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STATISTICAL-MECHANICAL INVESTIGATION OF VISCOELASTIC PROPERTIES OF SYSTEMS WITH NON-CENTRAL INTERMOJECULAR INTERACTIONS

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We obtain relations between the two stress tensors and the two velocity-strain tensors for a medium with non-cent. I interactions. An approximation method of integration of autocorrelation functions based on statistically calculated average relaxation times of coordinates and momenta is suggested.

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The existence of two stress tensors and corresponding velocity-strein tensors is characteristic of systems with non-central intermolecular interactions [1,2]. The strain tensors $\epsilon_{ik} = \partial u_i / \partial q_k - \delta_m e_{mki}$ and $\gamma_{ik} = \partial \delta_i / \partial q_k$ are expressed by kinematical j independent vectors of a small displacement u_i and of a small angle of rotation δ_i of a particle. Strong correlation between space and angular variables is an important feature of the sy tems. This correlation is evident in dielectric properties [3].

Relations between stress tensors and velocity-strain tensors are derived by the Kubo method [4] to describe the viscoelastic behaviour of the system, with spatial dispersion taken into account.

Similarly to [5], the canonical transformation method is used to overcome the main difficulty in the derivation of an explicit expression for an increment in the Hamiltonian. Applying a small deformation to the system and regarding the change of coordinates and momenta as an infinitesimal canonical transformation, we obtain

$$\Delta H = \int \Pi_{ik}(q') \epsilon_{ik}(q') \, dq' + \int \mathcal{P}_{ik}(q') \gamma_{ik}(q') \, dq' \,, \tag{1}$$

where Π_{ik} and \mathcal{P}_{ik} are dynamic quantities, representing microscopic linear momentum and angular momentum fluxes, respectively.

The expressions for the viscous stress tensor σ_{ib} and the couple-stress tensor π_{ib} are given by

$$\sigma_{ik}(q,t) = (k_{\rm B}T)^{-1} \int_{0}^{\infty} d\tau \int dq' \left\{ \langle \Pi_{mn}(q',0) \widetilde{\Pi}_{ik}(q,\tau) \rangle \dot{\epsilon}_{mn}(q',t-\tau) + \langle \mathcal{P}_{mn}(q',0) \widetilde{\Pi}_{ik}(q,\tau) \rangle \dot{\gamma}_{mn}(q',t-\tau) \right\},$$

$$\pi_{ik}(q,t) = (k_{\rm B}T)^{-1} \int_{0}^{\infty} d\tau \int dq' \left\{ \langle \Pi_{mn}(q',0) \widetilde{\mathcal{P}}_{ik}(q,\tau) \rangle \dot{\epsilon}_{mn}(q',t-\tau) + \langle \mathcal{P}_{mn}(q',0) \widetilde{\mathcal{P}}_{ik}(q,\tau) \rangle \dot{\gamma}_{mn}(q',t-\tau) \right\}.$$
(2)

In the above expressions, $\widetilde{\Pi}_{ik}$ and \widetilde{P}_{ik} are subtracted fluxes in the sense of [6]. The calculation of transport coefficients is faced with the difficulties of averaging and of determining the time dependence of dynamic quantities. This dependence can be approximated by $\exp(-t/\tau_i)$ where τ_i is some average relaxation time.

For the systems under consideration these are relaxation times of the linear momentum τ_p and the angular momentum τ_l as well as relaxation times of the centre of inertia coordinates τ_0 and angular coordinates T of a molecule.

The expressions for τ_0 and τ_{ω} are obtained [7, 8] by an approximate solution of the equation for the one-particle partition kinetic function

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$$\tau_{\sigma} = k_{\rm B} T / \langle \mathcal{F} \rangle \langle v \rangle, \qquad \tau_{\sigma} = k_{\rm B} T / \langle M \rangle \langle \omega \rangle$$

where the brackets $\langle \cdot \rangle$ represent an average over the equilibrium ensemble; \mathcal{F} and M represent the absolute values of the total force and torque on a molecule, respectively; v and ω are the absolute values of the linear and angular velocities of a molecule, respectively.

Kirkwood's method [9] extended to systems of orientable particles is used to derive the Langevin equations for Brownian motion, both translational and rotational, these equations being used to obtain the linear and angular momentum relaxation times.

These equations are

$$\frac{dp}{dl} = -\xi_{qq} \cdot (m^{-1}p) - \xi_{qq} \cdot (I^{-1} \cdot I) + \mathfrak{I}(t) ,$$

$$\frac{dI}{dt} = -\xi_{qq} \cdot (m^{-1}p) - \xi_{qq} \cdot (I^{-1} \cdot I) + \mathfrak{M}(t) , \qquad (4)$$

where p and l represent the linear and angular momentum, respectively; m is the mass of a particle: l represents its tensor of moments of inertia.

The following friction coefficient tensors are expressed by integrals of time autocorrelation functions

$$\zeta_{aa} = (k_{\rm B}T)^{-1} \int_{0}^{\infty} \langle \mathcal{F}(0)\mathcal{F}(t) \rangle dt, \qquad \zeta_{aaa} = (k_{\rm B}T)^{-1} \int_{0}^{\infty} \langle \mathcal{M}(0)\mathcal{M}(t) \rangle dt.$$
(5)

The other two friction coefficient tensors describe the mutual effect of rotational and translational motions. The effect disappears if some symmetry occurs in the system [10]. The friction coefficients for linear molecules can be represented as $\zeta_q = \langle \mathcal{F}^2 \tau_q / 3k_BT, \zeta_q \rangle =$

The friction coefficients for linear molecules can be represented as $\tau_p = M^2 \sigma_p/2k_BT$, the relaxation times being then defined as $\tau_p = m/\zeta_p$ and $\tau_l = l/\zeta_p$. The above mentioned relaxation times have been widely used [11-13]. In particular, the anisotropy

The above mentioned relaxation times have been widely used [11-13]. In particular, the anisotropy relaxation time $\tau_{an} = \langle M^2 \rangle \tau_{\sigma} / 12 (k_B T)^2$ for linear molecule systems can be obtained. The self-diffusion coefficient can be satisfactorily evaluated through the relaxation time τ_{dr} .

For isotropic non-gyrotropic media with non-central intermolecular interactions, with known relaxation times. use of relations (2) makes it possible to evaluate (while neglecting spatial dispersion) six viscosity coefficients, including both shear and bulk viscosities, commonly known.

The existence of additional viscosity coefficients leads to non-trivial peculiarities of sound wave propagation. In addition to longitudinal waves, there are also rotational waves and two types of transverse waves in the high-frequency range defined by the theory.

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