Physical criterion of the degree of non-Markovity of relaxation processes in liquids

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The microscopic parameter characterizing the degree of non-Markovity of irreversible processes is introduced. It is shown that the structure relaxation process in liquids is essentially non-Markovian in a wide range of wave vectors excluding the region near the first maximum of the static structure factor.

1. Historically the theory of irreversible phenomena was based on the probability notions about Markovian stochastic processes. Undoubtedly, it promoted the formation of the theory and permitted one to obtain the series of interesting results in describing transport processes and calculating transport coefficients (diffusion, shear and bulk viscosity, thermal conductivity) in terms of the time correlation functions (TCF) of the corresponding currents. Note that the Markovian property of the stochastic processes was formulated for the first time by Markov in ref. [1] published in Kazan. The basis of the general theory of Markovian processes with continuous time was founded by Kolmogorov [2]. Later the limitation of this approach was cleared up and during the last three decades beginning with the works of Zwanzig [3] and Mori [4] statistical physics developed by overcoming the old "Markovian" errors.

Earlier it was formally shown by some of the authors that the main relaxational processes in a condensed medium were non-Markovian and characterized by molecular memory effects. However, the statements about the non-Markovity were, as a rule, rather indefinite and hazy. Until this time there was no clear physical criterion characterizing the non-Markovity of irreversible processes.

The aim of this work is the presentation of such a criterion and the analysis of the latter by the example of the investigation of the space–time correlations of local number density fluctuations in liquid aluminium.

2. Let us consider the normalized TCF of the arbitrary dynamical variable $g(t)$,

$$G(t)=\frac{\langle g^*(0)g(t)\rangle}{\langle |g(0)|^2\rangle}\,. \qquad (1)$$

Following the Zwanzig–Mori formalism [3,4], we can write an equation of motion for the TCF $G(t)$ in the form

$$\frac{\mathrm{d}G(t)}{\mathrm{d}t}=-\Omega^2\int_0^t \mathrm{d}\tau\, M(\tau)G(t-\tau)\,, \qquad (2)$$

where Ω^2 is a parameter with the dimension of frequency squared and $M(\tau)$ is the memory function reflecting the non-Markovian time effects.

As a simple criterion of the non-Markovity of the relaxation process it is possible to consider the following microscopic parameter,

$$\epsilon_1=\tau_g/\tau_m\,,$$

$$\tau_g=\mathrm{Re}\int_0^\infty \mathrm{d}t\, G(t)\,,\quad \tau_m=\mathrm{Re}\int_0^\infty \mathrm{d}t\, M(t)\,, \qquad (3)$$

where τ_g is the correlation time of the dynamic variable $g(t)$ and τ_m is the correlation time of the memory function.