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R M Yulmetyev and N R Khusnutdinov†

Department of Theoretical Physics, Kazan State Pedagogical Institute, Kazan, PO Box 21, Mezhlauk 1, 420021, Russia

Abstract. The spectra of the non-Markovity parameter for three model systems are found: an ideal gas, weakly non-ideal gas and a medium in hydrodynamic limits. It is shown that the non-Markovian effects play the dominant role in all three above-mentioned cases. The effects of molecular memory are connected with the statistical appearance of intermolecular interactions in statistical systems.

1. Introduction

The theory of Markovian random processes that began with the well known article of Markov [1] served for a certain time as the fundamental basis for describing a wide range of statistical phenomena in physics and chemistry (e.g. [2, 3]). After the prominent articles of Zwanzig [4] and Mori [5], in principle it is quite clear that in statistical physics, non-Markovian processes and the statistical effects of molecular memory play a great role. However, the methods of strict quantitative evaluation of the effects of memory have not been elaborated for a long time. The quantitative criterion of numerical evaluation of the non-Markovian effects was firstly introduced only in [6, 7]. Recently, the notion of a spectrum of the non-Markovian parameter and Markovization depth was determined for the description of non-equilibrium processes in liquids.

In its usual meaning, a spectrum of physical quantities is a set of eigenvalues of corresponding operators. Yet the spectrum concept has another and wider meaning. Because the term 'spectrum' stems from the Latin word for 'representation' or 'image', in physics, therefore, 'spectrum' means an aggregate of all values of a physical quantity indicative of a system or a process.

Investigation of a spectrum of physical quantities is one of the most vital tasks of the physics of condensed media. The most traditional is a determination of an energy spectrum, a system of eigenfunctions, spectral invariants, spectral properties of a corresponding group of unitary shift operators, etc. We analyse in the present paper the spectral properties such as random density fluctuations that lead to structural relaxation.

The concept of a non-Markov spectrum reflects the infinite structure and hierarchy properties of an arbitrary relaxation process. The hierarchy of the equations is due to intermolecular interactions and to the static properties of the system. The presence of a definite ith level reflects only the existence of an ith equation of the chain. From the physical standpoint, we are interested in the Markov ($\epsilon \gg 1$) and non-Markov ($\epsilon \sim 1$ or

† e-mail: nail@univex.kazan.su

$\epsilon < 1$) regions of a spectrum. The number m of the level at which the change from a Markov to a non-Markov spectrum takes place can be called the depth of 'Markovization' $d_M = m$ [6, 7].

It is noteworthy that for quasi-Markov ($\epsilon \gg 1$) and purely Markov ($\epsilon \to \infty$) processes the initial time correlation function (TCF) cannot be determined from the first equation of the chain. The point being made is that the presence of non-Markov behaviour at deep levels plays an essential role in the behaviour of the experimentally observed physical quantities in the case of quasi-Markov and Markov processes at the first level. By way of example we refer to spin relaxation in liquids [8–11], where the spin relaxation itself is a Markov process. However, the presence of non-Markov behaviour in molecular processes ($\epsilon_1 \sim 1$ at the first level) leads to an unusual square root dependence of the spin relaxation time in liquefied inert gases, liquid metals, and semiconductors ($T_1, T_2 \sim T^{1/2}, T^{-1/2}$). The picture observed changes substantially when Markov molecular processes become responsible for the spin relaxation ($\epsilon_1 \to \infty$). The temperature dependence of T_1 and T_2 become of the traditional activation type.

The space dispersion of the non-Markovity parameter for structural relaxation was found in [7]. The spectrum of this parameter for vibrational, structural and dielectrical relaxation was obtained in [12, 13] and in [14] the spectra and their space dispersions for transport phenomena (viscosity, heat conduction) in liquids were calculated. The results which were obtained in [6, 7, 12–14] showed the fundamental role of non-Markovian effects in processes of relaxation in condensed matter.

The goal of this particular article is to calculate the spectrum of the non-Markovity parameter for three simple model systems: an ideal gas, a weakly non-ideal gas and a hydrodynamical system (in limits $k \to 0$, where k is a wavevector), when the calculations may be carried out exactly, without using approximations. Analysis of these three models is important for two reasons: firstly, for the best comprehension and explanation of the non-Markovian effects from the experimental spectrum, and, secondly, for the clarification of the fundamental role of interparticle potential interaction in random intermolecular processes.

The organization of this paper is as follows. In section 2 we deduce the infinite hierarchy of connected equations for the time correlation functions. In section 3 we give determinations of the spectrum of the non-Markovity parameter and depth of Markovization and calculate them for an ideal gas (subsection 3.1), weakly non-ideal gas (subsection 3.2) and for systems in the hydrodynamic limit (subsection 3.3). We will conclude in section 4 with some remarks.

2. General framework

Let us consider the time evolution of the equilibrium fluctuation $\delta A_0(t) = A_0(t) - \langle A_0(t) \rangle$ of the dynamical variable $A_0(t)$, which is the Fourier transformation over particle density (15), where the brackets $\langle \cdots \rangle$ denote the statistical average over the equilibrium distribution of Gibbs. The fluctuation obeys the Liouville equation

$$\frac{d}{dt}(\delta A_0(t)) = i\hat{L}\delta A_0(t) \tag{1}$$

where we introduce the Liouville operator $\hat{L}$

$$\hat{L} = \hat{L}_0 + \hat{L}_1 = -i\left\{ \sum_{j=1}^{N} \frac{p_j \nabla_j}{m} - \sum_{l>j}^{N} \sum_{j=1}^{N} \nabla_j U(r_{lj}) \left(\nabla_{p_j} - \nabla_{p_l} \right) \right\} \tag{2}$$

and operator $\hat{L}_1$ corresponds to the particle interactions, $U(r_{lj})$ is a pair potential, p_j is the momentum of jth particles, m is the mass and N is the total number of particles.

Successively applying the operator $\hat{L}$ to the dynamic variable $\delta A_0(0)$ we obtain the infinite set of dynamic functions

$$B_n(0) = (\hat{L})^n \delta A_0(0) \qquad n \geqslant 0. \tag{3}$$

Applying the Gram–Schmidt orthogonalization procedure [15] to the set of functions $B_n(0)$, we obtain the set of dynamical variables W_n:

$$\langle W_n^*(0), W_l(0) \rangle = \langle |W_n|^2 \rangle \delta_{n,l}$$

where $\delta_{n,l}$ is Kronecker's symbol.

We may easily infer the recurrent formulae in which the next values $W_n(t)$ are connected with the preceding values of smaller number:

$$W_0 = \delta A_0(0) \qquad W_1 = (\hat{L} - \omega_0^{(0)}) W_0$$
$$W_n = (\hat{L} - \omega_0^{(n-1)}) W_{n-1} - \Omega_{n-1}^2 W_{n-2} \qquad n > 1. \tag{4}$$

Here we introduce the following notation:

$$\omega_0^{(n)} = \frac{\langle W_n^* \hat{L} W_n \rangle}{\langle |W_n|^2 \rangle} \qquad \Omega_n^2 = \frac{\langle |W_n|^2 \rangle}{\langle |W_{n-1}|^2 \rangle} \tag{5}$$

where Ω_n are the main relaxation frequencies, and the frequencies $\omega_0^{(n)}$ describe the eigenspectrum of the Liouville operator $\hat{L}$.

Arbitrary variables W_n may be expressed directly through the zeroth variable W_0, using equations (4):

$$W_n = \begin{vmatrix} \hat{L} - \omega_0^{(0)} & \Omega_1 & 0 & \cdots & 0 \\ \Omega_1 & \hat{L} - \omega_0^{(1)} & \Omega_2 & \cdots & 0 \\ 0 & \Omega_2 & \hat{L} - \omega_0^{(2)} & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & \hat{L} - \omega_0^{(n-1)} \end{vmatrix} W_0. \tag{6}$$

The set of orthogonal functions (4) can be connected with the set of projectors, which project the arbitrary dynamic variable Y to the corresponding vector of set

$$\Pi_n = \frac{W_n \rangle \langle W_n^*}{\langle |W_n|^2 \rangle} \qquad P_n = 1 - \Pi_n \qquad \Pi_n \Pi_m = \delta_{nm} \Pi_n \tag{7}$$
$$P_n^2 = P_n \qquad \Pi_n P_n = P_n \Pi_n = 0.$$

Take into consideration that both sets (4) and (7) are infinite. If we execute the operations in the space of dynamic variables then the formal expression (7) must be understood as the following:

$$\Pi_n Y = W_n \frac{\langle W_n^* Y \rangle}{\langle |W_n|^2 \rangle} \qquad Y \Pi_n = W_n^* \frac{\langle Y W_n \rangle}{\langle |W_n|^2 \rangle}. \tag{8}$$

Applying successfully operators Π_n and P_n to equation (1) on the left and solving these systems of equations we obtain the infinite hierarchy of connected equations

$$\frac{\mathrm{d}M_n}{\mathrm{d}t} = \mathrm{i}\omega_0^{(n)} M_n - \Omega_{n+1}^2 \int_0^t \mathrm{d}\tau \, M_{n+1}(\tau) M_n(t-\tau) \qquad n \geqslant 0 \tag{9}$$

for the TCFs

$$M_n(t) = \frac{\langle W_n^* \exp\{\mathrm{i}\hat{L}_{22}^{(n)} t\} W_n \rangle}{\langle |W_n|^2 \rangle}. \tag{10}$$

Functions $M_n(t)$ are usually considered [4–7, 12, 13] as functions characterizing the statistical memory of the system. Here we determine the following notation for the diagonal matrix elements of Liouvillian

$$\begin{aligned} \hat{L}_{22}^{(0)} &= \hat{L} \\ \hat{L}_{22}^{(n)} &= P_{n-1} P_{n-2} \ldots P_0 \hat{L} P_0 \ldots P_{n-2} P_{n-1} \qquad n \geqslant 1. \end{aligned} \tag{11}$$

The TCFs (10) do not contain the Liouville operator, only the diagonal part $\hat{L}_{22}^{(n)}$ (11). In [4, 5] the TCFs (10) contain the operator

$$\hat{L}_2^{(n)} = P_{n-1} P_{n-2} \ldots P_0 \hat{L}$$

instead of the operator $\hat{L}_{22}^{(n)}$ (equation (11)). It can be shown that the TCFs (10) agree with one obtained in [4, 5]. Indeed, expanding the TCFs (10) in a Taylor series we derive the following expression:

$$M_n(t) = \sum_{k=0}^{\infty} \frac{1}{k! \langle |W_n|^2 \rangle} \langle W_n^* (\mathrm{i}t \hat{L}_{22}^{(n)})^k W_n \rangle.$$

This expression can be put in a form coinciding with the results of [4, 5], using the properties (8) and (9):

$$M_n(t) = \sum_{k=0}^{\infty} \frac{1}{k! \langle |W_n|^2 \rangle} \langle W_n^* (\mathrm{i}t \hat{L}_2^{(n)})^k W_n \rangle = \frac{\langle W_n^* \exp(\mathrm{i}t \hat{L}_2^{(n)}) W_n \rangle}{\langle |W_n|^2 \rangle}.$$

Applying the Fourier transformations to equations (9)

$$\widetilde{M}_n(s) = \int_0^{\infty} \mathrm{d}\tau \, \mathrm{e}^{-s\tau} M_n$$

and we may reduce this infinite integrodifferential hierarchy (9) to the infinite system of algebraic equations

$$\widetilde{M}_n(s) = \{s - \mathrm{i}\omega_0^{(n)} + \Omega_{n+1}^2 \widetilde{M}_{n+1}(s)\}^{-1}. \tag{12}$$

Solution of this system for M_0 has its persistent fraction form.

Although the resulting system of kinetic equations (9) coincides with that given by Mori and Zwanzig [4, 5], the method developed in this article differs from theirs in two ways. Firstly, we have used the infinite set of orthogonal dynamical variables W_n and the

orthogonal set of projectors (7) and (8). We have obtained the set of functions W_n in an explicit form with the help of the Gram–Schmidt orthogonal procedure. Secondly, in the inference system (9), the matrix representation of the Liouville operator and its splitting in various subspaces has been used.

It was this approach which was used in the functional analysis and quantum theory of scattering [21, 22]. Because of this, the diagonal matrix elements $\hat{L}_{22}^{(n)}$ ($n \geqslant 0$) have been produced in the evolution operator inside the TCFs (10). For TCFs, the initial space of dynamical variables is the Hilbert space, which is why there is no difference when using the operator $\hat{L}_{22}^{(n)}$ and $\hat{L}_2^{(n)}$ [23].

However, in the series of other important problems, for example in the quantum theory of scattering [22, 24, 25] and in equilibrium statistical physics [22, 26, 27], the initial space of variables is the Banach space. Therefore the difference between the operators $\hat{L}_{22}^{(n)}$ and $\hat{L}_2^{(n)}$ is essential when we calculate the evolution of states in various functional subspaces.

3. Spectra of parameter non-Markovity for the statistical systems

Previously, the hierarchy of equations (9) has been investigated repeatedly for various systems and dynamical variables W_0 [4–7, 12–14]. In particular, we showed that in many cases the basic role is played by the effects of non-Markovity, which describe hierarchy (9). In order to describe the non-Markovity of a system quantitatively we suggested calculation of the non-Markovity parameter [6, 7] and its spectrum [12, 13]. Briefly, the main point of these articles is the following.

We determine the time of relaxation τ_n of the TCFs $M_n(t)$ by the following correlation:

$$\tau_n = \text{Re} \int_0^\infty d\tau\, M_n(\tau) = \text{Re}\, \widetilde{M}_n(0). \tag{13}$$

The spectrum of the non-Markovity parameter describes the infinite set of dimensionless parameters

$$\epsilon_n = \tau_n/\tau_{n+1} \qquad n \geqslant 0 . \tag{14}$$

The integer n corresponds to the number of the equation (level) in systems (9). If the quantity of the parameter $\epsilon_n \gg 1$ for some integer n, then this level of relaxation is Markovian. In the opposite case, when we have ϵ_n ranging from zero to values of the order of unity, the relaxation is non-Markovian. For the number m of the first level with non-Markovian relaxations, the term depth of Markovization, $d_M = m$, was suggested [12, 13]. Some examples for simple liquids were investigated in [12, 13], from which it is shown that the relaxation of systems steadily approaches the non-Markovity regime, while the level number n increases. Here we investigate the simple situation when it is possible to calculate the spectrum of the non-Markovity parameter theoretically. The initial variable is the Fourier transformation over the fluctuation of the particle number density of a system

$$W_0 = W_0(k) = \frac{1}{V} \sum_{l=1}^N \exp(ikr_l) - \frac{N}{V} \delta_{k,0}. \tag{15}$$

It is obvious that all frequencies ω_0^n are equal to zero for the variable (15). In all three cases calculated in the present article the correlation time τ_0 is real and the spectrum of the non-Markovity parameter obeys the following equation:

$$\epsilon_n \epsilon_{n+1} = \frac{\Omega_{n+2}^2}{\Omega_{n+1}^2}.$$

This relation allows us to express ϵ_n in terms of the variables τ_0 and Ω_k:

$$\epsilon_0 = \tau_0^2 \Omega_1^2 \qquad \epsilon_1 = \frac{1}{\tau_0^2} \frac{\Omega_2^2}{\Omega_1^4} \qquad \epsilon_2 = \tau_0^2 \frac{\Omega_3^2 \Omega_1^4}{\Omega_2^4} \qquad \epsilon_3 = \frac{1}{\tau_0^2} \frac{\Omega_4^2 \Omega_2^4}{\Omega_3^4 \Omega_1^4} \qquad \text{etc.}$$

Hereafter we use the following notations: c_v, c_p, n, χ, κ, e which are the specific heat capacities in units of mass at constant volume and constant pressure, $n = N/V$ is the density of number particles, the coefficient of isothermal compressibility and energy by one particle, respectively. The quantity $\vartheta_s = \{(c_p/c_v)(\partial p/\partial \rho)_T\}^{1/2}$ is the velocity of sound in the matter, $\Gamma_s = \{4\eta/3 + \zeta + (1/c_v - 1/c_p)\kappa\}/2\rho$ is the absorption coefficient of sound and T is the temperature in units of energy.

3.1. Ideal gas $(U = 0)$

The initial TCF is calculated exactly in this case and has the following form:

$$M_0(t) = \exp\{-t^2/t_r^2\} \qquad t_r^2 = 2m/k^2 T. \tag{16}$$

The calculation will be up to the level $n = 4$. The main relaxation frequencies have the simple form

$$\Omega_n^2 = n\Omega_1^2 \qquad \Omega_1^2 = k^2 T/m \qquad k \neq 0. \tag{17}$$

Using equation (16) we can obtain the next TCF $M_n(t)$, and then the first four numbers in the spectrum of the non-Markovity parameter have the following form:

$$\epsilon_0 = \pi/2 \approx 1.57 \qquad \epsilon_1 = 4/\pi \approx 1.27$$

$$\epsilon_2 = 3\pi/8 \approx 1.17 \qquad \epsilon_3 = 32/9\pi \approx 1.13.$$

This spectrum is represented in figure 1, from which it is shown that the non-Markovity parameter steadily approaches unity while n increases.

We conclude with the following result: the relaxation of density in an ideal gas occurs in a non-Markovian regime with zeroth depth of Markovization $d_M = 0$. It seems to us that this is what one would expect. Actually, in this case statistics is introduced via the assumption that the equilibrium distribution is canonical at temperature T. After fixing the initial condition of a particle, which can be thought of as a system of a Gibbs ensemble, the motion of the particle turns out to be characterized by constant velocity (with only a sign inversion due to the collisions with the walls). In this case relaxation only stems from the average over the canonical distribution of initial conditions.

3.2. Weakly non-ideal gas

We will perform the calculation up to the linear approximation on particle interaction. Then, the approximate formula

$$\exp[it(\hat{L}_0 + \hat{L}_1)] \approx \exp[it\hat{L}_0] + \int_0^t dt_1 \, \exp[i(t - t_1)\hat{L}_0]i\hat{L}_1 \exp[it_1\hat{L}_0] \tag{18}$$

can be used to take into account the dynamic effect of the weakness of the interaction, where $\hat{L}_1$ is the interaction Liouvillian.
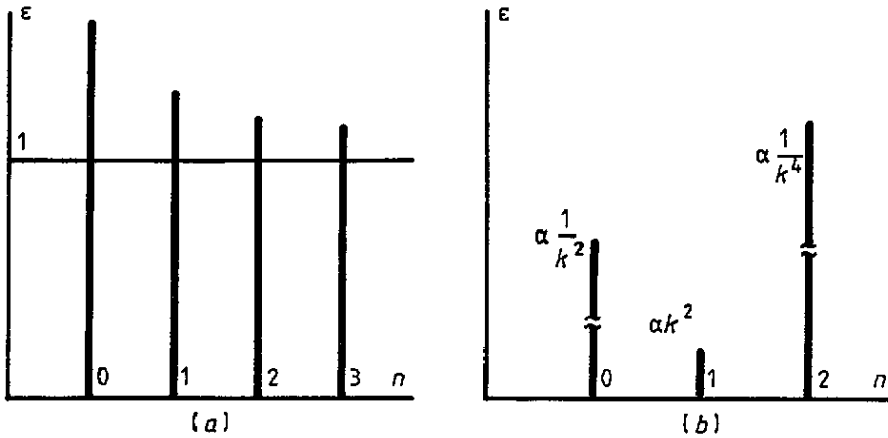
Figure 1. (a) Spectrum of the non-Markovity parameter for an ideal gas. Relaxation of density occurs in the non-Markovian regime with zeroth depth of Markovization $d_M = 0$. The non-Markovity parameter steadily approaches unity while n increases. (b) Spectrum of the non-Markovity parameter for continuous matter in hydrodynamic limits. The great oscillation of spectrum ϵ_n is the main peculiarity in this case. Neighbouring levels have a different behaviour: if the nth level is 'Markovian', then the neighbouring $(n + 1)$th level is without fail 'non-Markovian'.

The initial TCF has the following form:

$$M_0(t) = \exp\left\{-\frac{t^2}{t_r^2}\right\} + \frac{nk^2}{m} J(k)\Phi(t) \tag{19}$$

where

$$J(k) = \int dr\, g(r)U(r)\exp(ikr)$$

$$\Phi(t) = \int_0^t dt_1\, t_1 \exp\left\{-\frac{(t-t_1)^2 + t_1^2}{t_r^2}\right\}$$

and $g(r)$ is a radial distribution function of particles in a liquid.

The spectrum of the non-Markovity parameter is different from the preceding case at the first point only,

$$\epsilon_0 = \epsilon_{0(id)}\left(1 - \frac{nJ}{T}\right) \tag{20}$$

while at other points we have

$$\epsilon_{n>0} = \epsilon_{n(id)}.$$

The direction of alternation ϵ_1 depends on the sign of the value J_0, and may be given a thermodynamical mean in the limit $k \to 0$ [2],

$$J(k)_{|k\to 0} = \frac{2e - 3T}{n}. \tag{21}$$

Notice that the hierarchy of the equilibrium distribution function in liquids [2] was used to obtain expressions (19) and (20).

3.3. Hydrodynamic limits ($k \to 0$)

In this case the time fluctuation of the number particle density of a liquid obeys the well known Landau–Placzek formula:

$$M_0(t) = \frac{c_v}{c_p} \cos(\vartheta_s k t) \exp(-\Gamma_s k^2 t) + \left(1 - \frac{c_v}{c_p}\right) \exp\left\{-\frac{\kappa k^2 t}{\rho c_p}\right\}. \tag{22}$$

To gain a better understanding of the spectrum of the non-Markovity parameter we examine the calculations in detail. The time correlations τ_0 contain various degrees of the wavevector:

$$
\begin{aligned}
\tau_0 &= \frac{c_v}{c_p} \frac{\Gamma_s}{\Gamma_s^2 k^2 + \vartheta_s^2} + \left(1 - \frac{c_v}{c_p}\right) \frac{\rho c_p}{\kappa k^2} \\
&= \frac{1}{k^2} \left(1 - \frac{c_v}{c_p}\right) \frac{\rho c_p}{\kappa} + \frac{c_v}{c_p} \frac{\Gamma_s}{\vartheta_s^2} - k^2 \frac{c_v}{c_p} \frac{\Gamma_s^3}{\vartheta_s^4} + O(k^4).
\end{aligned}
\tag{23}
$$

The spectrum of the non-Markovity parameter is expressible in terms of the variables $\langle |\hat{L}^n W_0|^2 \rangle$ and the first four variables have the following form:

$$\langle |W_0|^2 \rangle = \frac{N}{V^2}(nT\chi + O(k^2))$$

$$\langle |\hat{L} W_0|^2 \rangle = \frac{N}{V^2} \frac{T}{m} k^2$$

$$\langle |\hat{L}^2 W_0|^2 \rangle = \frac{N}{V^2} \frac{T}{m} k^4 (F + O(k^2)) \tag{24}$$

$$\langle |\hat{L}^3 W_0|^2 \rangle = \frac{N}{V^2} \frac{T}{m} k^4 (A + O(k^2))$$

where we use the following notation

$$F = 3\frac{T}{m} + \frac{n}{2m} \int dr \frac{(kr)^2}{k^2} g(r) \frac{(k\nabla)^2}{k^2} U(r)$$

$$
\begin{aligned}
A = 15\frac{Tn}{m^2} &\int dr\, g(r) \frac{(k\nabla)^2}{k^2} U(r) + 6\frac{Tn}{m^2} \int dr\, g(r) \frac{(kr)}{k} \frac{(k\nabla)^3}{k^3} U(r) \\
&+ \frac{n}{m^2} \int dr\, g(r) \frac{(kr)^2}{k^2} \left(\nabla \frac{(k\nabla)}{k} U(r)\right)^2 \\
&+ \frac{n^2}{m^2} \int dr\, dr'\, g_3(r, r') \frac{(kr)(kr')}{k^2} \nabla \frac{(k\nabla U(r))}{k} \nabla' \frac{(k\nabla' U(r'))}{k}.
\end{aligned}
\tag{25}
$$

Furthermore, we may calculate the first three frequencies ω_n and Ω_n (equation (5)):

$$\omega_n^2 = \frac{\langle |\hat{L}^n W_0|^2 \rangle}{\langle |\hat{L}^{n-1} W_0|^2 \rangle} = \cdot \quad \omega_1^2 = \frac{k^2}{nm\chi}(1 + O(k^2))$$

$$\omega_2^2 = Fk^2 + O(k^4) \qquad \omega_3^2 = \frac{A}{F} + O(k^2)$$

$$\Omega_1^2 = \omega_1^2 = k^2/nm\chi \qquad \Omega_2^2 = \omega_2^2 - \omega_1^2 = k^2(F - 1/nm\chi) \tag{26}$$

$$\Omega_3^2 = \omega_2^2 \frac{\omega_3^2 - \omega_2^2}{\omega_2^2 - \omega_1^2} = \frac{A}{(F - 1/nm\chi)}.$$

Then, we obtain the first three points in the spectrum of the non-Markovity parameter:

$$
\begin{aligned}
\epsilon_0 &= \frac{1}{k^2} \frac{([1 - c_v/c_p]\rho c_p/\kappa)^2}{nm\chi} \\
\epsilon_1 &= k^2 \frac{(nm\chi)^2(F - 1/nm\chi)}{[1 - c_v/c_p](\rho c_p/\kappa)^2} \\
\epsilon_2 &= \frac{1}{k^4} \frac{A([1 - c_v/c_p]\rho c_p/\kappa)^2}{(F - 1/nm\chi)^3(nm\chi)^2}.
\end{aligned}
\tag{27}
$$

From equation (27) we extract various dependences of the spectrum level for the wavevector k:

$$
\epsilon_0 \propto k^{-2} \qquad \epsilon_1 \propto k^2 \qquad \epsilon_2 \propto k^{-4} \qquad \text{etc.}
$$

In figure 1 the first three points for the non-Markovity parameter of continuous matter in hydrodynamical limits ($k \to 0$) are represented schematically. The great oscillation of spectrum ϵ_n is the main peculiarity in this case. Neighbouring levels have a different behaviour: if the nth level is 'Markovian', then the neighbouring $(n + 1)$th level is without fail 'non-Markovian'. And vice versa, the next $(n + 2)$th level is also 'Markovian' considering irreversible processes. These oscillations deviate from the framework of our usual notions about Markovian relaxation processes in a continuous medium. Notice that the next degree over the wavevector k is outside the bound of the Landau–Placzek formula (22).

The resulting black and white picture of the spectrum of the non-Markovity parameter reflects the hierarchy of relaxation times which are peculiar to hydrodynamic systems. The relaxation of the number particle density fluctuation is accounted for firstly by sound propagation and secondly by heat transfer (first and second terms in equation (22), respectively). By this means, the time relaxation of the TCF of the number particle density fluctuation has the magnitude $\tau_0 \sim 1/k^2$ (at the expense of heat transfer). The equation for the TCF of the density fluctuation contains the TCF of the longitudinal flux of the number particle fluctuation M_1. The time relaxation τ_1 of this TCF M_1 is constant while $k \to 0$ [2]. In such a manner we have $\epsilon_0 = \tau_0/\tau_1 \sim 1/k^2$.

The TCF of the fluctuation of the longitudinal flux of the number particle obeys the equation which contains the TCF of the energy of longitudinal movements. Since $W_2 = -\ddot{\rho} - \Omega_1^2 \delta\rho$ (equation (4)) (where $\delta\rho = W_0$ is the number particle density fluctuation), the relaxation time τ_2 has a magnitude $\sim 1/k^2$. Consequently, we obtain $\epsilon_1 = \tau_1/\tau_2 \sim k^2$.

The TCF of the longitudinal movements of the energy fluctuation obeys the equation which contains the TCF of fluctuation of the flux of the energy of the longitudinal movement M_3 whose time relaxation τ_3 is proportional to k^2. Then $\epsilon_2 = \tau_2/\tau_3 \sim 1/k^4$. By this means the spectrum of the non-Markovity parameter within the hydrodynamic limits $k \to 0$ forms large oscillations owing to the great difference between relaxation times at neighbouring levels.

4. Remarks and conclusion

In the present article we found the spectrum of the non-Markovity parameter for simple model systems, namely an ideal gas, a weakly non-ideal gas and a medium in

hydrodynamical limits ($k \rightarrow 0$). In all three described cases our calculations show the stable non-Markovian effects which testify to the strong effects of molecular memory. In the first two cases (ideal and weakly non-ideal gases) the depth of Markovization $d_M = 0$, and the relaxation is already non-Markovian for the zeroth level. It also remains non-Markovian at the following levels, and what takes place is the smoothing of relaxation times while n increases. This statement confirms Bogolubov's idea about a hierarchy of relaxation times in statistical systems [16]. In hydrodynamical limits $k \rightarrow 0$ the relaxation acquires the black and white picture: in the limits ($k \rightarrow 0$) the level with Markovian relaxation successfully alternates with a level where the relaxation is non-Markovian. This alternation connects with specific manifestation statistical effects of memory for hydrodynamical systems.

Calculations were performed to obtain spectra for comparison. In real physical processes, the experimentally observed relaxation kinetics is relatively complicated. Current spectroscopic techniques (for example, femtosecond technique and slow neutron scattering) allow investigations to be made of the fast processes which take place in the microscopy region of space.

Our calculations have shown that in the absence of interaction (ideal gas) the whole spectrum is non-Markovian. The spectrum of the non-Markovity parameter undergoes essential transformations when the interaction has evolved. It acquires, as with hydrodynamics limits (section 3.3), the black and white form, or, more precisely, it takes the form of dumped oscillations. The surprising thing is that a similar picture is distinctive not only for hydrodynamics but for several relaxation processes as well which are studied by different spectroscopic methods. Here, we are referring to dielectric and NMR, NQR and EPR relaxations in liquids. For example, observations of dielectric relaxations in CH_3I [17] lead to dumping oscillations in the spectrum of the non-Markovity parameter (see figure 2 in [8]). In EPR relaxation, the observations of Vishnevskaya and collaborators [18–20] have shown [9] that over a wide range of varying viscosity (two orders) the picture of the non-Markovity parameter grossly changed. Whereas ϵ_0 ranges from infinity to zero, ϵ_1 ranges from 100 to unity.

In NQR relaxation in liquid metals, semiconductors and liquefied inert gases [10, 11] we have $\epsilon_0 \sim 10^{10}$ and $\epsilon_1 \sim 1$. This clearly demonstrates that the picture of relaxation for the two neighbouring levels is interrelated. Note the presence of non-Markovian behaviour in molecular processes at the first level ($\epsilon_1 \sim 1$) leads to an unusual square root dependence of the spin relaxation time in liquefied inert gases, liquid metals, and semiconductors (T_1, $T_2 \sim T^{1/2}$, $T^{-1/2}$), while the zeroth level is Markovian (the spin relaxation itself is a Markov process).

From the aforementioned, it is seen that the presence of spectra for comparison offers a clearer view of the correlation between the subtle details of intermolecular potential interactions and the spectrum of the non-Markovity of a system.

In particular, the production of interaction leads to a just as Markovian picture, so non-Markovian picture of relaxation at different levels of the spectrum (see figure 1). Detail in this picture essentially depends on a form of interaction—its shielding, and contributions from electrostatics, magnetic and quadruple forces, etc. Calculation and measurements of a spectrum of non-Markovity parameter for different interactions permits notable extension of our existing notions concerning the irreversible properties of media.

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