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The Spectrum of the Lagrange Velocity Autocorrelation Function in Confined Anisotropic Liquids

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Abstract: The results of our further analysis of the thermal hydrodynamic fluctuations in an anisotropic liquid under heterogeneous conditions are represented. The heterogeneity is modeled in the form of a plane-parallel layer, the liquid is considered is taken to be incompressible, and the rapid processes of the angular momentum relaxation to equilibrium are ignored. The extended system of hydrodynamics equations is linearized for small deviations from the equilibrium values. For the case of spontaneous fluctuation fields being present in the system of equations for the velocity and inertia tensor components, the boundary problem solution is found in the form of an expansion in the harmonic functions. The spectral densities of the fluctuation correlation functions are obtained by using the fluctuation dissipation theorem (FDT). A special attention is paid to the correlation functions (CFs) for the velocity field in the anisotropic liquid. The spectrum of the Lagrange velocity autocorrelation function (LVACF) and the collective part of the self–diffusion coefficient of the molecules are determined as functions of the coordinate normal to the confining planes.
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1. Introduction

The investigation of thermal hydrodynamic fluctuations in heterogeneous systems is an urgent question at present [1-8]. The heterogeneity can be caused by different external

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factors. Under natural conditions, such factors as geometrical restrictions on the system and imposition of external electromagnetic and gravitation fields are most frequently encountered. Despite the different nature of these factors, their influences are identical and reduce to some orientation ordering of the liquid's anisotropic molecules. In this connection, the need for studying heterogeneous anisotropic liquids, including confined ones, arises.

The influence of a geometrical restriction on the dynamic properties of the system is taken into account by supplementing the system of hydrodynamics equations with proper boundary conditions. The anisotropy of the liquid's molecules can incorporated by introducing into the above system the anisotropy tensor, which serves as an additional field variable and characterizes the deviations of the anisotropic molecule axes within a liquid volume element from the isotropic distribution. Such an approach was first offered and justified in [9], and then refined in [10]. Recently, with the participation of one of us [11], a complete system of hydrodynamics equations was developed in which along with the local traverse velocity, the internal angular momentum is taken into account and the inertia tensor is considered as the anisotropy tensor. The equations were used for the study of the space–time CF and the spectral density of the inertia tensor fluctuations of the liquid Lagrange particle in a homogeneous liquid under equilibrium and non-equilibrium conditions – against the background of a liquid flow with constant velocity gradient [11, 12].

In this report, the results of our further analysis of the thermal hydrodynamic fluctuations in an anisotropic liquid are presented. The fluctuations are studied for the heterogeneous conditions modeled, for the sake of simplicity, in the form of a plane-parallel layer. The extended system of hydrodynamics equations is linearized for small deviations from the equilibrium values, the liquid is taken to be incompressible, and the rapid processes of the angular momentum relaxation to equilibrium are ignored. The solution of the boundary problem with arbitrary initial conditions is found for the system of linked equations for the velocity and inertia tensor components by developing it in an expansion in the harmonic functions. The spectral densities of the fluctuation CFs for the expansion amplitudes are obtained by using FDT. The results obtained for the field variable CFs for the heterogeneous anisotropic liquid are compared with those for the bulk case. The LVACF spectrum for the anisotropic liquid and the collective part of the molecule self–diffusion coefficient are determined as functions of the coordinate normal to the restrictive planes. The transformation from the Euler to the Lagrange variables is carried out on the basis of the Malomuzh approach [13-15].

2. Analysis

The complete system of hydrodynamics equations for the anisotropic liquid was obtained in [11]. Let us assume that the liquid occupies the region between two parallel planes separated by distance d, and the z axis of the Cartesian coordinate system to be directed along the normal to the planes, so that $0 \leq z \leq d$. For the sake of simplicity, we consider the anisotropic liquid to be incompressible and ignore the rapid processes of the internal angular momentum relaxation to equilibrium [11]. Now, let us linearize the equation of motion for the velocity, pressure, and inertia tensor fluctuation fields, and add to them spontaneous sources of the fluctuations. As a result, we obtain the system of linked differential equations

$$\frac{\partial}{\partial t}\upsilon_\alpha = -\frac{1}{\rho_0}\nabla_\alpha p + \nu\,\Delta\upsilon_\alpha + \nu_{12}\nabla_\beta\delta\, I_{\alpha\beta} + \sigma_\alpha,$$

$$\frac{\partial}{\partial t}\delta I_{\alpha\beta} = -\frac{1}{\tau}\delta I_{\alpha\beta} + D\Delta\delta I_{\alpha\beta} + \nu_{21}(\nabla_\alpha\upsilon_\beta + \nabla_\beta\upsilon_\alpha) + R_{\alpha\beta}, \tag{1}$$

$$div\,\vec{\upsilon} = 0, \quad \nu_{ab} = {}^{\eta_{ab}}\!/_{\rho_0}, \quad \tau = {}^{\rho_0}\!/_{\eta_2}, \quad D = {}^{\mu_2}\!/_{\rho_0}.$$

Here ρ_0 is the equilibrium density, ν is the kinematics viscosity, τ is the relaxation time, D is the diffusion coefficient for the inertia tensor, δI is the deviation of the inertia tensor from its equilibrium value, and σ and R are the spontaneous fluctuation sources. The velocity field and the inertia tensor components, υ_α and $\delta I_{\alpha\beta}$, vanish at the restrictive planes:

$$\begin{aligned}&\vec{\upsilon}(t,x,y,z=0)=0, \quad \delta I_{\alpha\beta}(t,x,y,z=0)=0,\\ &\vec{\upsilon}(t,x,y,z=d)=0, \quad \delta I_{\alpha\beta}(t,x,y,z=d)=0.\end{aligned} \tag{2}$$

In equations (1) and boundary conditions (2), let us pass to the Fourier–transforms with respect to the time and the transversal radius-vector components:

$$\Phi(t,\vec{r}_\perp,z) = \int\limits_{d\omega\,\int\limits_{d\vec{k}_\perp}} e^{-i(\omega t-\vec{k}_\perp\vec{r}_\perp)}\Phi_{\omega k}(z). \tag{3}$$

Retaining the former designations for the amplitudes of the velocity and the inertia tensor fields, and taking into account that the Laplace operator in representation (3) is of the form

$$\Delta = \frac{\partial^2}{\partial z^2} - k_\perp^2, \qquad k_\perp^2 = k_x^2 + k_y^2, \tag{4}$$

after simple transformations we obtain these independent inhomogeneous equations:

$$\hat{f}\upsilon_\alpha(z) = \nu_{12}\nabla_\beta R_{\alpha\beta} + (-i\omega + \frac{1}{\tau} - D\Delta)\sigma_\alpha, \tag{5}$$

$$\hat{f}(-i\omega + \frac{1}{\tau} - D\Delta)\delta I_{\alpha\beta=} = \hat{f}R_{\alpha\beta} + \frac{1}{2}(F_{\alpha\beta} + F_{\beta\alpha}).$$

Here $F_{\alpha\beta}$ is the result of transformation of the following combination of the spontaneous fields

$$F_{\alpha\beta}(t,\vec{r}) = \nu_{12}\nu_{21}\nabla_\beta\nabla_{\beta'}R_{\alpha\beta'} + \nu_{21}(\frac{\partial}{\partial t} + \frac{1}{\tau} - D\Delta)\nabla_\alpha\sigma_\beta, \tag{6}$$

and the operator

$$\hat{f} = [(-i\omega - \nu\Delta)(-i\omega + \frac{1}{\tau} - D\Delta) - \frac{\nu_{12}\nu_{21}}{2}\Delta]. \tag{7}$$

It is convenient to represent the solution of the ordinary differential equation system (5) in the form of expansions in the harmonic functions. In view of the properties of these functions and boundary conditions (2), these expansion assume the form

$$\upsilon_\alpha(z) = \sum_m A_{\alpha m} \sin \mu_m z, \tag{8}$$

$$\delta I_{\alpha\beta}(z) = \sum_m B_{\alpha\beta m} \sin \mu_m z,$$

where the eigenvalues are $\mu_m = \pi m/d$. Let us represent the components of the spontaneous sources in equations (5) in the form of similar expansions with the expansion coefficients $A^0_{\alpha m}$, $B^0_{\alpha\beta m}$. With the orthogonality property and the normality condition for the harmonic functions, the amplitudes in (8) are simply expressed from (5) through the expansion amplitudes for the spontaneous fields. Based on these expressions and using the FDT, we find the spectral densities for the amplitudes of the velocity and inertia tensor fluctuations:

$$\langle A^*_{\alpha m} A_{\alpha' m'} \rangle_\omega = \Theta \delta_{\alpha\alpha'} \delta_{mm'} Re[-i\omega + \nu_{\omega\lambda}(k_\perp^2 + \mu_m^2)]^{-1}, \tag{9}$$

$$\left\langle B^*_{\alpha\beta m} B_{\alpha'\beta' m'} \right\rangle_\omega = 2\Theta \delta_{\alpha\alpha'} \delta_{\beta\beta'} \delta_{mm'} Re[-i\omega + \frac{1}{\tau} + D(k_\perp^2 + \mu_m^2)]^{-1},$$

where

$$\Theta = \frac{k_? T_0}{2\pi^2}, \quad \nu_{\omega\lambda} = \nu + \frac{\nu_{12}\,\nu_{21}}{2}\,[-i\omega + \frac{1}{\tau} + D(k_\perp^2 + \mu_m^2)]^{-1}. \tag{10}$$

The spectral density of the amplitudes for the inertia tensor fluctuations in (9) is obtained under the assumption that the velocity field fluctuations and the inertia tensor field fluctuations are independent. The difference of the result (9) from the those for the bulk case is only in the discrete values of the wave number $\vec{k}$ and the appearance of a frequency dependence of the kinematics viscosity coefficient.

The spectral densities of the thermal fluctuations of the Euler velocity and inertia tensor hydrodynamic fields are respectively given by

$$< \upsilon^*_\alpha(\vec{r}_\perp, z, t) \upsilon_{\alpha'}(\vec{r'}_\perp, z', t') >_\omega = \frac{1}{(2\pi)^3} \int d\vec{k}_\perp e^{i\vec{k}_\perp(\vec{r}_\perp - \vec{r'}_\perp)} \sum_m \sum_{m'} \langle A^*_{\alpha m} A_{\alpha' m'} \rangle_\omega \sin \mu_m z \cdot \sin \mu_{m'} z',$$

$$< I^*_{\alpha\beta}(\vec{r}_\perp, z, t) I_{\alpha'\beta'}(\vec{r'}_\perp, z', t') >_\omega = \frac{1}{(2\pi)^3} \int d\vec{k}_\perp e^{i\vec{k}_\perp(\vec{r}_\perp - \vec{r'}_\perp)} \sum_m \sum_{m'} \left\langle B^*_{\alpha\beta m} B_{\alpha'\beta' m'} \right\rangle_\omega \sin \mu_m z \cdot \sin \mu_{m'} z'. \tag{11}$$

Let us explore the spectral density of the autocorrelation function for the velocity thermal fluctuations in more detail. In the limiting case of coincident spatial arguments, the expression for the velocity CF from (11) reveals the logarithmic divergence $\sim \ln_{\rho \to 0} \rho$ ($\rho = |\vec{r}_\perp - \vec{r}'_\perp|$) and, because of this, cannot be used to estimate the self-diffusion coefficient. However, we can analyze the spectrum of the velocity autocorrelation function by changing from the Euler variables to the Lagrange ones. Moreover, since the velocity of the Lagrange particle is usually considered to equal the collective component of the velocity of the molecule [13, 14], the realization of such a change is actually equivalent to obtaining the hydrodynamic asymptotic for the spectrum of the velocity autocorrelation function for the velocity of the molecule.

To change to the LVACF, we take advantage of the Malomuzh approach [13], whose essence consists in taking into account nonlocal relation between the Lagrange and Euler variables. The derivation of the relation between the Lagrange and Euler velocity CFs is given in [13]. It is considerably simplified if we ignore small drifts of the centre of mass of the Lagrange particle, as in [12]; in this case, it assumes the form

$$\varphi_L(t) = \frac{1}{V_L^2}\int\limits_{V_L} d\vec{r}_1 \int\limits_{V_L} d\vec{r}_2 < \vec{v}(\vec{r}(t)+\vec{r}_1,t)\vec{v}(\vec{r}(0)+\vec{r}_2,0) > . \qquad (12)$$

where V_L is the volume of the Lagrange particle. The spectral density of the Lagrange velocity hydrodynamic field has, according to (11), (12), and in view of the presence of the delta-functions in the spectral densities of the velocity fluctuation amplitudes, the form

$$\varphi_{L\omega}(z) = \frac{R_L^4}{V_L^2}\sum_m \int\limits_0^\infty \frac{J_1^2(k_\perp R_L)}{k_\perp} < A_{\alpha m}^* A_{\alpha m} >_\omega \bar{S}_m^2(z) dk_\perp. \qquad (13)$$

Here $J_1(y)$ is the Bessel function, $R_L = \left(\frac{3}{4\pi}V_L\right)^{1/3}$, and

$$\bar{S}_m^2(z) = \frac{1}{R_L^2}\int\limits_0^{R_L} dz_1 \int\limits_0^{R_L} dz_2 \sin\mu_m(z+z_1)\sin\mu_m(z+z_2) = \qquad (14)$$

$$= (\mu_m R_L)^{-2} \cdot (\cos\mu_m z - \cos\mu_m (z+R_L))^2 .$$

After integration over the $k_\perp$ and in view of (9), we get:

$$\varphi_{L\omega}(z) = \frac{9\Theta}{16\pi^2\nu}\sum_m \sum_{l=1,2} a_l \frac{I_1(R_L\gamma_{ml})K_1(R_L\gamma_{ml})}{(R_L\gamma_{ml})^2} \cdot \bar{S}_m^2(z). \qquad (15)$$

Here $I_1(y)$ and $K_1(y)$ are the modified Bessel functions, and a_l and γ_{ml} are the solutions of these simple algebraic equations:

$$\begin{aligned} &\gamma_{m1}^2 = \mu_m^2 + C_1, && a_1 = \tfrac{C_2-C_3}{C_2-C_1}, \\ &\gamma_{m2}^2 = \mu_m^2 + C_2, && a_2 = \tfrac{C_3-C_1}{C_2-C_1}, \\ &C_1 = \lambda - \sqrt{\lambda^2 + \tfrac{\omega^2+i\omega/\tau}{D\nu}}, && \lambda = \tfrac{-i\omega(D+\nu)+\nu/\tau+\nu_{12}\nu_{21}/2}{2D\nu}, \\ &C_1 + C_2 = 2\lambda, && C_3 = D^{-1}(1/\tau - i\omega). \end{aligned} \qquad (16)$$

Since $R_L \ll d$, using the series expansion for the functions $I_1(y)$ and $K_1(y)$, result (15) is represented in the form

$$\varphi_{L\omega}(z) = \frac{9\Theta}{32\pi^2\nu}\sum_m \sum_{l=1,2} a_l \left(\frac{1}{2}\ln\frac{R_L\gamma_{ml}}{2} + (R_L\gamma_{ml})^{-2} + \frac{1}{2}\left(C_L - \frac{1}{4}\right)\right) \cdot \bar{S}_m^2(z), \qquad (17)$$

where C_L is the Euler constant.

After carrying out the summation, we finally derive:

$$\varphi_{L\omega}(z) = \frac{9\Theta}{128\pi^2\nu} \sum_{l=1,2} a_l \left(\frac{1}{R_L}\left(C_L - \frac{1}{4} \right) + \frac{1}{2R_L} \ln \frac{R_L^2 C_l}{4} + \frac{s\,(2C_l)}{R_L^2\,(2C_l)^{1/2}} + \frac{2}{R_L^3 C_l} + \frac{2s\,(C_l)}{R_L^4 C_l^{3/2}} \right), \tag{18}$$

where

$$s\,(x) = cth\,(d\sqrt{x})\,(ch\,((z+R_L)\,\sqrt{x}) - ch\,(z\sqrt{x}))^2 +$$
$$+ (sh\,((z+R_L)\,\sqrt{x}) + ch\,(z\sqrt{x}))^2 - ch\,(R_L\sqrt{x})\,(ch\,((2z+R_L)\,\sqrt{x}) + sh\,((2z+R_L)\,\sqrt{x}))\,. \tag{19}$$

The derived spectrum of the LVACF allows us to find the expression for the Lagrange self-diffusion coefficient, which is defined as

$$D_L\,(z) = \frac{1}{3}\varphi_{L,\omega=0}(z). \tag{20}$$

In the limit $\nu_{12}\,\nu_{21} \to 0$, when the fluctuations of the inertia tensor and velocity fields are independent, with the use of (15), (16) we obtain:

$$D_L\,(z) = \frac{9\Theta}{64\pi^2\nu}\frac{d}{R_L^2}\left(\frac{z}{d}\left(1 + o\left(\frac{R_L}{d}\right)^2\right) - \left(\frac{z}{d}\right)^2\left(1 + o\left(\frac{R_L}{d}\right)^2\right) + \frac{R_L}{d}\left(\frac{37}{12} - \frac{1}{2}\ln\frac{8\pi d}{R_L}\right) + o\left(\frac{R_L}{d}\right)^2 \right). \tag{21}$$

Expression (21) is given with an accuracy of up to the second order in the small ratio R_L/d; depending on the distance d between the parallel planes, this relation takes on values from $-\infty$ to 10^{-1}.

Conclusion

The spectrum of the Lagrange velocity hydrodynamic field as a function of the coordinate z normal to the restrictive planes is derived. It represents the hydrodynamic asymptotic form for $t \to \infty$ of the spectrum of the velocity autocorrelation function for the anisotropic molecules of a liquid confined by two parallel planes. The distance between the planes is a parameter for this dependence and can be taken to range from $d \sim 10R_L$ to $d \to \infty$. With the use of the expression for the spectrum, the Lagrange self-diffusion coefficient is determined as a function of z and dimensionless relation R_L/d. It is in good agreement with results [6], where the effect of confinement on the mode-coupling contribution to the self-diffusion coefficient (in the direction parallel to the walls) in a fluid slab was computed. In [6], these finite-size corrections are shown to reduce the bulk diffusion constant near the walls by an amount of $-(\sigma/d)\log(\sigma/d)$, where d is the thickness of the fluid slab and the physical interpretation of σ is given, based on intuitive considerations, as the atomic size.

Similar finite-size corrections near the walls with R_L instead of σ are obtained for the Lagrange self-diffusion coefficient in the present paper. In the limit $d \to \infty$, the results obtained transform into the self-diffusion coefficient for the bulk case.

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