Transport processes in Newtonian and non-Newtonian fluids and fluctuation-dissipation theorems

V Ya Rudyak
Novosibirsk State University of Architecture and Civil Engineering
113 Leningradskaya Str., Novosibirsk, 630008, Russia
Novosibirsk State University, 2 Pirogova Str., Novosibirsk, 630090, Russia
E-mail: valery.rudyak@mail.ru

Abstract. The subject of this paper is molecular modelling of the transport processes in liquids including nanofluids. The weak and strong nonequilibrium processes are considered. In the first case, the corresponding fluctuation-dissipation theorems are formulated. These theorems determine the relation between the dissipative processes and equilibrium thermal fluctuations of the mass, momentum, and energy in the molecular system. Two different formulations of these theorem are discussed in detail. Various systems are considered: molecular liquids, nanofluids, turbulent liquids, fluids in confined conditions, and microviscosity in biomembranes. In the last part the nonlinear transport processes and rheology of the non-Newtonian fluids are discussed.

1. Introduction
The transport processes determine both the nature of the gas and liquid flows and all their thermophysical properties. These flows usually have the macroscopic dimensions and their study, both experimental and theoretical, is carried out at the appropriate scales. For example, when modelling flows of liquids and gases (not too rarefied), macroscopic transport equations, often called hydrodynamic equations, are used. In this case, there is a certain logical dissatisfaction, since the formulation of the transport equations requires the introduction of transport coefficients. However, the mechanisms of formation of these coefficients are determined by intermolecular interactions and their determination requires microscopic analysis of these processes. To date, a wide range of experimental methods for measuring these quantities has been developed. The interpretation of the results obtained in this case is based on the known phenomenological theories, which themselves cannot determine these coefficients. Of course, the results of this interpretation, generally speaking, should be treated with a certain caution.

For the first time, a consistent theory of transport processes was created on the basis of the kinetic theory of rarefied gases. The kinetic theory of gases, having examined the transport processes from a molecular point of view, not only revealed the mechanisms of transport processes, but also gave a constructive way to calculate the corresponding transport coefficients [1]. Unfortunately, this can only be done for rarefied gases. In dense gases and liquids, such a consistent theory does not exist. A kinetic description, that is, a description by means of a one-particle distribution function is essentially impossible for either dense gases or liquids. There are quite objective reasons for this. Even in the equilibrium state, the calculation, for example, of the energy of such a fluid requires knowledge of at least a pair distribution function. The thing is that the interactions between molecules do not contribute into...
transport coefficients and the equation of state for the rarefied gas. Such contributions appear only in dense gases [2]. In addition, the transport processes in dense gases and liquids along with individual interactions of molecules, are also determined by some collective effects. The transport processes are no longer local.

The situation is even more complicated in various so-called non-Newtonian fluids. Non-Newtonian behavior is typical for different dispersed fluid, nanofluids, polymer liquids and etc. For such fluid the stress tensor is the function of the shear rate. How are the transport laws formulated in this case and how are the functions characterizing them related to the molecular motion of particles of the corresponding fluids? The widely used models here (Power law model, Hershel–Bulkly fluid and etc.) are simply an attempt to integrate them into the framework of a regular Newtonian fluid. At the same time, the question of the mechanisms of transport processes is not discussed at all.

Similar difficult situation arises when considering and studying strongly nonequilibrium processes, when the usual linear constitutive relations cease to work. Are there any general physical laws that allow us to consider all transport processes from a general point of view? The present work is devoted to the discussion of this questions and the search for appropriate answers.

2. Nonequilibrium statistical mechanics of simple liquids

This section will be discussing only the so called simple liquids. It can be either single-component or multicomponent liquids, including dispersed ones. In the latter case, however, we will talk about media in which dispersed particles are spherical or close to spherical. In all cases, it will be assumed that the interactions of all the medium particles are described by certain potential forces (although a similar approach is quite feasible for non-potential forces).

In the phenomenological mechanics of a continuous medium, the transport equations are formulated with respect to macroscopic variables, which are determined by the integral conservation laws. These equations, however, are not closed. The central problem of the entire phenomenological mechanics of a continuous medium is the derivation of the constitutive relations establishing the relationship between fluxes and thermodynamic forces. The latter are some functions of the macroscopic variables. Phenomenologically, this problem is solved by methods of thermodynamics of nonequilibrium processes [3]. In this case, it is possible to establish some functional relationship between the fluxes and gradients of macroscopic variables and thereby close the transport equations. However, the constitutive relations obtained include unknown transport coefficients, which phenomenological macroscopic physics cannot determine.

Since the nature of the transport processes is microscopic, it is possible to deduce the corresponding constitutive relations and transport coefficients only from the first principles or, in other words, from molecular point of view. Actually, this is exactly how Boltzmann’s kinetic theory was constructed [1]. Since in this paper we are interested in the constitutive relations for macroscopic transport equations, the corresponding equations should be derived from the first principles, considering the particle dynamics of a given liquid.

This can be done using methods of nonequilibrium statistical mechanics [2,4,5]. In this case all macroscopic observables are calculated using the N-particle distribution function. This function is a solution of the Liouville equation. To describe the transport processes in the system considered we have to construct the solution of the Liouville equation corresponding to the macroscopic level of the system description. Such solution can be constructed by using the projection method [6]. There are many different variants of this method [2,4,5,7]. However in all cases the similar generalized constitutive relations are obtained. These relations for the isotropic medium have the following form

$$J_i(r, t) = J_i(r, 0) + \sum_{n=1}^{3} \int_0^t dt_1 \int dr' dr'' K_{ni}(r, r', t - t_1|q_i(r'')) \cdot X_n(r', t_1), \quad i = 1, 2, 3. \quad (1)$$

Here $X_n$ are the so-called thermodynamical forces. These forces are equal to the gradients of the macroscopic variables $q_i$. The constitutive relations (1) are nonlinear, nonlocal and delaying. The nonlinearity of the relations (1) is due to that the transport kernels $K_{ni}$ are also the functionals of the ter-
modynamical forces. The delay is connected with the finite speed of disturbances propagation in the medium. The spatial nonlocality is associated with the correlation between dissipative fluxes \( J_i \) and thermodynamic forces and is due to the nonlocality of the particles interactions and statistical effects (interactions of the physical small fluid volumes).

In this section the weakly nonequilibrium processes will be considered. In this case the dissipative fluxes are proportional to gradients of the macroscopic variables \( \phi_i \)

\[
J_i(r, t) = -\mu_i \nabla \phi_i(r, t), \quad i = 1, 2, 3. \tag{2}
\]

The transport coefficients in linear constitutive relations (2) are the time integrals from the two-time correlation functions \( \chi_1 \) of the corresponding dynamical variables

\[
\mu_i = \int_0^t dt_1 \chi_1(r, t - t_1), \quad i = 1, 2, 3. \tag{3}
\]

These relations are called the fluctuation-dissipation theorems (FDT). In literature for the simple fluids these theorems are known as Green-Kubo formulas [2, 4, 5, 8, 9].

It is worth noting two important facts. The transport coefficients of the weakly nonequilibrium fluid flows are determined by the microfluctuations of the corresponding dynamical values. The correlation functions in equation (3) are calculated by means of equilibrium distribution function. Thus, the transport coefficients (3) are the properties of equilibrium state of the system.

3. FDT of the weakly nonequilibrium processes

The FDT (3) has universal character. The relations of such type describe the transport processes having place in different media and in different situations. In this section some such situations are discussed.

3.1. Diffusion of molecules and nanoparticles

The simplest FDT determines the self-diffusion coefficient

\[
D = \frac{1}{3} \int_0^{t_p} dt_1 \chi_1(r, t - t_1). \tag{4}
\]

The coefficient (4) is the function of time. This dependence is determined by the evolution of the velocity autocorrelation function (VACF)

\[
\chi_1(t) = \sum_{i=1}^{N} \langle v_i(0) \cdot v_i(t) \rangle. \tag{5}
\]

Here and below angular brackets indicate ensemble averaging. Thus, VACF as all other correlation functions is calculated using the \( N \)-particle equilibrium distribution function. The observed value of this coefficient is obtained when it reaches a plateau value \( t_p \) [10]. Therefore the existence of the transport coefficients means that the corresponding correlation function must be decaying. According to (4) the self-diffusion coefficient is to be a finite value if VACF decreases more rapidly than \( t^{-1} \).

Really, VACF of the rarefied gas damps exponentially [1, 5]. However the evolution of VACF of the dense gas is more complex, it has two different branches [11]

\[
\chi_1(t) = ae^{-t/t_*} + b(t - t_*)^{-3/2}. \tag{6}
\]

Here \( a, b \) and \( t_* \) are some constants [12]. The existing two different terms in Eq. (6) mean two different mechanisms of the molecule velocity relaxation in the dense gas. The first is determined by the individual interactions of the molecules, at the same time the second is related to collective effects of the molecules interactions. This second branch of the VACF decay is related to the molecules diffusion in a gas.
The behaviour of the VACF in liquids depends on liquid state. In metastable state the VACF is described by the function similar to (6). However, in main state the VACF has the negative tail which describes the so-called cage-effect [13]. The presence of a negative tail of VACF of molecules is associated with the existence of a short-range order in the liquid.

The relaxation mechanisms in dispersed liquids are determined by the interaction of the dispersed particles with the molecules of carrier fluid. The evolution of the Brownian particle in liquid is directly connected with the Stokes friction force. In this case there is a single mechanism of the velocity relaxation. Therefore the relaxation of the VACF of the Brownian particle has the following form

$$x_n(0, t) = \frac{(3kT/M)e^{-t/\tau_s}}{1 + e^{-t/\tau_s}},$$

(7)

where the relaxation time is equal to $\tau_s = M/(6\pi\mu R) = M/\gamma$, $R$ and $M$ are the radius and mass of the particle, respectively, $\mu$ is the viscosity coefficient of the carrier fluid and $\gamma$ is the Stokes friction force ($T$ is the fluid temperature, and $k$ is the Boltzmann constant).

The evolution of the VACF of nanoparticles is much more complex, because their relaxation depends not only on the collective friction force acting from the carrier fluid but also on the individual interactions with the fluid molecules. For this reason the relaxation of the VACF of a nanoparticle is the sum of two exponents [14]

$$x_n(0, t) = a_1e^{-t/\tau_1} + a_2e^{-t/\tau_2},$$

(8)

where $\tau_1, \tau_2$ are some constants depending on the characteristics of nanoparticles.

The presence of two branches of relaxation of the VACF (8) means the existence of two different mechanisms of velocity relaxation. The first of them is associated with individual interactions of a nanoparticle with carrier fluid molecules and has a characteristic time $\tau_1$. The second is due to the collective effects of the interaction of the nanoparticles with microfluctuations of the macroscopic fields of the carrier fluid (density and velocity) that form around the nanoparticle. The corresponding time of this interaction is $\tau_2$.

The diffusion coefficient of the Brownian is described by the following relation

$$D = kT/(M\gamma).$$

(9)

The formula (9) is another formulation of the FDT. This FDT formulation goes back to Einstein's famous work on Brownian motion [15]. Using the FDT (9) it is easy to show that the diffusion coefficient of the nanoparticle has the similar form

$$D = (kT/M)(a_1\tau_1 + a_2\tau_2).$$

(9a)

The carbon nanotube (CNT) is a special type of nanoparticles. The single-walled CNTs have a characteristic diameter of 1.6 nm but their length $L$ can reach hundreds of nanometers or more. Thus, the aspect ratio of the CNT may be very large. But the diffusion coefficient of the CNTs may be described by the relation similar to (9) [16]

$$D_t = \frac{kT}{6\pi\mu L}(\ln \frac{L}{2R} + 0.32).$$

(9b)

Another important circumstance in studying the diffusion of CNTs is the need to take into account rotational diffusion. In simplest case the diffusion coefficient of the CNT will be described by the following relation

$$D_t = \frac{3kTln(L/2R)}{\pi\mu L^3}.$$  

(9c)

3.2. The viscosity coefficient of nanofluids

The FDT (9) connects the diffusion coefficient of the Brownian particle with the friction force acting on it. In other words, according to the FDT (9), the diffusion coefficient is simply proportional to the mobility $l$ of the Brownian particle: $D = kTL$. The transport of the momentum and energy in rarefied gases is also proportional to the mobility of the molecules. The average force acting on an isolated
molecule generally depends on the laws of intermolecular interaction. Nevertheless, \( \mu \sim \rho D \) (here \( \rho \) is the gas density and \( D \) is the self-diffusion coefficient). Thus, it may formulate the FDT for the viscosity of rarefied gas

\[
\mu = a_\mu kTl, \tag{10}
\]

where the coefficient \( a_\mu \) is the function of the intermolecular forces. The similar FDT may be described for the thermal conductivity of rarefied gas.

Such a simple type of the FDT for a rarefied gas is due to the fact that the interaction of molecules does not directly contribute to the transport coefficients. Such a contribution appears only for a moderately dense gas [2]. Therefore the FDT for the viscosity coefficient of a rarefied gas nanosuspension has the following form

\[
\mu = \frac{1}{kTV} \sum_{\alpha, \beta = 1,2} t_p \left( \sum_{i=1}^{N_\alpha} m_\alpha v_{ix}(t) v_{iy}(t) \sum_{j=1}^{N_\beta} m_\beta v_{jx}(t) v_{jy}(t) \right).
\]

A similar FDT can be written for the thermal conductivity coefficient.

Contributions to the viscosity coefficient of the gas nanosuspension are determined by the FDT (11) of three grades. On the one hand, this is a contribution due to the interaction of molecules \( \mu_m \) and it is completely described by the kinetic theory of gases [1, 2]. On the other hand, this is the contribution of nanoparticles \( \mu_p \). Finally, there is a cross-contribution that determines the redistribution of momentum in the system due to the interaction of molecules with particles \( \mu_{mp} \). Averaging in (11) is performed over the equilibrium distribution function. Therefore, due to its parity, the cross contribution \( \mu_{mp} \) to the total viscosity coefficient is zero.

Next, we will consider the nanoparticle as Brownian. This can be done unless the gas is too rarefied. In this case, the usual Stokes force must be replaced by the force \( \gamma_* = \gamma C \), introducing the Cunningham–Milliken–Davis correction \( C \) [17]. Then, the contributions of nanoparticle velocities included in (11) can be calculated. As a result, the full viscosity coefficient of gas nanosuspension with a volume concentration of particles \( \varphi \) is equal to \( (\rho_p \) is the density of the particle material)

\[
\mu = \mu_m + \mu_p = \mu_m \left( 1 + \frac{kT \rho_p}{12 \pi \mu_m^2 C} \varphi \right). \tag{12}
\]

It should be noted that \( \mu_p \) included in formula (12) is effective; it takes into account the contribution of particles to the fluid viscosity. Moreover, interactions of nanoparticles with molecules of the carrier fluid are actually taken into account as well. The viscosity coefficient of the gas suspensions with CNT can be calculated in exactly the same way. In this case, the expression (12) is transformed into the following

\[
\mu = \mu_m \left[ 1 + \frac{kT \rho_p}{12 \pi \mu_m^2 C} \left( \ln \frac{L}{2R} + 0.32 \right) \varphi \right]. \tag{12a}
\]

The FDTs that determine the viscosity and thermal conductivity coefficients of liquids are much more complicated than expression (10). Now these processes are not only determined by the velocities of the particles of the system, but also depend on interparticle interactions. Below, the FDT for nanofluid viscosity is considered as an example

\[
\eta = \frac{1}{5kT} \int_0^{t_p} dt \left( J(0): J(t) \right), \tag{13}
\]

where \( J \) is the microscopic formula of the stress tensor

\[
J = \sum_{\alpha} \sum_{i=1}^{N_\alpha} m_\alpha v_i v_i + \frac{1}{2} \sum_{\alpha, \beta \neq \beta} (r_i - r_j) F_{ij},
\]
here \( \mathbf{r}_i \) and \( \mathbf{v}_i \) are the coordinate and velocity of the particle \( i \) of phase \( \alpha \), \( m_\alpha \) is its mass and \( \mathbf{F}_{ij} \) is the interparticle force. Here indexes \( \alpha = 1, 2 \) refer to base fluid molecules and nanoparticles, respectively.

### 3.3. Viscosity of the fluid in confined conditions

Extensive study of fluid flows under confined conditions in the last years has been motivated by the traditional interest to the flows in porous media on the one hand, and by emergence of many different microfluidics tools and systems on the other hand. One of the most important property of such flows is their viscosity. In papers [18, 19] the statistical mechanics of the fluid transport properties under confined conditions were developed. The considered system (fluid molecules and atoms of the walls of channel or pores) is modelled by two kinds of the particles. The evolution of this particles system is described by the Liouville equation. Solving this equation, the constitutive relations were derived. It has been established that the transport properties of fluids in nanochannels and nanopores are determined not only by the characteristics of the fluid, but also by the properties of the entire fluid-channel (pore) wall system. In particular, the effective viscosity coefficient of the fluid is described by the following FDT

\[
\eta = \frac{1}{5kT} \sum_{i,j=1,2, i \neq j} t_p \int_0^t dt \left( \mathbf{J}_i(0) : \mathbf{J}_f(t) + \mathbf{J}_i(0) : \mathbf{J}_b(t) \right).
\]

Here the subscript \( f \) corresponds to the fluid molecules, and \( b \) to the molecules (atoms) of the channel walls. In addition, new type stress tensor of the the microscopic fluxes appeared:

\[
\mathbf{I}_{fb} = -\frac{1}{4} \sum_{\alpha}^2 \sum_i \sum_j (\mathbf{r}_i - \mathbf{r}_j) \mathbf{F}_{ij}.
\]

The equation (14) is the generalization of the known Green–Kubo formula for fluid in the bulk (the latter is obtained from equation (14) for \( \alpha = 1 \)). The effective viscosity coefficient is due to the interactions not only between the fluid molecules. The interactions of the fluid molecules with the walls play a key role. This should be taken into account, and it should be realized that the fluid viscosity in nanochannels is not determined only by the fluid properties. This system is a special two-phase medium in which transport processes are in a sense similar to those in two-phase suspensions, where it is also necessary to introduce effective transport coefficients.

### 3.4. Microviscosity of biomembranes

Biomembranes are a very interesting and, for obvious reasons, extremely important dispersed system. They are usually built from two layers of lipids, in which proteins are embedded. This is a typical nanosystem, since usually the thickness of the lipid layers does not exceed 10 nm. The structural state of the biomembrane is very complex. In the normal state, the membrane is in the liquid crystal state, but depending on external conditions, it may undergo a phase transition to the gel phase. In general, lipids perform quite complex movements, including lateral diffusion, rotational motion around an axis, and some others. The lateral diffusion coefficient of spin-labeled or fluorescent phospholipid probes can be measured by several methods: EPR, NMR, and fluorescent method. The root mean square displacement of such a probe is determined by the Einstein’s relation: \( \bar{r}^2 = 4D_\perp t \) (two-dimensional system). The values of the diffusion coefficient are quite high: \( D = 10^{-7} - 10^{-9} \) sm²/s [20].

Since a biomembrane can be considered as a specific dispersed fluid, many traditional properties for liquids are quite suitable for its characterization. In particular, it turns out that one of the most important integral properties is the so-called microviscosity. It plays an important physiological role in the adaptation of various organisms to external influences, for example, to thermal stress. Microviscosity change, in particular, is a good marker of cell health. When we talk about microviscosity we actually mean mobility. Thus the microviscosity coefficient is determined by the FDT in the form (9)
\[ \eta_t = \frac{1}{5kT} \int_0^{t_p} dt \langle \delta u(0) \delta u(0) : \delta u(t) \delta u(t) \rangle, \]  
\[ \lambda_t = \frac{1}{3} \int_0^{t_p} dt \langle \delta u^2(0) \delta u(0) \cdot \delta u^2(t) \delta u(t) \rangle, \]  
\[ D_{ct} = \frac{1}{3} \int_0^{t_p} dt \langle \delta u^2(0) \delta u(0) \cdot \delta u(t) \rangle. \]  

3.5. **Turbulent viscosity**

The FDTs are the fundamental relations of the theory of dissipative processes. In all cases of introducing the transport coefficients describing given dissipative process these coefficients will be integrals from two-time correlation functions of appropriate microfluctuations. In particular, we may consider the transport processes in turbulent fluid flows. In turbulent flows the instant velocity field \( u \) may be presented as superposition of the average velocity \( U \) and fluctuation \( \delta u : u = U + \delta u \). In simplest case the turbulent dissipative processes will be determined namely by these fluctuations. Therefore it is possible to introduce the coefficient of turbulent viscosity coefficient

\[ \eta_t = \frac{1}{5kT} \int_0^{t_p} dt \langle \delta u(0) \delta u(0) : \delta u(t) \delta u(t) \rangle, \]  

coefficient of the turbulent energy transfer

\[ \lambda_t = \frac{1}{3} \int_0^{t_p} dt \langle \delta u^2(0) \delta u(0) \cdot \delta u^2(t) \delta u(t) \rangle, \]  

and coefficient of thermal diffusion

\[ D_{ct} = \frac{1}{3} \int_0^{t_p} dt \langle \delta u^2(0) \delta u(0) \cdot \delta u(t) \rangle. \]  

Certainty, in general case the transport processes in turbulent flows are rather complex. Therefore the formulas (15)–(17) will have more complicated form. One has to take into account the presence of pressure and density fluctuations. In addition, all fluctuations will interact with each other. Finally, there are fluctuations of different scales. For this reason it will be convenient to formulate the corresponding transport coefficient in Fourier representation. However, all FDT will have the form similar to the formulas (15)–(17).

4. **Strongly nonequilibrium processes**

Generally speaking, strongly nonequilibrium processes may have different nature. On the one hand, these are processes in which flows are already non-linear in the gradients of macroscopic variables or, in other words, in thermodynamic forces. The difficulty lies in the fact that in the general case this dependence is determined not even by a function, but by some functional. The Eq. (1) defines such functional. Two types of nonlocality contained in the generalized constitutive relations (1) should be distinguished. This is the nonlocality associated with the spatial and temporal correlation of dissipative fluxes and thermodynamic forces, and nonlocality caused by the nonlocality of the transport kernels \( K_{ni}(r,r',t-t_1|\varphi_i(r'')) \), which themselves are rather complex functionals of macroscopic variable and thermodynamic forces.

In the simplest case, neglecting the nonlocality of the transport kernels, the Eq. (1) can be localized and it can be represented as a series in gradients

\[ J_i(r, t) = -\mu_i \nabla \varphi_i(r, t) + \sum_n \left[ \mu_{in}^{(1)} \nabla \varphi_i(r, t) \nabla \varphi_n(r, t) + \mu_{in}^{(2)} \nabla \varphi_n(r, t) \right] + \cdots, \quad i = 1,2,3. \]  

A feature of the nonlinear constitutive relations (18) is that all dissipative fluxes now depend on all thermodynamic forces. This dependence is governed by Curie's theorem [3], according to which the
tensor dimension of the flux is consistent with the tensor dimension of the thermodynamic forces entering the right-hand side. One of the first examples of such nonlinear constitutive relations is the Burnett equation in the kinetic theory of rarefied gases [1, 21]. However, these equations need to be adjusted and take into account the terms associated with the delay [22]. The transport coefficients in the Eqs. (18) will again be determined by some FDTs, which, however, turn out to be much more complicated (3). In kinetic theory, they are determined by explicit analytic formulas [1].

Some fundamental difficulty lies in the fact that the transport coefficients appearing in (18) turn out to be immeasurable (even if we can calculate them!). Therefore, it is worth understanding when such equations can be applied. In the rarefied gas dynamics the second-order terms can be useful, on the one hand, in the description of supersonic flows. On the other hand, they must be taken into account at very small Mach numbers, when the so-called thermostresses transport phenomena become important [23]. Similar phenomena may well be observable.

The appearance of nonlinear transport equations in the rarefied gas dynamics was expected to enable the advancement towards moderate Knudsen numbers. These hopes have not materialized. This is due not only to the fact that the corresponding hydrodynamic equations turn out to be extremely complex. Even today they cannot be solved with the help of the best existing programs. The thing is different. There are very few processes that would have to be described using nonlinear transport laws in the rarefied gas dynamics. On the other hand, series (18) are not convergent in the usual sense. All terms above the first are almost of the same order. Therefore, taking into account only quadratic terms, we make almost the same mistake that does not take them into account. In addition, it should be understood that the use of higher-order transport equations requires the formulation of corresponding boundary conditions. Thus, in rarefied gases, strongly nonequilibrium states should be described by means of the Boltzmann equation. On the other hand, in all other cases when the Knudsen numbers are sufficiently small, the Navier–Stokes equations should be used.

Is it necessary to apply higher order transport equations in the description of liquids flows? Simple estimates show that the nonlinear velocity contributions to the stress tensor will be of the first order terms only at pressures of about a million atmospheres or more. Therefore, in the study of ordinary liquid flows, the use of higher order transport equations is not relevant. In liquids, however, other nonlinear phenomena are possible.

In the constitutive relations (1), the relaxation transport kernels $K_{nl}(\mathbf{r}, \mathbf{r}', t - t_0 | \varphi_i(\mathbf{r}''))$ are nonlocal functionals of macroscopic variables and thermodynamic forces. There are both spatial and temporary nonlocalities. A characteristic type of spatial nonlocality is associated with the sizes of the internal structural elements of the medium. The temporal nonlocality in normal conditions is determined by the interaction times of the medium particles. These times are small as a rule and therefore the temporal nonlocality can be neglected. If in this case the spatial and temporal nonlocality of dissipative flows and thermodynamic forces can be neglected, then, for example, the stress tensor has the following form

$$J_2(\mathbf{r}, t) = J_2(\mathbf{r}, 0) + \mu_2(\mathbf{r}, t|\nabla \mathbf{u})\nabla \mathbf{u}(\mathbf{r}, t),$$

(19)

the vertical line here, as before, means functional dependence.

Thus, in Eq. (19) a certain analogue of the usual molecular viscosity appears. Actually, the coefficient $\mu_2$ also has a molecular nature, however, unlike the usual one, it is also a functional of the shear rate tensor. In addition, expression (19) includes some initial value of the stress tensor $J_2(\mathbf{r}, 0)$, which depends on the initial data. In ordinary liquids and media with damped memory, this component decays rather quickly and the stress tensor takes its usual form. However, there are liquids in which the fluid flow begins only when the stresses become greater than some predetermined value. These are non-Newtonian fluids with yield strength $J_{10}$. Fragments $J_2(\mathbf{r}, 0)$ in such liquids turn out to be undamped and they form the yield point.

The dependence of the pseudo-viscosity $\mu_2(\mathbf{r}, t|\nabla \mathbf{u})$ on the shear rate tensor is extremely complex and requires special discussion. In the simplest case, localizing this functional, it can be represented as
the product of a certain constant by a function of the strain rate tensor. Since it must be a scalar, the final stress tensor can be written as

$$J_2(r, t) = J_{20} + k \dot{\gamma}^{n-1} S(r, t),$$

(19a)

where $S$ is the symmetrized stress rate tensor, $\dot{\gamma} = S : S$.

The constitutive relation (19a) is intentionally presented in the form typical of the Herschel–Bulkley fluid. If $J_{20} = 0$, then the constitutive relation of the power-law fluid model follows from (19a), where $k$ is the consistency parameter and $n$ is the fluid index. It should be noted that the consistency parameter is also determined by some analog of the FDT, since it is also calculated as a certain time integral of the correlation function, although this relation is much more complex than (13).

Conclusion

The most important characteristic of all transport processes is the corresponding transport coefficients. In both linear and nonlinear processes, they are determined by FDTs. In the simplest case, these theorems have the form (3) and indicate that the cause of the dissipative processes is the equilibrium thermal fluctuations of the mass, momentum, and energy that take place in the molecular system. Dissipation is associated with the redistribution of mass, momentum and energy in the system, due to the presence of precisely equilibrium molecular fluctuations. And this is the law of the nature.

The following remark is also useful. The diffusion coefficient is a macroscopically observable, measurable and completely deterministic quantity. On the contrary, the velocity field of a Brownian particle (and nanoparticle in particular) is random, and only its average displacement is observable. Deterministic measurable quantity (instantly measurable!) cannot depend on the random value.

The situation with non-Newtonian fluids is fundamentally different. In Newtonian fluids, dissipative processes are determined by equilibrium thermal molecular fluctuations. The flows of non-Newtonian fluids are an open system. The viscosity of these fluids changes with changing the shear rate. For each specific steady-state value of the shear rate, a completely specific and unchanged viscosity value is obtained, which is due to all the same thermal fluctuations. Why does viscosity change when the shear rate changes? This is due to a change of the liquid structure under the action of shear stresses. This effect is well known in shear flows of polymer or dispersed liquids. Therefore, further study of transport processes in such liquids requires a systematic study of their structure and its change under the action of shear stresses.

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