

# Fluid Transport Properties under Confined Conditions

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**Abstract** The problem of adequate description of transport processes of fluids in confined conditions is solved using methods of nonequilibrium statistical mechanics. The «fluid–channel wall» system is regarded as a two-phase medium, in which each phase has a particular velocity and temperature. The obtained results show that the transfer equations describing transport processes in confined spaces should contain not only the stress tensor and the heat flux vector, but also the interfacial forces responsible for the transfer of momentum and heat due to the interaction with the wall surfaces. The stress tensor and the heat flux vector fluid can be expressed in terms of the effective viscosity and thermal conductivity. However, the constitutive relations contain additive terms that correspond to the fluid–surface interactions. Thus, not only do the fluid transport coefficients in nanochannels differ from the bulk transport coefficients, but also they are not determined only by the parameters of the fluid.

**Keywords:** Micro Flow, Transport Coefficients, Nonequilibrium Statistical Mechanics, Molecular Dynamics

## 1. Introduction

Extensive study of liquid and gas microflows in the last two decades has been motivated by the emergence of a large number of microelectromechanical systems (MEMS) and then nanotechnologies. These flows are currently used in biochemistry, medicine, pharmacology, biology, thermal engineering, instrument making, catalysis, etc. An important aspect of the active use of various micro- and nanosystems is the development of a new generation of resource-saving technologies with low power consumption. The performance of such devices is largely determined by the transport processes occurring in the fluid. Thus, for example, mixing in micromixers is due to diffusion processes, and the energy spent for fluid circulation depends on the fluid viscosity. Today, however, it is known that transport processes in confined geometry are significantly different from those in the bulk. Diffusion, for example, is anisotropic (Andryushchenko, Rudyak, 2011, Rudyak et al., 2011), and the viscosity is much higher than that in the bulk (Karnidakis et al., 2011).

Transport processes are processes of relaxation of large-scale fluctuations, such as gradients of observed macroscopic density, velocity, temperature, etc. Fluctuations can be maintained, in particular, by external forces with respect to the system. Transport processes in rarefied gases are easily interpreted: they are due to transfer of the corresponding microscopic characteristics on scales of the order of the mean free path of the molecules. In liquids, transport processes are much more complicated. For example, the viscosity is due not only to the momentum transfer in collisions of molecules, but also to the destruction of short-range order and diffusion processes of momentum transfer in the system. In the vicinity of the surface, an important factor in the equalization of momentum in flow is the interaction of fluid molecules with the surface molecules. In a nanochannel with a characteristic cross-sectional area of the order of 5 nm, almost half of all interactions of fluid molecules are their collisions with the molecules of the channel walls. Under such conditions, it becomes meaningless to speak of the viscosity of the fluid separately. The viscosity of the fluid becomes a property of the

entire «fluid–nanochannel wall» system. Of course, it is not easy to study this «viscosity» experimentally. However, to develop an appropriate apparatus, it is first necessary to construct an adequate theory of transport processes, which should be used in interpreting experimental data. The aim of this work is to develop such a theory. It is constructed from the first principles using methods of nonequilibrium statistical mechanics.

## 2. Dynamic description of the «fluid–surface» system

Since the states of the molecules of the fluid and the channel walls are significantly different (in particular, the walls are at rest and the fluid moves), the system is a peculiar two-phase medium. The properties of this medium are described in this paper using the apparatus that we developed previously to describe dispersed media (Rudyak, 1987, Rudyak, Belkin, 2011). In this case, the «liquid–channel wall» system is treated as a two-phase medium, each of which phases consists of the same type of molecules and is characterized by their macroscopic variables: density, velocity, and temperature. The dynamics of the system is described by the  $N$ -particle distribution function  $F_N$  which satisfies the Liouville equation

$$\partial F_N / \partial t + L_N F_N = 0, \quad (1)$$

in which the Liouville operator is defined as

$$L_N = \sum_{\alpha, \varphi=1}^2 \sum_{i=1}^{N_\alpha} \left[ \frac{\mathbf{p}_i}{m_\alpha} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \frac{1}{2} \sum_{j=1}^{N_\varphi} \mathbf{F}_{ij} \cdot \left( \frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \right].$$

Here  $m_i$ ,  $\mathbf{r}_i$ , and  $\mathbf{p}_i$  are the mass, coordinate of the center of mass, and momentum of the  $i$ -th molecule of phase  $\alpha$ . The intermolecular interaction force  $\mathbf{F}_{ij}$  can generally be nonpotential, and the structure of the Liouville operator does not change in this case.

We will characterize the state of the system by partial values of the density  $n_\alpha$ ,

momentum  $\mathbf{p}_\alpha$ , and energy  $E_\alpha$ . These quantities are the averages of the corresponding dynamical variables

$$\hat{n}_\alpha(\mathbf{r}) = \sum_{i=1}^{N_\alpha} \delta(\mathbf{r}_i - \mathbf{r}), \quad \hat{\mathbf{p}}_\alpha(\mathbf{r}) = \sum_{i=1}^{N_\alpha} \mathbf{p}_i \delta(\mathbf{r}_i - \mathbf{r}),$$

$$\hat{E}_\alpha(\mathbf{r}) = \sum_{i=1}^{N_\alpha} E_i \delta(\mathbf{r}_i - \mathbf{r}). \quad (2)$$

Here  $E_i$  the energy of the  $i$ -th molecule. Applying the Liouville operator to the dynamic densities (2), we obtain the following transport equation for them:

$$\dot{\hat{n}}_\alpha = -\nabla \cdot \hat{\mathbf{J}}_{1\alpha}, \quad \dot{\hat{\mathbf{p}}}_\alpha = -\nabla \cdot \hat{\mathbf{J}}_{2\alpha} + \hat{\mathbf{j}}_{2\alpha},$$

$$\dot{\hat{E}}_\alpha = -\nabla \cdot \hat{\mathbf{J}}_{3\alpha} + \hat{j}_{3\alpha}. \quad (3)$$

The operators of the number flux of molecules  $\hat{\mathbf{J}}_{1\alpha}$ , momentum flux  $\hat{\mathbf{J}}_{2\alpha}$ , the energy flux  $\hat{\mathbf{J}}_{3\alpha}$ , and the interfacial force operators  $\hat{\mathbf{j}}_{2\alpha}$  and  $\hat{j}_{3\alpha}$  are defined as follows:

$$\hat{\mathbf{J}}_{1\alpha} = \sum_{i=1}^{N_\alpha} \frac{\mathbf{p}_i}{m_\alpha} \delta(\mathbf{r}_i - \mathbf{r}), \quad \hat{\mathbf{J}}_{2\alpha} = \sum_{i=1}^{N_\alpha} \frac{\mathbf{p}_i \mathbf{p}_i}{m_\alpha} \delta(\mathbf{r}_i - \mathbf{r}) + \frac{1}{2} \sum_{i=1}^{N_\alpha} \sum_{\varphi}^{f,b} \sum_{j=1}^{N_\varphi} \mathbf{r}_{ij} \mathbf{F}_{ij} \int_0^1 d\eta \delta(\mathbf{r}_j - \mathbf{r} + \eta \mathbf{r}_{ij}),$$

$$\hat{\mathbf{J}}_{2\alpha} = \frac{1}{2} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_{\varphi \neq \alpha}} \mathbf{F}_{ij} [\delta(\mathbf{r}_i - \mathbf{r}) + \delta(\mathbf{r}_j - \mathbf{r})],$$

$$\hat{\mathbf{J}}_{3\alpha} = \sum_{i=1}^{N_\alpha} \frac{\mathbf{p}_i E_i}{m_\alpha} \delta(\mathbf{r}_i - \mathbf{r}) + \frac{1}{4} \sum_{i=1}^{N_\alpha} \sum_{\varphi=1}^l \sum_{j=1}^{N_\varphi} \left( \frac{\mathbf{p}_i}{m_\alpha} + \frac{\mathbf{p}_j}{m_\varphi} \right) \cdot \mathbf{r}_{ij} \mathbf{F}_{ij} \int_0^1 d\eta \delta(\mathbf{r}_j - \mathbf{r} + \eta \mathbf{r}_{ij}),$$

$$\hat{j}_{3\alpha} = \frac{1}{4} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_{\varphi \neq \alpha}} \mathbf{F}_{ij} \cdot \left( \frac{\mathbf{p}_i}{m_\alpha} + \frac{\mathbf{p}_j}{m_\varphi} \right) [\delta(\mathbf{r}_i - \mathbf{r}) + \delta(\mathbf{r}_j - \mathbf{r})].$$

The hydrodynamic velocities of the fluid (hereinafter, we use the subscript  $f$ ) and the walls (subscript  $b$ ) are defined as follows:

$$\mathbf{u}_f(\mathbf{r}, t) = \mathbf{p}_f(\mathbf{r}, t) / m_f n_f, \quad \mathbf{u}_b(\mathbf{r}, t) = 0.$$

Transport equations of the hydrodynamic characteristics can be obtained by averaging the density transport equations over the

ensemble  $F_N$  and using a locally accompanying coordinate system for the fluid which moves relative to the laboratory system with velocity  $\mathbf{u}_f$

$$\begin{aligned} \frac{dn_f}{dt} &= -n_f \nabla \cdot \mathbf{u}_f, \quad \frac{dn_b}{dt} = 0, \quad \frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u}_f \cdot \nabla, \\ \rho_f \frac{d\mathbf{u}_f}{dt} &= -\nabla \cdot \mathbf{J}'_{2f} + \mathbf{j}'_{2f}, \quad \frac{d\mathbf{u}_b}{dt} = 0, \\ \frac{dE'_f}{dt} &= -E'_f \nabla \cdot \mathbf{u}_f - \nabla \cdot \mathbf{J}'_{3f} - \\ &\quad -(\mathbf{J}'_{2f} + \mathbf{J}_{fb}) : \nabla \mathbf{u}_f - \mathbf{j}_{fb} \cdot \mathbf{u}_f + j'_{3f}, \\ \frac{dE'_b}{dt} &= -\nabla \cdot \mathbf{J}'_{3b} - j'_{3f} + \mathbf{J}_{fb} : \nabla \mathbf{u}_f. \end{aligned} \quad (4)$$

Here  $\mathbf{A} = \langle \hat{\mathbf{A}} \rangle$ , the angle brackets denote an average over the ensemble  $F_N$ , and all primed quantities were obtained from the corresponding unprimed quantities by the momentum transformation:  $\mathbf{p}'_i = \mathbf{p}_i - m_\alpha \mathbf{u}_\alpha$ . Moreover, additional microscopic densities are introduced:

$$\begin{aligned} \hat{\mathbf{J}}_{fb} &= -\frac{1}{4} \sum_{i=1}^{N_f} \sum_{j=1}^{N_b} \mathbf{r}_{ij} \mathbf{F}_{ij} \int_0^1 d\eta \delta(\mathbf{r}_j - \mathbf{r} + \eta \mathbf{r}_{ij}), \\ \hat{\mathbf{j}}_{fb} &= \frac{1}{2} \sum_{i=1}^{N_f} \sum_{j=1}^{N_b} \mathbf{F}_{ij} \delta(\mathbf{r}_i - \mathbf{r}). \end{aligned}$$

### 3. Nonequilibrium distribution function

The problem of deriving the hydrodynamic equations and constitutive relations reduces to finding a solution of equation (1) for an appropriately chosen shortened description. Due to the linearity of equation (1), its solution can be sought in the form of the sum of the quasi-equilibrium distribution function  $F_{N0}$  and the dissipation function  $F_{N1}$ :

$$F_N = F_{N0} + F_{N1}.$$

The function  $F_{N0}$  is obtained from the extremum condition for the information entropy  $S = -k \langle \ln F_{N0} \rangle$  ( $k$  is Boltzmann's constant) for the given average values of the

number of particles, momentum, and energy of the particles of each phase. The distribution function obtained in this way corresponds to the two-fluid description of the system. In the derivation of  $F_{N0}$ , it should only be taken into account that the macroscopic velocity of the wall is equal to zero and that the temperatures of the walls and the fluid can be different.

$$\begin{aligned} F_{N0} &= Q_0^{-1} \exp \left\{ - \int d\mathbf{r} \left[ \beta_f(\mathbf{r}, t) \hat{E}'_f(\mathbf{r}) - \nu_f(\mathbf{r}, t) \hat{n}_f(\mathbf{r}) + \right. \right. \\ &\quad \left. \left. + \beta_b(\mathbf{r}, t) \hat{E}'_b(\mathbf{r}) - \nu_b(\mathbf{r}, t) \hat{n}_b(\mathbf{r}) \right] \right\}, \\ Q_0 &= \left\langle \exp \left\{ - \sum_{\alpha=1}^l \sum_{k=1}^3 \int g_{k\alpha}(\mathbf{r}, t) \hat{G}'_{k\alpha}(\mathbf{r}) \right\} \right\rangle \end{aligned} \quad (5)$$

the Lagrange multipliers  $g_{k\alpha}$  are chosen so that  $g_{3\alpha} = \beta_\alpha = 1/kT_\alpha$  is the local inverse temperature of the component  $\alpha$ ,  $g_{1\alpha} = \beta_\alpha (-\mu_\alpha + m_\alpha \mathbf{u}_\alpha^2 / 2)$ ,  $g_{2\alpha} = -\beta_\alpha \mathbf{u}_\alpha$ ,  $\nu_\alpha = -\beta_\alpha \mu_\alpha$ , and  $\mu_\alpha$  is the local chemical potential. The average values of the particle number density of the component and its energy calculated for the quasi-equilibrium ensemble (5) are

$$\langle \hat{n}_\alpha(\mathbf{r}) \rangle_0 = \frac{\delta \ln Q_0}{\delta \nu_\alpha(\mathbf{r})}, \quad \langle \hat{E}'_\alpha(\mathbf{r}) \rangle_0 = \frac{\delta \ln Q_0}{\delta \beta_\alpha(\mathbf{r})}.$$

Here averaging over the ensemble (5) is denoted by the subscript 0 in the angle brackets. For the thermodynamics of the system to be defined by the function  $F_{N0}$ , it is necessary that the macroscopic variables coincide with their quasi-equilibrium values

$$n_\alpha(\mathbf{r}, t) = \langle \hat{n}_\alpha(\mathbf{r}) \rangle_0, \quad E_f(\mathbf{r}, t) = \langle \hat{E}'_f(\mathbf{r}) \rangle_0.$$

Because  $F_{N0}$  is an even function of the momentums  $\mathbf{p}'_i$  and the coordinates  $\mathbf{r}_{ij}$ , the mean values of the nondiagonal elements of the stress tensor and the tensor  $\mathbf{J}_{fb}$  calculated from it are equal to zero:

$$\mathbf{J}_{2f}^0(\mathbf{r}, t) = \frac{1}{3} \langle \hat{\mathbf{J}}'_{2f}(\mathbf{r}) : \mathbf{U} \rangle_0 = p_f(\mathbf{r}, t) \mathbf{U},$$

$$\mathbf{J}_{fb}^0(\mathbf{r}, t) = \frac{1}{3} \langle \hat{\mathbf{J}}'_{fb}(\mathbf{r}) : \mathbf{U} \rangle_0 = p_{fb}(\mathbf{r}, t) \mathbf{U}.$$

Here  $p_f$  is the partial pressure of the fluid, which we assume to be isotropic and  $\mathbf{U}$  is the unit tensor of second rank. For the same reason, the other fluxes and interfacial forces are equal to zero, and the equations of multifluid hydrodynamics of the Euler approximation have the following form

$$\begin{aligned}\frac{dn_f}{dt_0} &= -n_f \nabla \cdot \mathbf{u}_f, \quad \rho_f \frac{d\mathbf{u}_f}{dt_0} = -\nabla p_f, \\ \frac{dE'_f}{dt_0} &= -(E'_f + p_f + p_{fb}) \nabla \cdot \mathbf{u}_f, \\ \frac{dE'_b}{dt_0} &= p_{fb} \nabla \cdot \mathbf{u}_f.\end{aligned}$$

It is evident that these equations derived for the ensemble  $F_{N0}$  do not describe dissipative processes in the system. To construct the nonequilibrium distribution function, it is necessary to solve the linear inhomogeneous equation

$$\partial F_{N1} / \partial t + L_N F_{N1} = -(\partial F_{N0} / \partial t + L_N F_{N0}). \quad (6)$$

The right side of this equation contains time derivatives of hydrodynamic quantities which are determined from the transport equations (4) using the complete distribution function

$$\begin{aligned}\rho_f \frac{d\mathbf{u}_f}{dt_1} &= -\nabla \cdot \mathbf{J}_{2f}^1 + \mathbf{j}_{2f}^1, \\ \rho_b \frac{d\mathbf{u}_b}{dt_1} &= -\nabla \cdot \mathbf{J}_{2b}^1 - \mathbf{j}_{2f}^1 = 0, \\ \frac{dE'_f}{dt_1} &= -\nabla \cdot \mathbf{J}_{3f}^1 - (\mathbf{J}_{2f}^1 + \mathbf{J}_{fb}^1) : \nabla \mathbf{u}_f - \mathbf{j}_{fb}^1 \cdot \mathbf{u}_f + j_{3f}^1, \\ \frac{dE'_b}{dt_1} &= -\nabla \cdot \mathbf{J}_{3b}^1 + \mathbf{J}_{fb}^1 : \nabla \mathbf{u}_f + \mathbf{j}_{fb}^1 \cdot \mathbf{u}_f - j_{3f}^1.\end{aligned}$$

A method for solving equation (6) was developed and described in detail in (Rudyak, 1987). Omitting cumbersome calculations, we give the explicit form of the nonequilibrium distribution function obtained using this method for the system of nonspherical particles considered:

$$F_{N1}(t) = \pi(t, t_0) S_{(t-t_0)}^{(N)} F_{N1}(t_0) +$$

$$\begin{aligned}\sum_{\alpha} \sum_{k=1}^5 \int_{t_0}^t dt_1 \int d\mathbf{r} \int d\mathbf{r}' \pi(t, t_1) S_{(t-t_1)}^{(N)} F_{N0}(t_1) \Delta \mathbf{I}_{k\alpha} \cdot \mathbf{Y}_{k\alpha}(\mathbf{r}', t_1), \\ \Delta \mathbf{I}_{k\alpha} = \hat{\mathbf{I}}_{k\alpha}(\mathbf{r}, \mathbf{r}') - \mathbf{I}_{k\alpha}^0(\mathbf{r}, \mathbf{r}'), \quad \mathbf{I}_{ia}^0 = \langle \hat{\mathbf{I}}_{ia} \rangle_0.\end{aligned} \quad (7)$$

Here  $S_{(t-t_1)}^{(N)}$  is the displacement operator along the trajectory of  $N$  particles. The operator  $\pi(t, t_1)$  has the form of an infinite series in the thermodynamic forces (Rudyak, 1987). For weakly nonequilibrium systems (in ordinary hydrodynamics, this corresponds to the Navier-Stokes approximation), this series can be truncated to the first term, which is equal to unity. The fluxes  $\hat{\mathbf{I}}_{k\alpha}$  and thermodynamic forces  $\hat{\mathbf{Y}}_{k\alpha}$  are given by

$$\begin{aligned}\hat{\mathbf{I}}_{1f} &= \hat{\mathbf{J}}_{1f}(\mathbf{r}) \left( \delta(\mathbf{r} - \mathbf{r}') - \frac{\beta_f(\mathbf{r})}{n_f(\mathbf{r})} \frac{\delta p_f(\mathbf{r})}{\delta v_f(\mathbf{r}')} \right), \\ \hat{\mathbf{I}}_{1b} &= \hat{\mathbf{J}}_{1b}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'), \quad \mathbf{Y}_{1\alpha} = -\nabla' v_\alpha, \\ \hat{\mathbf{I}}_{2f} &= (\hat{\mathbf{J}}_{2f}(\mathbf{r}) + \hat{\mathbf{J}}_{fb}(\mathbf{r})) \beta_f \delta(\mathbf{r} - \mathbf{r}') - \\ &\quad - [E'_f(\mathbf{r}') + p_f(\mathbf{r}') + p_{fb}(\mathbf{r}')] \times \\ &\quad \times \left[ \hat{n}_f(\mathbf{r}) \frac{\delta v_f}{\delta E'_f n_f} - \hat{E}'_f(\mathbf{r}) \frac{\delta \beta_f(\mathbf{r})}{\delta E'_f(\mathbf{r}') n_f} \right] \mathbf{U} - \\ &\quad - n_f(\mathbf{r}') \left[ \hat{n}_f(\mathbf{r}) \frac{\delta v_f(\mathbf{r})}{\delta n_f(\mathbf{r}') n_f} - \hat{E}'_f(\mathbf{r}) \frac{\delta \beta_f(\mathbf{r})}{\delta n_f(\mathbf{r}') n_f} \right] \mathbf{U}, \\ \hat{\mathbf{I}}_{2b} &= p_{fb}(\mathbf{r}') \left[ \hat{n}_b(\mathbf{r}) \frac{\delta v_b(\mathbf{r})}{\delta E'_b(\mathbf{r}') n_b} - \right. \\ &\quad \left. - \hat{E}'_b(\mathbf{r}) \frac{\delta \beta_b(\mathbf{r})}{\delta E'_b(\mathbf{r}') n_b} \right] \mathbf{U}, \quad \mathbf{Y}_{2\alpha} = -\nabla' \cdot \mathbf{u}_\alpha, \\ \hat{\mathbf{I}}_{3f} &= \hat{\mathbf{J}}_{3f}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') + \\ &\quad + \hat{\mathbf{p}}_f(\mathbf{r}) \frac{\beta_f(\mathbf{r})}{m_f n_f(\mathbf{r})} \left( \frac{\delta p_f(\mathbf{r})}{\delta \beta_f(\mathbf{r}') v_f} \right)_{v_f}, \\ \hat{\mathbf{I}}_{3b} &= \hat{\mathbf{J}}_{3b}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'), \quad \mathbf{Y}_{3\alpha} = -\nabla' \beta_\alpha, \\ \hat{\mathbf{I}}_{4f} &= -\hat{\mathbf{j}}_{2f}(\mathbf{r}) \beta_f \delta(\mathbf{r} - \mathbf{r}'), \\ \mathbf{Y}_{4f} &= \mathbf{u}_f, \quad \mathbf{Y}_{4b} = 0,\end{aligned} \quad (8)$$

$$\hat{I}_{5f} = \left( \hat{j}_{3f} + \frac{1}{2} \hat{\mathbf{j}}_{2f}(\mathbf{r}) \cdot \mathbf{u}_f \right) \delta(\mathbf{r} - \mathbf{r}'),$$

$$Y_{5f} = \beta_f - \beta_b.$$

In these expressions, the subscript  $n_f$  indicates that the expression is determined for a fixed concentration of fluid molecules.

#### 4. Constitutive relations and transport coefficients

Using the nonequilibrium ensemble (7), we obtain fluid transport equations in flows bounded by surfaces. The constitutive relations for the stress tensor, heat flux vector, and interfacial forces entering these equations are generally nonlocal and retarded.

$$\mathbf{f}_{ia}(\mathbf{r}, t) = \mathbf{f}_{ia}(\mathbf{r}, t_0) + \mathbf{f}_{ia}^0(\mathbf{r}, t) + \sum_{k=1}^5 \sum_{\beta, \varphi} \int_{t_0}^t dt_1 \cdot$$

$$\cdot \int d\mathbf{r}' \int d\mathbf{r}'' \mathbf{M}_{ia}^{k\beta}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', t - t_1) \cdot \mathbf{Y}_{k\beta}(\mathbf{r}'', t_1), \quad (8)$$

$$\hat{\mathbf{f}}_{1a} = \hat{\mathbf{J}}_{1a}, \quad \hat{\mathbf{f}}_{2a} = \hat{\mathbf{J}}_{2a}, \quad \hat{\mathbf{f}}_{3a} = \hat{\mathbf{J}}_{3a}, \quad \hat{\mathbf{f}}_{4a} = \hat{\mathbf{J}}_{2a},$$

$$\hat{\mathbf{f}}_{5a} = \hat{\mathbf{J}}_{3a}, \quad \hat{\mathbf{f}}_{6f} = \hat{\mathbf{J}}_{fb}, \quad \hat{\mathbf{f}}_{7f} = \hat{\mathbf{J}}_{fb}, \quad \hat{\mathbf{f}}_{6b} = \hat{\mathbf{f}}_{7b} = 0.$$

The relaxation transport kernels included in these formulas are given by the relations

$$\mathbf{M}_{ia}^{k\beta}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', t - t_1) = \left( \hat{\mathbf{f}}_{ia}(\mathbf{r}) \pi(t, t_1) \times \right.$$

$$\left. \times S_{(t-t_1)}^{(N)} \hat{\mathbf{f}}_{k\beta}(\mathbf{r}) \Delta \mathbf{I}_{k\beta}(\mathbf{r}', \mathbf{r}'') \right) \Big|_0, \quad (9)$$

Given that the quasi-equilibrium distribution function is even in momentums and relative coordinates of the molecules, we can show that the uneven transport kernels (9) in these quantities are equal to zero. Moreover, if the bulk viscosity can be neglected, the constitutive relations (8) are simplified by retaining only the symmetric nondivergent part (denoted below by subscript  $^s$ ) of the stress tensor and the tensor  $\mathbf{J}_{fb}$

$$\mathbf{J}_{2f}^s(\mathbf{r}, t) = \int_{t_0}^t dt_1 \int d\mathbf{r}' \left\langle \hat{\mathbf{J}}_{2f}^s(\mathbf{r}) \pi(t, t_1) S_{(t-t_1)}^{(N)} \times \right.$$

$$\left. \Delta \left( \hat{\mathbf{J}}_{2f}^s(\mathbf{r}') + \hat{\mathbf{J}}_{fb}^s(\mathbf{r}') \right) : \beta_f \nabla \mathbf{u}_f(\mathbf{r}') \right\rangle_0$$

$$\mathbf{j}_{2f}(\mathbf{r}, t) = \frac{1}{2} \int_{t_0}^t dt_1 \int d\mathbf{r}' \left\langle \hat{\mathbf{j}}_{2f}(\mathbf{r}) \pi(t, t_1) S_{(t-t_1)}^{(N)} \hat{\mathbf{j}}_{2f}(\mathbf{r}') \times \right.$$

$$\left. \times (\beta_f + \beta_p) \mathbf{u}_f(\mathbf{r}') \right\rangle_0$$

$$\mathbf{J}_{3f}(\mathbf{r}, t) = - \int_{t_0}^t dt_1 \int d\mathbf{r}' \int d\mathbf{r}'' \left\langle \hat{\mathbf{J}}_{3f}(\mathbf{r}) \pi(t, t_1) S_{(t-t_1)}^{(N)} \times \right.$$

$$\left. \times \Delta \left( \hat{\mathbf{J}}_{3f}(\mathbf{r}') + \hat{\mathbf{p}}_f(\mathbf{r}') \frac{\beta_f(\mathbf{r})}{m_f n_f(\mathbf{r})} \frac{\delta p_f(\mathbf{r}')}{\delta \beta_f(\mathbf{r}'')_{v_f}} \right) \cdot \nabla \beta_f(\mathbf{r}'') \right\rangle_0,$$

$$\hat{j}_{3f}(\mathbf{r}, t) =$$

$$= \int_{t_0}^t dt_1 \int d\mathbf{r}' \left\langle \hat{j}_{3f}(\mathbf{r}) \pi(t, t_1) S_{(t-t_1)}^{(N)} \Delta \hat{j}_{3f}(\mathbf{r}') (\beta_f - \beta_b) \right\rangle_0,$$

$$\mathbf{J}_{fb}^s(\mathbf{r}, t) = \int_{t_0}^t dt_1 \int d\mathbf{r}' \left\langle \hat{\mathbf{J}}_{fb}^s(\mathbf{r}) \pi(t, t_1) \times \right.$$

$$\left. \times S_{(t-t_1)}^{(N)} \Delta \left( \hat{\mathbf{J}}_{2f}^s(\mathbf{r}') + \hat{\mathbf{J}}_{fb}^s(\mathbf{r}') \right) : \beta_f \nabla \mathbf{u}_f(\mathbf{r}') \right\rangle_0,$$

$$\mathbf{j}_{fb}(\mathbf{r}, t) = \frac{1}{2} \int_{t_0}^t dt_1 \int d\mathbf{r}' \times \quad (10)$$

$$\times \left\langle \hat{\mathbf{j}}_{fb}(\mathbf{r}) \pi(t, t_1) S_{(t-t_1)}^{(N)} \hat{\mathbf{j}}_{2f}(\mathbf{r}') \cdot (\beta_f + \beta_b) \mathbf{u}_f(\mathbf{r}') \right\rangle_0$$

Equations (10) are generally nonlinear, nonlocal, and retarded rheological relations. They contain several types of nonlocality. The first is the spatial and temporal nonlocality of the relaxation transport kernels (9). Its characteristic scales are the size of the internal structural elements of the medium and the time of their interaction. Nonlocality of the second type is associated with the correlation between dissipative fluxes and thermodynamic forces and is due to the finite speed of propagation of disturbances in the medium. For a one-component gas away from the critical point, the scale of this nonlocality is of the order of the mean free path and time of the molecule.

Transport coefficients can be introduced to the constitutive relations only if the nonlocality and retardation of thermodynamic forces can be neglected by removing them from under the integral sign in (10). Furthermore, in the linear approximation in the thermodynamic forces, we can set  $\pi(t, t_0) = 1$  and neglect the initial values of the fluxes and interfacial forces. If we neglect the bulk viscosity in this case, the time evolution of the

fluid velocity is described by the equation

$$\begin{aligned} \rho_f \frac{d\mathbf{u}_f}{dt} &= -\nabla p_f - \nabla \cdot (\boldsymbol{\mu}_{ff}^s + \boldsymbol{\mu}_{fb}^s) : \nabla \mathbf{u}_f - \mathbf{v} \cdot \mathbf{u}_f, \\ \frac{dE_f}{dt} &= -E_f \nabla \cdot \mathbf{u}_f - \nabla \cdot (\boldsymbol{\lambda}_f \cdot \nabla \beta_f + \boldsymbol{\lambda}_f \cdot \nabla \beta_b) - \\ &\quad - (\boldsymbol{\mu}_{ff}^s + \boldsymbol{\mu}_{fb}^s + \boldsymbol{\mu}_{bf}^s + \boldsymbol{\mu}_{bb}^s) : \nabla \mathbf{u}_f : \nabla \mathbf{u}_f + \\ &\quad + \boldsymbol{\sigma} : \mathbf{u}_f \mathbf{u}_f + \varpi (\beta_f - \beta_b). \end{aligned} \quad (11)$$

Here  $\boldsymbol{\mu}_{ff}^s$ ,  $\boldsymbol{\mu}_{fb}^s$ ,  $\boldsymbol{\mu}_{bf}^s$ , and  $\boldsymbol{\mu}_{bb}^s$  are fourth-rank tensors,  $\mathbf{v}$ ,  $\boldsymbol{\lambda}_f$ ,  $\boldsymbol{\lambda}_b$  and  $\boldsymbol{\sigma}$  are second-rank tensors, and  $\varpi$  is a scalar. All these quantities depend on the spatial coordinate and are given by the relations

$$\begin{aligned} \boldsymbol{\mu}_{ff}^s(\mathbf{r}) &= \beta_f \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \hat{\mathbf{J}}_{2f}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} \Delta \hat{\mathbf{J}}_{2f}^s(\mathbf{r}') \rangle_0, \\ \boldsymbol{\mu}_{fb}^s(\mathbf{r}) &= \beta_f \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \hat{\mathbf{J}}_{2f}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} \Delta \hat{\mathbf{J}}_{fb}^s(\mathbf{r}') \rangle_0, \\ \boldsymbol{\mu}_{bf}^s(\mathbf{r}) &= \beta_f \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \hat{\mathbf{J}}_{fb}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} \Delta \hat{\mathbf{J}}_{2f}^s(\mathbf{r}') \rangle_0, \\ \boldsymbol{\mu}_{bb}^s(\mathbf{r}) &= \beta_f \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \hat{\mathbf{J}}_{fb}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} \Delta \hat{\mathbf{J}}_{fb}^s(\mathbf{r}') \rangle_0, \\ \boldsymbol{\lambda}_f(\mathbf{r}) &= \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \hat{\mathbf{J}}_{3f}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} (\Delta \hat{\mathbf{J}}_{3f}^s(\mathbf{r}') + \\ &\quad + \hat{\mathbf{p}}_f(\mathbf{r}') \frac{\beta_f(\mathbf{r}')}{m_f n_f(\mathbf{r}')} \frac{\delta p_f(\mathbf{r}')}{\delta \beta_f(\mathbf{r}')_{\mathbf{v}_f}}) \rangle_0, \\ \boldsymbol{\lambda}_b(\mathbf{r}) &= \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \Delta \hat{\mathbf{J}}_{3f}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} \hat{\mathbf{J}}_{3b}^s(\mathbf{r}') \rangle_0, \\ \varpi(\mathbf{r}) &= \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \hat{j}_{3f}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} \hat{j}_{3f}^s(\mathbf{r}') \rangle_0, \\ \boldsymbol{\sigma}(\mathbf{r}) &= \frac{1}{2} (\beta_f + \beta_b) \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \hat{\mathbf{j}}_{fb}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} \hat{\mathbf{j}}_{2f}^s(\mathbf{r}') \rangle_0, \\ \mathbf{v}(\mathbf{r}) &= \frac{1}{2} (\beta_f + \beta_b) \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \hat{\mathbf{j}}_{2f}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} \Delta \hat{\mathbf{j}}_{2f}^s(\mathbf{r}') \rangle_0. \end{aligned} \quad (12)$$

Note that in the case of incompressible channel walls, the hydrodynamic velocity equals zero. The condition that the magnitudes

of the interfacial forces  $\mathbf{j}_{2f} = \mathbf{j}_{2b}$  and the equation

$$\rho_b \frac{d\mathbf{u}_b}{dt} = -\nabla \cdot \mathbf{J}'_{2b} + \mathbf{j}_{2b} = 0$$

imply that  $\mathbf{j}'_{2f} = -\nabla \cdot \mathbf{J}'_{2b}$ , and the evolution equation of the fluid velocity can be written in divergent form

$$\rho_f \frac{d\mathbf{u}_f}{dt} = -\nabla p_f - \nabla \cdot (\boldsymbol{\mu}_{ff}^s + \boldsymbol{\mu}_{fb}^s + \boldsymbol{\mu}_b^s) : \nabla \mathbf{u}_f. \quad (13)$$

Thus, the viscosity of the fluid in confined geometry depends not only on the interaction between the fluid molecules (responsible tensor coefficient  $\boldsymbol{\mu}_{ff}^s$ ). The effective viscosity contains the contributions due to the interaction with the surface, the coefficient  $\boldsymbol{\mu}_b^s$  is given by the relation

$$\boldsymbol{\mu}_b^s(\mathbf{r}) = \beta_b \int d\mathbf{r}' \int_{t_0}^t dt_1 \langle \hat{\mathbf{J}}_{2b}^s(\mathbf{r}) S_{(t-t_1)}^{(N)} \Delta \hat{\mathbf{J}}_{fb}^s(\mathbf{r}') \rangle_0.$$

Further simplification of the transport equations is possible in systems having symmetry properties. For an isotropic medium, the transport kernel (8) and the corresponding transport coefficients (12) are scalars multiplied by the isotropic tensors. Thus, for an isotropic medium, the local constitutive relations reduce to

$$\begin{aligned} \mathbf{J}'_{2f}(\mathbf{r}, t) &= p_f(\mathbf{r}, t) \mathbf{U} - (\mu_{ff}^s + \mu_{fb}^s + \mu_b^s) \nabla \mathbf{u}_f, \\ \mathbf{J}'_{3f}(\mathbf{r}, t) &= \lambda_f \nabla \beta_f + \lambda_b \nabla \beta_b, \\ \mathbf{j}_{2f}(\mathbf{r}, t) &= 0, \quad \mathbf{j}'_{3f}(\mathbf{r}, t) = \varpi (\beta_f - \beta_b), \\ \mathbf{J}_{fb}(\mathbf{r}, t) &= -(\mu_{bf}^s + \mu_{bb}^s) \nabla \mathbf{u}_f, \\ \mathbf{j}_{fb}(\mathbf{r}, t) &= -\boldsymbol{\sigma} \mathbf{u}_f. \end{aligned} \quad (14)$$

The scalar transport coefficients are obtained by convolution of the tensor coefficients. For example, the components of the shear viscosity and thermal conductivity due to the interaction between the fluid molecules are defined by the relations

$$\mu_{ff}^s = \frac{\beta_f}{5} \int d\mathbf{r}' \int_{t_0}^t dt \langle \hat{\mathbf{J}}_{2f}^s(\mathbf{r}) : S_{(t-t_1)}^{(N)} \hat{\mathbf{J}}_{2f}^s(\mathbf{r}') \rangle,$$

$$\lambda_f = \frac{1}{3} \int d\mathbf{r}' \int_{t_0}^t dt_1 \left\langle \hat{\mathbf{J}}'_{3f}(\mathbf{r}') \cdot S_{(t-t_1)}^{(N)} \left( \Delta \hat{\mathbf{J}}'_{3f}(\mathbf{r}') + \hat{\mathbf{p}}'_f(\mathbf{r}') \frac{\beta_f(\mathbf{r}')}{m_f n_f(\mathbf{r}')} \frac{\delta p_f(\mathbf{r}')}{\delta \beta_f(\mathbf{r}')_{v_f}} \right) \right\rangle_0.$$

The formulas for the other transport coefficients have a similar form.

## 5. Discussion of results

The technique developed in this paper to describe transport processes in confined geometries allows deriving closed equations based on the first principles. It is important that the characteristics in these equations, such as the stress tensor, are expressed in terms of the parameters of the fluid-fluid and fluid-surface interaction potentials. Therefore, specifying real material parameters, we can predict how the process of momentum and energy transfer in particular microsystems will occur. In this sense, the constructed equations are fairly universal.

On the other hand, the constitutive relations (8), (10) generally have a rather complicated structure and may be unusual for experts speaking in terms of transport coefficients. The traditional hydrodynamic approach is characterized by scalar, homogeneous and isotropic transfer coefficients. It should be understood that it is not possible to use them for flow in carbon nanotubes, where all fluid molecules constantly interact with the molecules of the walls. Spatial and temporal nonlocality of the transport processes and their anisotropy are fundamental for this system. However, these effects will be weaker with increasing size of the system. In terms of the constitutive relations, this means sequential transition from formula (8) to relations of type (14). In the limiting case of macroscopic systems, we naturally obtain the classical equations of hydrodynamics and the fluid-surface interaction is described only by slip or no-slip boundary conditions. Let us consider in detail what relations will work in systems of different sizes.

As noted above, for nanochannels with a diameter of a few nanometers or for similar nanoporous systems, it is necessary to use relations (8). For an accurate study of the transport processes in this case, the only alternative method seems to be the use of molecular dynamics (MD) simulations, and extensive work in this direction has recently been done. It is this simulation that, for example, has revealed the presence of subcontinual regimes in nanotubes (Thomas, McGaughey, 2009) and the anisotropy features of transport processes (Andryushchenko, Rudyak, 2011, Rudyak et al., 2011).

Nevertheless, the molecular dynamics method itself does not provide an answer to the question of what is the viscosity coefficient and thermal conductivity and whether it is possible to determine them for a particular system. In MD simulation studies of the characteristics of nanoflows, attempts are sometimes made to write the usual equations of hydrodynamics and the Green-Kubo formula for transport coefficients. It is clear that in such small systems, this approach is unreasonable.

In nanochannels with a diameter of about ten nanometers, it is possible to distinguish the boundary zone and the region where fluid molecules do not directly interact with the wall. Here we can neglect the nonlocal nature and retardation of thermodynamic forces and introduce transport coefficients, but, their anisotropy (i.e., the coefficients are tensors) and inhomogeneity must be taken into account. Such systems are described by the transport equations (11).

The influence of anisotropy and inhomogeneity will decrease with further increase in the size of the system. The transport equation (14) seems to be valid for channels and pores with a typical size of several tens of nanometers. However, in this case, too, the volume of the boundary zones with the strong interaction of the fluid with the wall is not infinitely small. Therefore, the most accurate description of the transport processes may require a combined description using different equations for the wall and inner regions. Attempts to construct such a

description has been made, in particular, in studies of gas and liquid flows in microchannels, where the classical equations of hydrodynamics and kinetics are used for the inner region and MD simulation for the wall area (Gaastra-Nedea et al., 2009).

In the approach developed in the present paper, the transport equation for the wall region will determine the boundary conditions for the classical equations of hydrodynamics of the fluid in the inner region. It is the presence of the wall area that will be responsible for the transition from the boundary no-slip conditions on the channel walls to the slip conditions typical of microflows. Thus, the results of this work can be useful in analyzing the effect of various microflow characteristics on the slip length and the momentum and energy accommodation coefficients.

Even if the stress tensor and the fluid heat flux vector can be expressed in terms of the effective viscosity coefficient and thermal conductivity, the constitutive relations will contain the additive terms corresponding to the fluid–surface interactions. Thus, the transport coefficients of a liquid or gas in a nanochannel not only do not coincide with the bulk values, but they are not determined only by the parameters of the fluid. In studies of the momentum and energy transfer of the fluid, it is necessary to introduce the viscosity and thermal conductivity of the fluid–surface system.

We note in conclusion that in describing transport processes in microflows bounded by solid surfaces, it is necessary to use transport equations which, in addition to the stress tensor and the heat flux vector, contain interfacial forces responsible for the transfer of momentum and heat in the interaction with the surfaces of the walls.

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