiewicz theorem [7, 8]. This theorem which is based on the requirement that the probability density function has to be given by a non-negative definite integrable function states that: If

$P_m(k)$ is a polynomial of degree $m > 2$ then the function $\exp[P_m(k)]$ cannot be a characteristic function. Thus as long as we are interested in the probability density functions it is clear that no use can be made of any systematic expansion of transport coefficients which would lead in consequence to this kind of expression for the characteristic function.

It seems interesting to consider how good representation the real distribution can be obtained if one use the gaussian approximation defined by the equation

$$\partial_t \hat{f}^0(k, t) = ik\,\hat{u}_0(t)\hat{f}^0(k, t) - k^2\hat{D}_0(t)\hat{f}^0(k, t) \tag{2.39}$$

for the characteristic function or equivalently by the Fokker-Planck equation for the displacement distribution

$$\partial_t f^0(x, t) + \nabla_x \hat{u}_0(t) f^0(x, t) = \nabla_x^2 \hat{D}_0(t) f^0(x, t) \tag{2.40}$$

$$f^0(x, t) = (2\pi)^{-1/2}\Big[\int_0^t dt'\hat{D}_0(t')\Big]^{-1/2} \exp\Big[-\Big(x - \int_0^t dt'\hat{u}_0(t')\Big)^2\Big/\Big(\int_0^t dt'\hat{D}_0(t')\Big)\Big] \tag{2.41}$$

In spirit of the central limit theorem it can be expected that the true distribution asymptotically tends to the gaussian for large values of the displacement variable. In fact let us assume that $X(t)$ is a bounded random variable, which means that for any time t exists a constant L such that $|X(t)| < L$. Then one can always choose such a set Q_L that for $k \in Q_L$ we have $Lk \ll 1$ and the trigonometric functions in (2.20) and (2.21) can be replaced by the first terms of their expansion in the Taylor series. Thus for $k \in Q_L$ we have

$$\hat{f}(k, t) \simeq \hat{f}^0(k, t), \qquad (k \in Q_L). \tag{2.42}$$

Now let us consider the inverse Fourier transform

$$f(x, t) = (2\pi)^{-1} \int_{-\infty}^{\infty} dk \exp(-ikx)\hat{f}(k, t)$$
$$= (2\pi)^{-1} \int_{Q_L} dk \exp(-ikx)\hat{f}(k, t) + (2\pi)^{-1} \int_{\bar{Q}_L} dk \exp(-ikx)\hat{f}(k, t) \tag{2.43}$$

where $\bar{Q}_L$ is a set complementary to Q_L. Using (2.42) we can obtain an approximate relation

$$f(x, t) \simeq (2\pi)^{-1} \int_{Q_L} dk \exp(-ikx)\hat{f}^0(k, t) + (2\pi)^{-1} \int_{\bar{Q}_L} dk \exp(-ikx)\hat{f}(k, t). \tag{2.44}$$

For large values of x the second term on the right-hand side of (2.44) will give a negligible contribution due to the rapid oscillation of the trigonometric functions. Thus an asymptotic form of the displacement distribution is given by

$$f^{as}(x, t) \sim (2\pi)^{-1} \int_{Q_L} dk \exp(-ikx)\hat{f}^0(k, t), \qquad x \to \infty$$
$$\simeq (2\pi)^{-1} \int dk \exp(-ikx)\hat{f}^0(k, t) = f^0(x, t), \tag{2.45}$$

where the integral was extended to the whole space since the complementary set $\bar{Q}_L$ is expected to give an unimportant contribution.

Let us consider now the transport coefficients as functions of the parameter λ introduced in Eq. (2.5). Since this parameter can be considered as a measure of change in time of the physical quantity $Y(\Gamma, t)$ (if $\lambda \to 0$ Y is a constant of motion), then for slowly changing quantities one can expect a reasonable approximation if we restrict ourselves to terms of order λ^2 only in the calculation of these coefficients. In this approximation we obtain again the gaussian distribution with

$$\hat{u}(k, t) = \hat{u}_0(t) = \langle \delta L(t) Y(\Gamma, 0)\rangle + \lambda^2 \int_0^t dt' \langle \delta L(t) \delta L(t') Y(\Gamma, 0)\rangle \tag{2.46}$$

and

$$\hat{D}(k, t) = \hat{D}_0(t) = \lambda^2 \{\langle [\delta L(t) Y(\Gamma, 0)] [\int_0^t dt' \delta L(t') Y(\Gamma, 0)]\rangle$$
$$- \langle \delta L(t) Y(\Gamma, 0)\rangle \int_0^t dt' \langle \delta L(t') Y(\Gamma, 0)\rangle. \tag{2.47}$$

It should be noted that higher order terms of the λ-expansion lead to the polynomial expansion of the transport coefficients with respect to the wave vector and therefore are excluded on the basis of the Marcinkiewicz theorem.

Results of this section shows more clearly why the gaussian distribution plays so important a role in the theory of time-dependent correlations. It appears as an asymptotic distribution in (a) short time limit (Eqs. (2.35), (2.37)) (b) long displacement limit (Eq. 2.45) (c) slow time changing limit ((Eqs. (2.46), (2.47)) and also in an unlikely event when (d) all the cumulants of order higher than the second vanish identically. It is important to note that the gaussian distribution cannot be considered as a first step result of any systematic procedure which would allow eventually to calculate further nongaussian corrections. We return to this problem in the last section.

3. *Multidimensional random processes*

Results of the preceding section can be readily generalized to the case of multidimensional random dynamical variables. Introducing an n-dimensional vector formed by the set of functions $\boldsymbol{Y}(\Gamma, t) = [Y_1(\Gamma, t), Y_2(\Gamma, t), \ldots, Y_n(\Gamma, t)]$ each of them changing in time according to the Poisson–Liouville equation we can define the time-dependent fluctuation vector $\boldsymbol{X}(\Gamma, t)$ by

$$\boldsymbol{X}(\Gamma, t) = \boldsymbol{Y}(\Gamma, t) - \boldsymbol{Y}(\Gamma, 0). \tag{3.1}$$

This vector has the following matrix evolution equation

$$d\boldsymbol{X}/dt = (\boldsymbol{L}_0 + \lambda \delta \boldsymbol{L}) \cdot \boldsymbol{X}(\Gamma, t) + \lambda \delta \boldsymbol{L} \cdot \boldsymbol{Y}(\Gamma, 0), \tag{3.2}$$

where $\boldsymbol{L}_0$ is the diagonal operator matrix with elements defined by

$$(\boldsymbol{L}_0)_{ii} Y_i(\Gamma, 0) = 0 \tag{3.3}$$

and $\lambda \delta \boldsymbol{L}$ is the diagonal operator matrix given by

$$\delta \lambda \boldsymbol{L} = \boldsymbol{L} - \boldsymbol{L}_0. \tag{3.4}$$

$\boldsymbol{L}$ is the non dimensional diagonal matrix formed by the Liouville operator for the sytem

$$(\boldsymbol{L})_{ij} = \delta_{ij}^{Kr} L. \tag{3.5}$$

The characteristic function of the n-dimensional distribution is given by

$$\hat{f}(\boldsymbol{k}, t) = \langle \exp (i\boldsymbol{k} \cdot \boldsymbol{X}(\Gamma, t)) \rangle \tag{3.6}$$

and fulfils the equation of evolution of the form

$$\partial_t \hat{f}(\boldsymbol{k}, t) = i\boldsymbol{k} \cdot \hat{\boldsymbol{u}}(\boldsymbol{k}, t)\hat{f}(\boldsymbol{k}, t) - \boldsymbol{k}\boldsymbol{k}:\hat{\boldsymbol{D}}(\boldsymbol{k}, t)\hat{f}(\boldsymbol{k}, t) \tag{3.7}$$

analogous to the equation (2.16). By a dot we denote the matrix product defined by

$$\boldsymbol{a} \cdot \boldsymbol{b} = \sum_{i=1}^{n} a_i b_i$$

and $\hat{\boldsymbol{u}}(\boldsymbol{k}, t)$ is a vector defined by

$$\hat{\boldsymbol{u}}(\boldsymbol{k}, t) = \{\langle \dot{\boldsymbol{X}}(t) \cos \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle \langle \cos \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle + \langle \dot{\boldsymbol{X}}(t) \sin \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle \langle \sin \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle\} \{\langle \sin \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle^2 + \langle \cos \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle^2\}^{-1}. \tag{3.8}$$

By $\hat{\boldsymbol{D}}(\boldsymbol{k}, t)$ we denote a dyade

$$\hat{\boldsymbol{D}}(\boldsymbol{k}, t) = \left\{ \left\langle \dot{\boldsymbol{X}}(t)\boldsymbol{X}(t) \frac{\sin \boldsymbol{k} \cdot \boldsymbol{X}(t)}{\boldsymbol{k} \cdot \boldsymbol{X}(t)} \right\rangle \langle \cos \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle - \langle \dot{\boldsymbol{X}}(t) \cos \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle \left\langle \boldsymbol{X}(t) \frac{\sin \boldsymbol{k} \cdot \boldsymbol{X}(t)}{\boldsymbol{k} \cdot \boldsymbol{X}(t)} \right\rangle \right\} \{\langle \sin \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle^2 + \langle \cos \boldsymbol{k} \cdot \boldsymbol{X}(t)\rangle^2\}^{-1}. \tag{3.9}$$

It is simple to obtain from (3.8) and (3.9) appropriate limiting formulas similar to the one obtained in Section 2. However, since we consider now n parallel dynamical processes each of which is characterized by a separate rate parameter λ_i ($i \in [1, n]$), we have to take into account that in general these parameters may not be of the same order. If we enumerate these processes according to the decreasing rate of change in time $\lambda_1 > \lambda_2 > \lambda_3 > \ldots > \lambda_n$ we have the following possibilities to consider: (a) All processes have about the same rate of change $-\lambda_i = \lambda$ for any i. (b) The rate constant fulfills the inequality $\lambda_1 > \lambda_2 > \ldots \lambda_m > \lambda_1^2, > \lambda_{m+1} > \ldots > \lambda_n$.

In the first case we have to keep terms of the order λ^2 for all the processes in the expansion of the transport coefficients with respect to the rate constant. Thus we obtain the N-dimensional gaussian distribution [9]

$$f^0(\boldsymbol{x}, t) = (2\pi)^{-n/2}[\operatorname{Det} \int_0^t dt' \boldsymbol{D}_0(t')]^{-1/2} \exp \{-1/2 \times (\boldsymbol{x} - \int_0^t dt' \hat{\boldsymbol{u}}_0(t')) \cdot [\int_0^t dt' \hat{\boldsymbol{D}}_0(t')]^{-1} \cdot (\boldsymbol{x} - \int_0^t dt' \hat{\boldsymbol{u}}_0(t'))\}. \tag{3.10}$$

In the second case it is sufficient to keep only terms proportional to the second power of the rate parameter λ_1. For the processes 2, 3, ..., m we have to calculate the transport coefficient in the linear (with respect to the rate parameter) approximation. Processes numbered by $m+1, \ldots n$ are in this time scale a constants of motion.

4. Time-dependent momentum and position displacements in equilibrium macroparticle solution

Let us consider an equilibrium system consisting of N macroparticles immersed in the heat bath of light solvent particles. We assume that the mass of macroparticles is very much larger than the mass of light environment particles. It may be expected, that due to the inertial effect, momentum change of the thermalized macroparticle is slow and oscillates around the mean value. On the basis of the results of the previous section we obtain the following kinetic equation for the probability density of finding a set of momentum displacements $\delta \boldsymbol{P}^N$ during the time period t

$$\partial_t f(\delta \boldsymbol{P}^N, t) = \sum_{i,j=1}^{N} \int_0^t dt' \langle \boldsymbol{F}_i(t) \boldsymbol{F}_j(t') \rangle_{\text{eq}} : \partial/\partial\delta \boldsymbol{P}_i \partial/\partial\delta \boldsymbol{P}_j f, \tag{4.1}$$

where

$$\boldsymbol{F}_i(t) = \exp(tL_0)\boldsymbol{F}_i(0) = \exp(tL_0)\delta L \boldsymbol{P}_i \tag{4.2}$$

is the actual force acting on the i-th macroparticle moving with a constant momentum $\boldsymbol{P}_i \cdot L_0$ is the Liouville operator of the "unperturbed" system in which the macroparticles are freely moving in the fluid that is in their potential field

$$L_0 = L_f + \sum_{i=1}^{N} \boldsymbol{P}_i/M \cdot \nabla_{\boldsymbol{R}_i}. \tag{4.3}$$

L_f is the Liouville operator of fluid particles moving in the field of force of stationary macroparticles and δL is the operator of infinitesimal momentum change of macroparticles due to their mutual interaction and interaction with the fluid particles.

$$\delta L = -\sum_{i<j} \partial U(|\boldsymbol{R}_i - \boldsymbol{R}_j|)/\partial \boldsymbol{R}_i \cdot (\partial/\partial \boldsymbol{P}_i - \partial/\partial \boldsymbol{P}_j)$$
$$- \sum_{i=1}^{N} \sum_j \partial U(|\boldsymbol{R}_i - \boldsymbol{r}_j|)/\partial \boldsymbol{R}_i \cdot \partial/\partial \boldsymbol{P}_i. \tag{4.4}$$

$U(|\boldsymbol{R}|)$ is a central interaction potential.

Since the motion of macroparticles is slow compared to the motion of light solvent particles, the position vectors of macroparticles also form a slowly varying random process. For the probability distribution of position displacements $\delta \boldsymbol{R}^N$ we obtain respectively

$$\partial_t f(\delta \boldsymbol{R}^N, t) = \sum_{i,j}^{N} \int_0^t dt' \langle \boldsymbol{P}_i(t)/M \boldsymbol{P}_j(t')/M \rangle_{\text{eq}} : \partial/\partial\delta \boldsymbol{R}_i \partial/\partial\delta \boldsymbol{R}_j f, \tag{4.5}$$

where

$$\boldsymbol{P}_i(t) = \exp[t(L_f + \delta L)]\boldsymbol{P}_i(0) = \lim_{\varepsilon \to 0} \exp[t(L_f + \delta L + \varepsilon \sum_j \boldsymbol{P}_j/M \cdot \nabla_{\boldsymbol{R}_j})]\boldsymbol{P}_i. \tag{4.6}$$

The macroparticle velocity correlation function can be calculated using hydrodynamic method which is frequently applied in the statistical theory of polymer dynamics [10].

5. *Discussion*

In recent years the brownian motion problem and the theory of time-dependent fluctuations received a great deal of attention. Statistical methods developed in this field were found useful not only for the description of many particle systems but also for characterization of complex technical units and in several nonphysical problems [11–13]. The Fokker-Planck equation plays a central role in the theory. It is therefore especially important to know exactly under what assumptions physical processes can be described by this equation and if there is a chance of improving this theory for example by the use of higher order differential operators instead of the usual second order diffusion equation. In the present note we discussed the problem of approximating of the real distribution of time-dependent displacement by the gaussian random process. It was shown that the gaussian distribution can be considered as an asymptote of the true displacement distributions and by no mean forms a first step of any systematic procedure. Especially, it does not seem justified to generalize the diffusion equation by the introduction of higher order derivatives and so called Burnett and super Burnett transport coefficients. This problem has been recently studied [4, 14] and it was shown that the higher order transport coefficient for the hard core particle self-diffusion problem are divergent for the limit of long time. However, even if we retain them as arbitrary functions of time, the "Burnett" diffusion equation would lead to a nonpositively defined distribution function according to the Marcinkiewicz theorem. This points out that one must be very careful in the application of apparently obvious systematic methods of derivation of the kinetic equations such as a gradient or coupling constant expansion since they do not always guarantee a correct result. Elaboration of the systematic procedure leading toward a properly defined kinetic equations on every step of approximation is still a challenge for nonequilibrium statistical mechanics.

REFERENCES

[1] A. Einstein, *Ann. Phys.* (Germany) **19**, 371 (1906); **22**, 569 (1907).

[2] M. Smoluchowski, *Z. Phys.* (Germany) **13**, 1069 (1912); *Sitzungsberichte der Akad. d. Wiss.* in Wien **123**, 2381 (1914).

[3] J. A. McLennan, *Phys. Rev.* **A8**, 1479 (1973).

[4] I. de Schepper, *Generalized Hydrodynamics for the Diffusion Processes*, Ph. D. Thesis, University of Nijmegen, The Nederlands 1974.

[5] J. R. Dorfman, *Fundamental Problems in Statistical Mechanics III*, E. G. D. Cohen Ed., North Holland, Amsterdam 1975, p. 227.

[6] A. R. Altenberger, *Acta Phys. Pol.* **A46**, 661 (1974).

[7] J. Marcinkiewicz, *Math. Zeits.* **44**, 612 (1938).

[8] E. Lukacs, *Characteristic Functions*, Griffin and Comp. Ltd. London 1970.

[9] M. Rosenblatt, *Random Processes*, Oxford University Press, New York 1962.

[10] A. R. Altenberger, *Acta Phys. Pol.* **A47**, 861 (1975).

[11] H. Haken, *Rev. Mod. Phys.* **47**, 67 (1975).

[12] R. L. Stratonovič, *Izbrannyie voprosy teorii fluktuacii v radiotekhnikie*, Sovietskie Radio, Moskva 1961.

[13] N. G. Van Kampen, *Adv. Chem. Phys.* **39**, 245 (1976).

[14] I. M. de Schepper, G. Van Beyeren, M. H. Ernst, *Physica* **75**, 1 (1974).