Fluid Viscosity under Confined Conditions

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Abstract—Closed equations of fluid transfer in confined conditions are constructed in this study using ab initio methods of nonequilibrium statistical mechanics. It is shown that the fluid viscosity is not determined by the fluid properties alone, but becomes a property of the “fluid–nanochannel walls” system as a whole. Relations for the tensor of stresses and the interphase force, which specifies the exchange by momentum of fluid molecules with the channel-wall molecules, are derived. It is shown that the coefficient of viscosity is now determined by the sum of three contributions. The first contribution coincides with the expression for the coefficient of the viscosity of fluid in the bulk being specified by the interaction of fluid molecules with each other. The second contribution has the same structure as the first one but is determined by the interaction of fluid molecules with the channel-wall molecules. Finally, the third contribution has no analog in the usual statistical mechanics of transport processes of a simple fluid. It is associated with the correlation of intermolecular forces of the fluid and the channel walls. Thus, it is established that the coefficient of viscosity of fluid in sufficiently small channels will substantially differ from its bulk value.

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The miniaturization of facilities of various indentation, which is caused by the necessity to lower their material consumption and to increase the energy efficiency, has led to the rapid development of microsystem and microchannel techniques. The applicability of nanoelectromechanical facilities simultaneously rises. In almost all cases, fluid flows occur in working elements of these facilities, the character of which is determined by transfer processes. Such flows have already been applied in biochemistry, medicine, pharmacology, biology, thermal engineering, instrument making, catalysis, water and air purification systems, etc. It is already known today that the transport processes in the bulk and in confined conditions differ substantially. For example, the diffusion is anisotropic [1–4], while the viscosity substantially differs from its value in the bulk [5]. Diffusion anisotropy is quite natural physical; however, the cause of varying viscosity is not so evident. This study is aimed at construction of a static theory of transfer processes of a fluid momentum in confined conditions (microchannels and nanochannels, nanopores). It is shown that the shear-viscosity coefficient of the fluid in confined conditions includes additional terms caused by the interaction of its molecules with channel-wall molecules in addition to the usual terms.

The dynamics of the “fluid–channel walls” system is described by the N-particle distribution function \( F_N \), which satisfies the Liouville equation

\[
\frac{\partial F_N}{\partial t} + L_N F_N = 0, \tag{1}
\]

the Liouville operator in which is determined as follows:

\[
L_N = \sum_{\alpha=1}^{2} \sum_{i=1}^{N_\alpha} \frac{\mathbf{p}_i}{m_\alpha} \frac{\partial}{\partial \mathbf{r}_i} + \frac{1}{2} \sum_{\alpha=1}^{2} \sum_{i=1}^{N_\alpha} \left\{ F_{\alpha i} \left( \frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \right\}.
\]

Here, \( m_i, \mathbf{r}_i, \) and \( \mathbf{p}_i \) are the mass, radius-vector of the center of mass, and momentum of the \( i \)th particle belonging to phase \( \alpha \) (below, index \( f \) corresponds to fluid and \( b \) to channel walls), and \( F_{\alpha i} \) is the intermolecular interaction force.

Since the states of fluid molecules and channel walls are substantially different (particularly, walls rest while the fluid flows), we have a peculiar two-fluid medium. Therefore, we will characterize the state of the system under consideration by partial values of density \( n_\alpha \), momentum \( \mathbf{p}_\alpha \), and energy \( E_\alpha \). These quantities are the average of the corresponding dynamic variables:
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\[ \hat{n}_a (r) = \sum_{i=1}^{N_a} \delta (r_i - r), \quad \hat{p}_a (r) = \sum_{i=1}^{N_a} p_i \delta (r_i - r), \]

\[ \hat{E}_a (r) = \sum_{i=1}^{N_a} \left( \frac{1}{2m_i} + \frac{1}{2} \frac{N_i}{j} U_j \right) \delta (r_i - r). \]  

(2)

Here, \( U_j \) is the interaction potential of molecules \( i \) and \( j \). Macroscopic variables, which determine the state of the system, are obtained by averaging of (2) over distribution function \( F_N \). The transfer equations of dynamic densities (2) have the form (see [6–9])

\[ \hat{n}_a = -\nabla \cdot \hat{J}_{1a}, \quad \hat{p}_a = -\nabla \cdot \hat{J}_{2a} + \hat{j}_{2a}, \]

\[ \hat{E}_a = -\nabla \cdot \hat{J}_{3a} + \hat{j}_{3a}. \]  

(3)

The operators of the flow of the number of molecules \( \hat{J}_{1a} \), momentum \( \hat{J}_{2a} \), energy \( \hat{J}_{3a} \), and interphase forces \( \hat{j}_{2a} \) and \( \hat{j}_{3a} \) are determined similarly to [6–9]; particularly,

\[ \hat{J}_{1a} = \sum_{i=1}^{N_a} \left[ \frac{p_i}{m_i} \delta (r_i - r) + \frac{1}{2} \sum_{j=1}^{N_a} r_{ij} F_{ij} \int_0^1 d\eta \delta (r_j - r + \eta r_{ij}) \right], \]

\[ \hat{J}_{2a} = \frac{1}{2} \sum_{i=1}^{N_a} \sum_{j=1}^{N_a} F_{ij} \left[ \delta (r_i - r) + \delta (r_j - r) \right]. \]

Transport equations for macroscopic variables are derived from the average of Eqs. (3) over distribution function \( F_N \). Following [6–9], we will seek the solution in the form of the sum of quasi-equilibrium \( F_{N0} \) and dissipative \( F_{N1} \) distribution functions: \( F_N = F_{N0} + F_{N1} \). In this case, function \( F_{N0} \) is found from the extremum condition of information entropy \( S = -k \langle \ln F_{N0} \rangle \) (\( k \) is the Boltzmann constant) at a specified average number of particles, momentum, and particle energy of each phase [6, 10]. Since the system under consideration is rather specific, the fluid in the channel moves with velocity \( u_j \), while the channel walls rest, i.e., \( u_s = 0 \), we can easily be convinced that

\[ F_{N0} = Q^{-1} \exp \left[ -\int_0^t d\tau \left[ \beta_f (r, \tau) \hat{E}_f (r) \right] \right], \]

\[ -\nu_f (r, \tau) \hat{n}_f (r) + \beta_b (r, \tau) \hat{E}_b (r) - \nu_b (r, \tau) \hat{n}_b (r) \right]\]  

(5)

Here, \( \beta_a = \frac{1}{kT_a} \) is the local inverse temperature of component \( a \), while \( \nu_a = -\beta_a \mu_a, \mu_a \) is the local chemical potential, and \( Q \) is the normalization multiplier.

The dissipative distribution function can be derived from the solution of Eq. (1) allowing for function (5). The found expression is rather cumbersome. Since we are interested only in the shear fluid viscosity in this article, we will limit ourselves to the corresponding part of function \( F_{N1} \). We will further take into account only terms linear by thermodynamic forces \( Y_{ka} \) (gradients of macroscopic variables) and will neglect their internal nonlocality. In this approximation, the distribution function responsible for the momentum transport has the form

\[ F_{N1} (t) = S_{(t-t_0)}^{(N)} F_{N1} (t_0) \]

\[ + \sum_{k=1}^{N} \int_0^t d t_1 \int d r S_{(t-t_1)}^{(N)} F_{N0} (t_1) \Delta \mathbf{I}_{ka} \cdot \mathbf{Y}_{ka} (r, t_1), \]

\[ \Delta \mathbf{I}_k = \mathbf{I}_k - \langle \mathbf{I}_k \rangle_0, \quad \mathbf{i}_1 = (\hat{J}_{2f} + \hat{j}_{2b}) \beta_f, \quad \mathbf{i}_2 = -\hat{J}_{2f} \beta_f, \]

\[ \mathbf{Y}_1 = -\nabla \cdot \mathbf{u}_f, \quad \mathbf{Y}_2 = \mathbf{u}_f, \quad \hat{J}_{j_{2f}} = \frac{1}{4} \sum_{i=1}^{N_f} \sum_{j=1}^{N_f} r_{ij} F_{ij} \int_0^1 d\eta \delta (r_j - r + \eta r_{ij}). \]

Here, \( S_{(t-t_0)}^{(N)} \) is the streaming operator along the trajectory of \( N \) particles.

The constructed nonequilibrium ensemble allows us to find the closed fluid transport equation in flows confined by surfaces. Finally, the stress tensor and interphase force for the incompressible fluid have the form

\[ \mathbf{J}_{2f} (r, t) = \mathbf{p}_f U + \beta_f \int_0^t d t_1 \left[ \int d r \mathbf{J}_{2f} (r) \right] \mathbf{S}_{(t-t_0)}^{(N)} \Delta \mathbf{J}_{2f}^{(N)} (r_0) \]

\[ \mathbf{j}_{2f} (r, t) = \frac{1}{2} \left( \beta_f + \beta_b \right) \]

\[ \times \int_0^t d t_1 \left[ \int d r \mathbf{j}_{2f} (r) \right] \mathbf{S}_{(t-t_0)}^{(N)} \mathbf{j}_{2f} (r_0) \cdot \mathbf{u}_f (r, t_1), \]  

(6)