

Calculation of the autocorrelation function of the angular velocity of liquid molecules in the long-wavelength approximation

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A method is presented for calculating in the long-wavelength approximation of the autocorrelation function of the angular velocity of molecules of a liquid. This autocorrelation function calculated for water is in agreement with experiments on the inelastic scattering of slow electrons.

The autocorrelation function of the angular velocity of water molecules at a temperature of 300 K has been obtained by the method of slow-neutron inelastic scattering.¹ Existing models of the autocorrelation function of the angular velocity² do not reflect important details of the experimental curves. If the equation chain of Mori is

used according to the method of Refs. 3–5, then the first two equations of the autocorrelation function $\psi(t) = \langle \omega(0)\omega(t) \rangle / \langle \omega(0)^2 \rangle$ can be written

$$\frac{d\psi(t)}{dt} = -\omega_1^2 \int_0^t f(t-\tau)\psi(\tau)d\tau, \quad (1)$$

$$\frac{d\psi(t)}{dt} = - \int_0^t R(t-\tau)f(\tau)d\tau,$$

where $f(t) = \langle \dot{\omega}(0)\dot{\omega}(t) \rangle / \langle \dot{\omega}(0)^2 \rangle$, $\omega_1^2 = \langle \dot{\omega}(0)^2 \rangle / \langle \omega(0)^2 \rangle$, and $\omega(t)$ is a component of the angular momentum vector of the molecule.

To derive Eqs. (1) it is necessary, following the work of Refs. 3–5, to eliminate the projection operators and in the long-wavelength approximation ignore the unsymmetric correlation functions.⁴ Here the long-wavelength region means the region where the wavelength of the external perturbations is considerably larger than the correlation length of the different particles. If we use the explicit form of the classical Liouville operator, then for linear molecules it is easy to find

$$\omega_1^2 = L^2 / K_B T I, \quad f(t) = \langle L(0)L(t) \rangle / \langle L(0)^2 \rangle,$$

$$R(t) = \langle \omega(0) \nabla L(0) \omega(t) \nabla L(t) \rangle / \langle L(0)^2 \rangle, \quad L^2 = \langle L(0)^2 \rangle, \quad (2)$$

where $L(t) = \dot{\omega}(t)I$ is the torque acting on a molecule from its surroundings, $\nabla L(t) = \dot{\omega}(t)I$ is the angular gradient of the torque, I is the moment of inertia, and K_B is the Boltzmann constant.

Let us introduce the correlation time τ_ω of the angular velocity and the correlation time $\tau_{\nabla L}$ of the torque gradient by the expressions

$$\tau_\omega = \int_0^\infty \psi(\tau)d\tau, \quad \tau_{\nabla L} = \int_0^\infty h(\tau)d\tau, \quad (3)$$

where $h(t) = \langle \nabla L(0)\nabla L(t) \rangle / \langle \nabla(0)^2 \rangle$.

The main assumption that permits the chain of equations to be closed reduces to the inequality

$$\tau_\omega \ll \tau_{\nabla L}. \quad (4)$$

For most liquids inequality (4) is a natural one, since from physical considerations the quantity $\tau_{\nabla L}$ should be of the same order of magnitude as the reorientation time of a molecule, and it can be estimated to be $\tau_{\nabla L} \propto 10^{-12}$ s (Ref. 6), which is two orders of magnitude greater than the value $\tau_\omega \propto 10^{-14}$ s (Ref. 1). In general, inequality (4) may not be satisfied. The existence of a hierarchy of times τ_ω and $\tau_{\nabla L}$ in a liquid may be related to the particular features of the spatial structure of the intermolecular interactions. A typical pair potential of the interactions consists of a superposition of the short-range forces of repulsion and the long-range forces of attraction. Presumably,

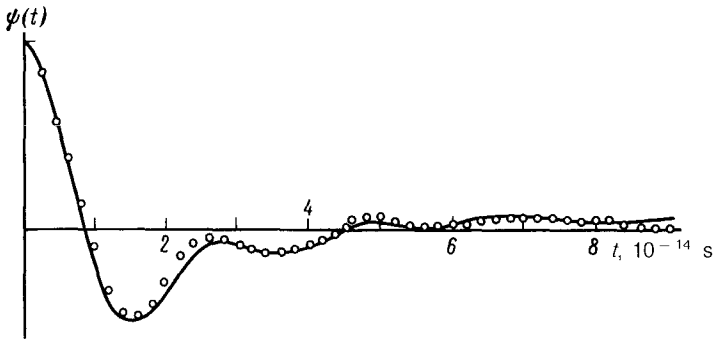


FIG. 1. Autocorrelation function of the angular velocity of water molecules at 300 K. Solid lines represent the numerical solution of Eq. (5); the points represent the experimental data of Ref. 1.

the short-range forces provide a fast relaxation of the angular velocity of a molecule long before it hops to a neighboring site, while at the same time the correlation of the torque gradient is still conserved through the long-range part of the potential. A quantitative analysis of this process may be the subject of a separate investigation.

Assuming that inequality (4) is satisfied, we separate the variables in $R(t)$ and disregard the time dependence of the slowly varying function $h(t)$. Finally, in place of Eq. (1) we have

$$\begin{aligned} \frac{d\psi(t)}{dt} &= -\omega_1^2 \int_0^t f(t-\tau)\psi(\tau)d\tau, \\ \frac{d\psi(t)}{dt} &= -\omega_2^2 \int_0^t \psi(t-\tau)f(\tau)d\tau, \end{aligned} \quad (5)$$

where $\omega_2^2 = \langle \nabla L(0)^2 \rangle K_B T / \langle L(0)^2 \rangle I$. A similar means of closing the Mori equations was used in the calculation of the structure factor of liquid rubidium.⁴

The curve obtained by a numerical solution of Eqs. (5) (solid line) is shown in Fig. 1, which also shows the experimental curve (points) from Ref. 1.

The parameter $\langle L(0)^2 \rangle^{1/2} = 5.2 \times 10^{-20}$ N·m is taken from Ref. 1, and the parameter $\langle \nabla L(0)^2 \rangle^{1/2} = 4.7 \times 10^{-19}$ N·m was chosen to make the theoretical curve coincide with the experimental curve. The quantity I was chosen to be equal to the average moment of inertia of water, $I = 2 \times 10^{-47}$ m·kg (Ref. 1).

In conclusion I note that with the Laplace transform one can obtain a solution of Eqs. (5) in the form of a combination of normal elliptical integrals.

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