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The spectrum of the non-Markovity parameter for relaxation processes in liquids

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A general theory of the spectrum of the non-Markovity parameter is introduced for the detailed analysis of non-Markovian peculiarities of relaxation processes in liquids. The numerical calculations have been carried out for vibrational, dielectrical and structural relaxation. It is shown that the non-Markovian time effects play the main role in the kinetics of the relaxation processes in liquids.

1. Introduction

The theory of non-equilibrium processes up to recent times has been based on the Markovian theory of random molecular processes in statistical systems. So, for example, the fundamental equations of transport phenomena, kinetics, spin and galvanomagnetic effects are Markovian and molecular memory effects were not taken into account.

This theory has been used by experimentalists for observations related to relatively slow processes and to the long-wavelength part of the electromagnetic spectrum. This theory changed essentially after the fast accumulation of data concerning the short-wavelength part of the spectrum and with the registration of relatively fast processes. It has become possible to extract detailed information about the kinetics of non-Markovian processes when molecular memory effects play the most important role.

Unfortunately, the modern theory of the non-Markovian processes is underdeveloped both from the physical and the mathematical point of view. A general theory of the spectrum of the non-Markovity parameter is introduced in the present paper. It is

concretely analyzed for vibrational, dielectrical and structural relaxation in classical liquids.

2. General theory

Let us consider a well known chain of coupled non-Markovian kinetic equations for the time correlation functions (TCFs) $a(t)$ [1],

$$\begin{aligned} \frac{da(t)}{dt} &= -\Omega_1^2 \int_0^t d\tau M_1(\tau) a(t-\tau), \\ \frac{dM_1(t)}{dt} &= -\Omega_2^2 \int_0^t d\tau M_2(\tau) M_1(t-\tau), \\ \frac{dM_2(t)}{dt} &= -\Omega_3^2 \int_0^t d\tau M_3(\tau) M_2(t-\tau), \end{aligned} \quad (1)$$

etc. Here $M_1(\tau)$, $M_2(\tau)$, $M_3(\tau)$ are the first-, second-, third-order memory functions, respectively, and Ω_1 , Ω_2 , Ω_3 are the frequency relaxation parameters related to the first three even frequency moments I_{2n} of the spectral density of the TCF $a(t)$,