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TRANSFORMATION OF NON-MARKOVIAN KINETIC EQUATION FOR TCF TO MARKOVIAN TYPE

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It is shown that the non-Markovian kinetic equation of relaxation takes on the Markovian form if the non-Markovity parameter (*Phys. Lett.* **A148**, 199 (1990)) goes to infinity.

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1. Introduction

In the present paper we discuss transformation properties of Zwanzig–Mori type equation for Time Correlation Function (TCF) [1,2] in a new way. Specifically we are dealing with a transformation of general non-Markov kinetic equation to the Markov structure under relevant behaviour of non-Markovity parameter. This topic is very important for solving many applied problems. In particular, it may be used for theoretical analysis of many spectral functions which are experimentally observed by methods of optical, vibrational, magnetic resonance and slow neutron scattering spectroscopy. For example, the low-frequency spectra give valuable information about longtime irreversible relaxation of spin density fluctuation in the magnetic resonance theory, and about the density fluctuation in the scattering of low energy neutrons, and the fluctuation of longitudinal and transversal molecular fluxes in the transport phenomena in Markov relaxation scenario.

The low frequency behaviour of TCF in statistical physics is closely related to the Markovian properties of molecular random processes. Starting with the famous paper by Markov [3], the theory of Markov random processes forms the basis of a great number of statistical processes in physics and chemistry (see, *e.g.*, Refs [4–6]). In physics [7–9] the Markov processes are understood as processes without after effects. In the theory of random processes the conditional mathematical expectations play a key role in modern representations of the Markov property. In statistical physics [10, 11] beginning with the papers by Prigogine [7], van Hove [8], Zwanzig [1], Mori [2], and others, the random processes are said to be non-Markov if the kinetic equations for distributions, the density matrices, the advanced or retarded Green functions, and the TCF's contain collision integral and the kinetic coefficients, or the dissipative parameters which describe the entire evolution of the system. It is most convenient to study the non-Markov properties in the terms of Green functions and TCF's since they express the important physical characteristics of a system, such as the spectrum of collective excitations, the relaxation times, the attenuation constants, and *etc.*, [10, 11], and the TCF's are measured by direct methods in spectroscopy [6, 11].

After the papers by Zwanzig [1] and Mori [2], it became clear that the non-Markovian processes and the statistical effects of macroscopic systems play a leading role in macroscopic systems. It has turned out that the non-Markov processes reflect the collective properties of systems and of multiparticle interactions. However, no methods for rigorous quantitative estimation of memory effects were available for a long time. The first quantitative criterion for the numerical estimation of non-Markovian effects was introduced in terms of TCF in Refs [12, 13] only. In the later papers [14, 15] the notion of the spectrum of non-Markov parameter ε and the degree of Markovization were defined for non-equilibrium processes in a fluid. These parameters are related via TCF to the fundamental characteristics of the system such as the memory function, the memory lifetime, and the de-Markovization.

The aim of this paper is to indicate various ways for transformation of the original non-Markov kinetic equation of Zwanzig and Mori for TCF's to the Markov type in response to the non-Markovian parameter ε which was introduced in Refs [12–17]. It is emphasized that the non-Markovian parameter ε regulates the systems relaxation type. The modification of kinetic equation structure for TCF is due to behaviour of this parameter, so that the transformation of originally non-Markovian kinetic equation for TCF to the Markovian one takes place in specific domain of ε ($\varepsilon \to \infty$).

The layout of the paper is as follows. In Section 2 we give the infinite hierarchy of connected kinetic equations for TCF's. In Section 3 we present the so-called “slow-time” van Hove approximation in terms of the non-Markovity parameter ε. Section 4 contains an example of transformation of the general equations for TCF at the delta-like behaviour memory functions of the n-th and $(n+1)$-th levels. In Section 5 we introduce the exponential majorant of memory function. The Tauber theorem and Laurent expansion of the Laplace image of memory function are used in Section 6. The Section 7 gives an example of Markov and non-Markov relaxation scenario for the molecular variables in NMR. The final Section 8 contains an assessment of the method and the results as well as an outlook on further possible developments.

2. Infinite hierarchy of kinetic equations for TCF's

The application of the equations of non-Markovian type for the description of irreversible phenomena originated in the famous papers of Zwanzig [1] and Mori [2]. Following the Zwanzig-Mori assumption, we can derive the infinite chain of non-Markovian kinetic equations for the time correlation function $M_0(t)$. It has the following form when the system did not have the eigen-frequencies

$$\frac{dM_n(t)}{dt} = -\Omega_{n+1}^2 \int\limits_0^t d\tau M_{n+1}(\tau) M_n(t-\tau)\ ,\ n=0,1,2\ldots\ , \tag{1}$$

where $M_{n+1}(\tau)$ are memory functions, reflecting the non-Markovity properties of the process and statistical molecular memory effects in the system, Ω_{n+1}^2 are the general frequency relaxation parameters. The chain given by Eq. (1) was used many times for the description of the wide range of relaxation processes in many-body systems (see, for example, Refs [16–22]).

In the preceding papers [12–15] we have introduced the microscopic non-Markovity parameter ε_0 and the spectrum of this parameter $\varepsilon = \{\varepsilon_n\}$ for the quantitative evaluation of memory effects

$$\varepsilon_n = \tau_n/\tau_{n+1}\ ,\ n=0,1,2,\ldots\ . \tag{2}$$

Here the relaxation (correlation) times of initial TCF ($n=0$) and of various order memory functions ($n>1$) are introduced by relations below

$$\begin{aligned} \tau_n &= \Re \int\limits_0^\infty dt M_n(t) = \Re \widetilde{M_n}(0)\ , \\ \widetilde{M_n}(s) &= \int\limits_0^\infty dt \mathrm{e}^{-st} M_n(t)\,, \end{aligned} \tag{3}$$

where the symbol $\Re$ means the real part. Let us note that the relaxation (correlation) times τ_n may be introduced using another, more delicate way which was considered in Refs [12,13]. In the case of $\varepsilon_n \sim 1$ the process is definitely non-Markovian on this level. However, if $\varepsilon_n > 1$, and $\varepsilon \gg 1$ the process can be regarded as quasi-Markovian. It will be a Markovian process in the limit as $\varepsilon_n \to \infty$.

In the last case ($\varepsilon_n \to \infty$) the statistical memory effects will disappear and the non-Markovian equation of motion (1) will transform into the ordinary Markovian differential equation. The establishment of this fact is the principal purpose of this article.

3. The modified "slow-time" van Hove approxomation

The transition in equations of type given by Eq. (1) to the Markovian limit was performed first by Zwanzig [1] and van Hove [8]. If the closed system consists of two subsystems which are weakly interacting with each other, then the non-Markovian kinetic equation (1) at the number n takes the form

$$\frac{dM_n(t)}{dt} = -\lambda_{n+1}^2 \sigma_{n+1}^2 \int_0^t d\tau M_{n+1}(\tau) M_n(t-\tau) \,. \tag{4}$$

Here λ_{n+1} is the constant of the interaction strength, σ_{n+1} is the relaxation frequency. Following van-Hove (Ref. [8]), let us introduce the so-called "slow-time" approximation: $T = \lambda_{n+1}^2 t$, with $t \to \infty, \lambda_{n+1} \to 0$ and $T =$const. If in this scale we define the equality $M_n(t) = \mu_n(T)$, then, instead of Eq. (4), we have

$$\frac{d\mu_n(T)}{dT} = -\sigma_{n+1}^2 \int_0^{T/\lambda_{n+1}^2} d\tau M_{n+1}(\tau) \mu_n(T - \lambda_{n+1}^2 \tau) \,. \tag{5}$$

Taking in Eq. (5) the limit $t \to \infty, \lambda_{n+1} \to 0$ while T is constant, we can obtain the Markovian equation

$$\frac{d\mu_n(T)}{dT} = -\tau_{n+1} \sigma_{n+1}^2 \mu_n(T) \,. \tag{6}$$

Coming back to the usual time t, when $t \to \infty$, we obtain

$$\begin{aligned} \frac{dM_n(t)}{dt} &= -\gamma_n M_n(t), \\ \gamma_n &= \sigma_{n+1}^2 \lambda_{n+1}^2 \tau_{n+1} = \Omega_{n+1}^2 \tau_{n+1} \ , \ \tau_{n+1} = \Re \widetilde{M}_{n+1}(0) \,. \end{aligned} \tag{7}$$

It is seen from Eqs (3), (7), that the relaxation time of the function $M_n(t)$ is

$$\tau_n = \Omega_{n+1}^{-2} \tau_{n+1}^{-1} \ , \tag{8}$$

then we have

$$\varepsilon_n = 1/\tau_{n+1}^2 \Omega_{n+1}^2 \sim 1/\lambda_{n+1}^2 \tag{9}$$

for the non-Markovity parameter given by Eq. (2) of nth order. From Eq. (9) follows, that the van-Hove approximation of weak interaction ($\lambda_{n+1} \to 0$) means the transition to the Markovian relaxation regime on the nth level, when the corresponding non-Markovian parameter $\varepsilon_n \to \infty$. Here, the relaxation on the nth order level is caused by the memory effects on the next $(n+1)$th level.

4. δ-like behaviour of the memory function

Here, we give an example how the general non-Markovian equation (1) is transformed into the Markovian one under strong assumptions about properties of the memory function. Alongside with first derivative in Eq. (1), we write out the second derivative of both parts of Eq. (1)

$$\frac{d^2 M_n(t)}{dt^2} = -\Omega_{n+1}^2 M_n(t) + \Omega_{n+1}^2 \Omega_{n+2}^2 \int_0^t d\tau \int_0^\tau d\tau' M_{n+2}(t-\tau) M_{n+1}(\tau-\tau') M_n(\tau'). \tag{10}$$

In this equation there are three memory functions with indexes $n, n+1$ and $n+2$. For two higher order memory functions we assume the following approximation (see Refs [23, 24])

$$M_k(\tau) = M_k^{(\mathrm{sm})}(\tau) + M_k^{(\mathrm{lm})}(\tau) \ , \tag{11}$$

where the first part $M_k^{(\mathrm{sm})}(\tau)$ accounts for the short-time and the second one $M_k^{(\mathrm{lm})}(\tau)$ reflects the long-time behaviour of memory.

According to Refs [23,24] it is satisfactory here to represent such a memory by the expression

$$M_k(\tau) = \triangle_k^{\mathrm{sm}} \delta(\tau) + \xi_k \exp(-\tau/\tau_k^{\mathrm{lm}}) \ , \tag{12}$$

where $\triangle_k^{\mathrm{sm}}$ are the short-memory relaxation times, τ_k^{lm} are the long-memory times and ξ is the dimensionless partition parameter. The equation (12) should be real as denoting the relaxation time of memory functions

$$\tau_{n+1} = \lim_{t\to\infty} \int_0^t d\tau M_{n+1}(\tau) = \triangle_{n+1}^{\mathrm{sm}} + \xi_{n+1} \tau_{n+1}^{\mathrm{lm}} \ , \tag{13}$$

$$\tau_{n+2} = \lim_{t\to\infty} \int_0^t d\tau M_{n+2}(\tau) = \triangle_{n+2}^{\mathrm{sm}} + \xi_{n+2} \tau_{n+2}^{\mathrm{lm}} \ . \tag{14}$$

For the Markov limit we have

$$\xi_{n+1} \to 0 \ , \ \xi_{n+2} \to 0 \ , \ \tau_{n+1} \to \triangle^{\rm sm}_{n+1} \ , \ \tau_{n+2} \to \triangle^{\rm sm}_{n+2} \ . \tag{15}$$

The last expression means that in the limit $t \to \infty$, namely when $t \gg \tau_{n+1}$ and $t \gg \tau_{n+2}$, both higher memory functions have delta-like singularity. Then the memory function M_n obeys the Markovian equation

$$\frac{\partial^2 M_n(t)}{\partial t^2} = -\Omega^2_{n+1} M_n(t) + \Omega^2_{n+1}\Omega^2_{n+2}\tau_{n+1}\tau_{n+2} M_n(t) \ . \tag{16}$$

From the foregoing formulae it is seen that the gain in differential equation order takes into account memory functions of higher orders. As it can be seen from comparison of Eq. (16) with Eqs (6)–(9), the "slow-time" van Hove approximation is equivalent to the assumption of delta-like behaviour of higher memory functions in long-time region. It corresponds physically to short-range memory. The analysis of physical examples shows us that it is effective only for lowest indexes n; as the number n of kinetic equation in infinity hierarchy (1) increases then the condition (16) becomes incorrect (see, for examples Refs [13,14]). Consideration of higher relaxation levels in Eq. (16) leads to "renormalization" of relaxation time of nth level. Then we arrive at

$$\tau_n^{-2} = \{\Omega^2_{n+1}\Omega^2_{n+2}\tau_{n+1}\tau_{n+2} - \Omega^2_{n+1}\} \ , \tag{17}$$

instead of Eq. (8), and

$$\varepsilon_n = \{\tau_{n+1}\sqrt{\Omega^2_{n+1}(\Omega^2_{n+2}\tau_{n+1}\tau_{n+2} - 1)}\}^{-1} \ , \tag{18}$$

instead of Eq. (9) for the non-Markovity parameter.

If we take into account two exact relations

$$\varepsilon_n\varepsilon_{n+1} = \frac{\Omega^2_{n+2}}{\Omega^2_{n+1}} \ , \ \tau_n\tau_{n+1} = \Omega^{-2}_{n+1} \ , \tag{19}$$

which arise from definitions (1)–(3), then we obtain the Markovian limit for the non-Markovity parameter ε_n of nth level

$$\lim_{\tau_{n+2}\to\tau^{-1}_{n+1}\Omega^{-2}_{n+2}+0} \varepsilon_n \to \infty \ , \quad \lim_{\tau_{n+2}\to\tau^{-1}_{n+1}\Omega^{-2}_{n+2}+0} \tau_n \to \infty \ . \tag{20}$$

Above limits are due to the assumptions (10)–(14). On the other hand, the "slow-time" van Hove approximation maintains the Markovian limit ($\varepsilon_n \to \infty, \tau_n \to \infty$) in the limit of weak interaction ($\lambda_{n+1} \to 0$) only, as it is seen from Eqs (8), (9). This means that the assumption of delta-like behaviour of single memory function of n-th level is lacking in order to obtain the Markovian relaxation. It is sufficient that two neighbouring memory functions M_{n+1} and M_{n+2} have delta-like behaviour. The simple analysis above also indicates that the single exponential regime of relaxation does not provide the Markovian relaxation.

5. Exponential majorant of the memory function

Let us show now that the Eq. (1) takes on the Markovian form also for another strong assumption about the properties of the functions $M_n(t)$ and $M_{n+1}(t)$. Using the property of the time shift operator in Eq. (1), we get

$$\int_0^t d\tau M_{n+1}(\tau)M_n(t-\tau) = \widehat{R}(t)M_n(t) \ , \tag{21}$$

where we introduced the operator $\widehat{R}(t) = \int_0^t d\tau M_{n+1}(\tau)\exp(-\tau d/dt)$. In what follows we shall take into consideration that the memory functions M_i are the normalized TCF's, that is the relations

$$\lim_{\tau\to 0} M_i(\tau)=1, \ \lim_{\tau\to\infty} M_i(\tau)=0, -1 \le M_i(\tau) \le 1, |M_i(\tau)| \le 1 \text{for } \tau \in (0,\infty), \tag{22}$$

are fulfilled for $i = 0,1,2,\dots n, n+1, n+2,\dots$ Let us consider the two temporal scales

$$\tau_n = \Re\int_0^\infty dt M_n(t) \ , \ T_n = \int_0^\infty dt|M_n(t)| \ .$$

The estimation $\tau_n \le T_n$ is valid due to Eq. (22), where $\tau_n = (\Omega_{n+1}^2\tau_{n+1})^{-1}$. Because our analysis presupposes the Markovian regime we can use estimation $|M_n(t)| \le \exp(-t/\tau_n)$ for $t \gg \tau_n$. It allows us to use the exponents as majorant functions for longtime limit $t \to \infty$, when $t \gg \tau_n, T_n$. Taking into consideration the exponential relaxation regime in the limit $t \to \infty$, we can obtain the following inequality

$$\left|\Re\frac{d^m}{dt^m}M_n(t)\right| \le (\tau_n)^{-m}M_n(t) \ . \tag{23}$$

From Eqs (10) and (11) follows that

$$\left|\int_0^t d\tau M_{n+1}(\tau)M_n(t-\tau)\right| \le \int_0^t d\tau M_{n+1}(\tau)\sum_{m=0}^{\infty}(\tau_{n+1}/\tau_n)^m M_n(t) \ , \tag{24}$$

where we used the assumption (23) for the $(n+1)$-th order memory function given below

$$\left|\int_0^t d\tau\tau^m M_{n+1}(\tau)\right| \le m!\tau_{n+1}^m\int_0^\infty d\tau M_{n+1}(\tau) \ . \tag{25}$$

Going then to the limit $t \to \infty$ in the Eq. (24), we arrive at the following inequality

$$\Big| \int_0^t d\tau M_{n+1}(\tau) M_n(t-\tau) \Big| \leq \int_0^\infty d\tau M_{n+1}(\tau)(1-\varepsilon_n^{-1})^{-1} M_n(t) \ . \qquad (26)$$

The inequalities (23)–(26) are valid only for longtime regime $t \to \infty$ and $t \gg \tau_n, T_n$. The non Markovity parameter $\varepsilon_n = \tau_n/\tau_{n+1}$ has been introduced in above estimations. We obtain the Markovian kinetic equation for $M_n(t)$ in the form given by Eq. (7) in the case when $\varepsilon_n \to \infty$.

Therefore, the estimations obtained above show that the Markovian relaxation regime in kinetic equation for TCF $M_n(t)$ depends on the variable ε_n. It becomes Markovian in the limit $\varepsilon_n \to \infty$ only.

6. Laurent expansion of the Laplace image

Let us consider now the transformation of the type of non-linear kinetic equation (1) using the Laurent expansion of the Laplace image $\widetilde{M}_n(s)$ in case of $\varepsilon_n \to \infty$.

If a function $M_n(t)$ in the limit $t \to \infty$ is described by an exponential function, the Laplace image $\widetilde{M}_n(s)$ may possess poles-like singularities. Let us use now the Tauber theorem about the restitution of the arbitrary function $f(t)$ when $t \to \infty$ by the properties of its Laplace image [25]. Let us assume, that the function $\widetilde{M}_n(s)$ possesses a finite number of singular points (s_ν) and it has the following form of the Laurent expansion in the neighbourhood of these points

$$\widetilde{M}_n(s) = \sum_{k=0}^{\infty} \mu_k^{(\nu)} (s - s_\nu)^{n_k^{(\nu)}}, \qquad (27)$$

where $n_k^{(\nu)}$ are the integer numbers which satisfy the conditions $-\infty < n_0^{(\nu)}, n_1^{(\nu)}, \ldots < +\infty$. Then, the function $M_n(t)$ in the limit $t \to \infty$ has the form

$$M_n(t) = \sum_{\nu} \exp(s_\nu t) \sum_{k=0}^{\infty} \mu_k^{(\nu)} \{\Gamma(-n_k^{(\nu)})\}^{-1} t^{-(1+n_k^{(\nu)})}, \qquad (28)$$

where we sum over all singular points. Using Eq. (27), we obtain the expansion of the Laplace image in the neighbourhood of the first order pole

$$\widetilde{M}_{n+1}(s) = \widetilde{M}_{n+1}(s_\nu) + (s-s_\nu) M'_{n+1}(s_\nu) + \frac{1}{2!}(s-s_\nu)^2 M''_{n+1}(s_\nu) + \ldots, \quad (29)$$

where the prime denotes the derivative with respect to the variable s_ν. Taking into account the division rule for the power series [25], we obtain from Eqs (1), (29)

$$\begin{aligned}\widetilde{M}'_n(s) &= \frac{1}{s-s_\nu}\left\{1+\Omega^2_{n+1}\widetilde{M}'_{n+1}(s_\nu)\right\}^{-1} - \frac{1}{2}\Omega^2_{n+1}\widetilde{M}''_{n+1}(s_\nu)\\ &\quad+\frac{s-s_\nu}{1-\Omega^2_{n+1}\widetilde{M}'_{n+1}(s_\nu)}\left\{\frac{1}{4}\frac{[\Omega^2_{n+1}\widetilde{M}''_{n+1}(s_\nu)]^2}{1+\Omega^2_{n+1}\widetilde{M}'_{n+1}(s_\nu)}\right.\\ &\quad\left.-\frac{1}{6}\Omega^2_{n+1}\widetilde{M}'''_{n+1}(s_\nu)\right\}+\dots\ .\end{aligned} \tag{30}$$

Then, using the Tauber theorem given by Eq. (28), we have the following equation instead of Eq. (1)

$$\begin{aligned}\frac{dM_n(t)}{dt} &= -\Omega^2_{n+1}\int_0^t d\tau M_{n+1}(\tau)\sum_{l=0}^{\infty}\frac{(-1)^l\tau^l}{l!}\sum_\nu\sum_{k=0}^{\infty}\mu_k^{(\nu)}\left\{\Gamma\left(-n_k^{(\nu)}\right)\right\}^{-1}\\ &\quad\times\sum_{r=0}^{l}\frac{l!}{r!(l-r)!}(-1)^{l+r}\left\{1+n_k^{(\nu)}\right\}\left\{2+n_k^{(\nu)}\right\}\dots\left\{l+1-r+n_k^{(\nu)}\right\}\\ &\quad\times s_\nu^r \mathrm{e}^{s_\nu t}t^{-\left(1+n_k^{(\nu)}\right)+l-r}\ .\end{aligned} \tag{31}$$

As it is evident from estimation (25) for the integral $\int_0^\infty d\tau M_{n+1}(\tau)\tau^l$, the series over indices r and l contain, in fact, the power expansion over the small parameter $\varepsilon_n^{-1} = \tau_{n+1}/\tau_n \to 0$ when $\varepsilon_n \to \infty$. Then, the first term only survives in Eq. (30) and the non-Markovian equation (1) is transformed into the Markovian one given by Eq. (7).

7. Spin relaxation in NMR as an example of the Markov and the non-Markov relaxation scenario

The results obtained in Sections 3–5 have shown that the integro-differential equation of non-Markovian type given Eq. (1) are transformed, in fact, to the differential Markovian equation (7) in the case, when the statistical memory in system is very short and the non-Markovity parameter tends to infinity $\varepsilon_n \to \infty$.

In the conclusion it is necessary to stress that all results obtained are also correct in the case, when the system possesses eigen frequencies.

As it has already been indicated that the chain of kinetic equations (1) is infinite, so the whole spectrum of non-Markovity parameter ε_n is required for more sophisticated investigation of relaxation processes under discussion. The point is that, in spite of the first level of relaxation is Markovian one ($\varepsilon_0 \to \infty$), the ability of non-Markovian behaviour in the deeper levels $\varepsilon_n \sim 1$ for $n > 0$ could result in essential changes in experimentally observed spectra. The existence of non-Markovian behaviour, as an example, in the first level ($\varepsilon_1 \sim 1$) brings into existence the unusual temperature dependence of the magnetic spin relaxation times T_1 and T_2 such as the square root type ($T_1, T_2 \sim \sqrt{T}, 1/\sqrt{T}$) in the liquified noble gases and the liquid metals and semiconductors [26, 27], whereas the spin relaxation itself is the Markovian process ($\varepsilon_0 \to \infty$). The temperature dependence of the relaxation times T_1 and T_2 is rendered to the usual activation type dependence at the transition in the Markovian relaxation scenario in the first level $\varepsilon_1 \to \infty$. A set of similar particularities as well as other interesting and important singularities make themselves evident in the treatment of the spectrum of non-Markovity parameter in the structure [12–15], the dielectric [13,15,18] and the vibration [13, 15] relaxation, in the kinetics of microscopic vortices in classical liquids [19, 22], the hydrodynamics and the ideal systems [21], *etc.*

There is one example of physical phenomenon which accompanies the transformation of non-Markovian equation for TCF to the Markovian type. Let us consider the spin relaxation of nuclear spins in the liquid. According to the Abragam [28], Kubo and Tomita [29], we have the following formulae for longitudinal T_1 and transverse T_2 relaxation times in the semiclassical limit

$$\begin{aligned}
T_1^{-1} &= \sum \sigma_{0\beta}^2 \tau_{0\beta}\,, \\
T_2^{-1} &= \sum \sigma_{1\beta}^2 \tau_{1\beta}\,, \\
\sigma_{\alpha\beta}^2 &= \frac{\langle |[\hat{S}_\alpha, \hat{\mathcal{H}}_\beta]|^2 \rangle}{\hbar^2 \langle |\hat{S}_\alpha|^2 \rangle}\,, \\
\tau_{\alpha\beta} &= \Re \int_0^\infty dt e^{i\omega_\beta t} f_{\alpha\beta}(t)\,, \\
f_{\alpha\beta}(t) &= \frac{\langle R_{\alpha\beta}^*(0) R_{\alpha\beta}(t) \rangle}{\langle |R_{\alpha\beta}(0)|^2 \rangle}\,.
\end{aligned} \tag{32}$$

Here, $\hat{S}_\alpha$ is α-component of system's total spin, $\sigma_{\alpha\beta}^2$ is the static moment of spin-lattice interaction, ω_β is eigen frequency of β-component of $\hat{\mathcal{H}}_\beta$ of Hamiltonian $\hat{\mathcal{H}} = \sum_\beta \hat{\mathcal{H}}_\beta$ which describes the spin relaxation, and $f_{\alpha\beta}(t)$ is the time correlation function of lattice (molecular) variables of the total system, namely spins + medium moleculae. For simplicity restrict ourselves to the case of intermolecular interactions $\hat{\mathcal{H}}$. Then, the lattice part of operators $\hat{\mathcal{H}}_\beta$ contains spatial molecular coordinates. According to Eq. (1), we obtain the following equation for lattice (molecular) variables

$$\frac{\partial f(t)}{\partial t} = -\Omega^2 \int_0^t d\tau M_1(t-\tau) f(\tau) \ . \tag{33}$$

The first memory function has a simple form given below

$$M_1(t) = \frac{\langle (\vec{p}_{12}(0)\vec{p}_{12}(t))(\nabla_1 \mathcal{F}(1,2;0)\nabla_1 \mathcal{F}(1,2;t))\rangle}{\langle |\vec{p}_{12}(0)|^2\rangle\langle |\nabla_1 \mathcal{F}(1,2;0)|^2\rangle} \ , \ \vec{p}_{12} = \vec{p}_1 - \vec{p}_2 \ , \tag{34}$$

where $\vec{p}_i$ is the momentum and $\mathcal{F}(1,2)$ is the lattice part of spin-lattice interaction which is responsible for spin relaxation. In the denominator we have taken into account that statistical average values over coordinates and momenta are separated and they are easily calculated by parts. There is no such separation in the nominator of the above fraction because temporal evolution of coordinates and momenta takes place, in general, in the same temporal scale. According to the Bogolubov's idea about hierarchy of relaxation times we have to consider three different cases, namely

(a) fast momenta relaxation as compared with coordinates "relaxation" (lattice functions $\mathcal{F}$ or $\nabla_1\mathcal{F}$)

$$\tau_p \ll \tau_{\mathcal{F}}; \tag{35}$$

(b) coordinated (combined) relaxation of momenta and lattice functions; they relax in the same temporal scale

$$\tau_p \sim \tau_{\mathcal{F}}; \tag{36}$$

(c) slow relaxation of momenta

$$\tau_p \gg \tau_{\mathcal{F}}. \tag{37}$$

Then, the kinetic equations (33), (34) are transformed to the following equations according to three cases above

$$\text{(a)} \qquad \frac{\partial f(t)}{\partial t} = -\Omega^2 \int_0^t d\tau \pi(\tau) f(t-\tau) \ , \tag{38}$$

$$\text{(b)} \qquad \frac{\partial f(t)}{\partial t} = -\Omega^2 \int_0^t d\tau M_1(t-\tau) f(\tau) \ , \tag{39}$$

$$\text{(c)} \qquad \frac{\partial f(t)}{\partial t} = -\Omega^2 \int_0^t d\tau \mathcal{F}(t-\tau) f(\tau) \ , \tag{40}$$

where we have introduced the normalized TCF's

$$\pi(t) = \frac{\langle \vec{p}(0)\vec{p}(t)\rangle}{\langle |\vec{p}(0)|^2\rangle} \ , \ \mathcal{F}(t) = \frac{\langle \nabla\mathcal{F}(0)\nabla\mathcal{F}(t)\rangle}{\langle |\nabla\mathcal{F}(0)|^2\rangle} \ .$$

Equation (38) has Markovian type in the longtime range due to the condition (35), because the function $\pi(t)$ possesses delta-like singularity as in Eq. (10). Then, the lattice (molecular) function $f(t)$ has a simple exponential form

$$f(t) \sim \exp(-t/\tau_{\mathrm{c}}) \, , \ \tau_{\mathrm{c}} \sim \int_0^\infty \pi(t) dt \sim D_{\mathrm{s}} \, , \tag{41}$$

where D_{s} is the molecular self-diffusion coefficient. For many liquids the parameter D_{s} obeys the Arrhenius law [28]

$$D_{\mathrm{s}}(T) = D_0 \exp(\Delta E/kT) \ , \tag{42}$$

where ΔE is the molecular activation energy. Therefore, the correlation time τ_{c} and the rate of spin relaxation have also the dependence of usual activation type, as it is seen from Eqs (41), (42).

In the cases (b) and (c) the situations are changed dramatically. The numerical estimations show that the case (c) has never been experimentally observed in real liquids. In the case (b), in fact, one assumes the equality of all correlation times that is $\tau_p \sim \tau_{\mathcal{F}} \sim \tau_f$. Then, it is suitable to describe the correlation by non-Markovian non-linear equation

$$\text{(b)} \ \frac{\partial f(t)}{\partial t} = -\Omega^2 \int_0^t d\tau f(t-\tau) f(\tau) \ . \tag{43}$$

Applying the Laplace transformation

$$\tilde{f}(p) = \int_0^\infty dt \mathrm{e}^{-pt} f(t) \ ,$$

to the above equation [30], we obtain the solution

$$\tilde{f}(p) = \frac{1}{2\Omega^2}\left\{-p \pm \sqrt{p^2+4\Omega^2}\right\} \ , \ f(t) = \frac{1}{\Omega t}J_1(2\Omega t), \text{with}\, f(0) = 1 \ , \quad (44)$$

where J_1 is the Bessel function of the first kind.

The solution given by Eq. (44) leads to unusual behaviour of correlation time

$$\tau_\mathrm{c} = \lim_{p\to 0} \tilde{f}(p) = \Omega^{-1} \ . \quad (45)$$

This relation gives the weak temperature dependence of the square root kind $\tau_\mathrm{c} \sim T^{-1/2}$, $\tau_\mathrm{c} \sim T^{1/2}$ for well-known mechanisms of relaxation, namely quadrupole interaction of nuclear spins in liquid metals, semiconductors and liquefied inert gases, and the quasimolecular spin-rotational interaction in the liquid xenon-129. Such dependences have been experimentally observed, in fact, in a number of liquids (see Ref. [27]).

The transformation of NMR parameters T_1 and T_2 from activation temperature dependence to square root one is very interesting because it means the transformation of Markovian ($\varepsilon \gg 1$) scenario of relaxation to the non-Markovian ($\varepsilon \sim 1$) relaxation of lattice variables. That is why the non-Markovian phenomena, in principle, are easily experimentally observed in the temperature dependence of NMR parameters.

In this way, the analysis of the spectrum of non-Markovity parameter for a variety of systems and processes allows us to extend significantly the existing presentations of the non-equilibrium phenomena in physics of condensed matter.

8. Concluding remarks and conclusion

In the framework of the theory of statistical spectrum of non-Markovity parameter $\{\varepsilon_n\}$, suggested by authors in Refs [12–15] we have shown that the transformation of general non-Markovian equation for TCF in a level n to the Markovian type is derived in the limit $\varepsilon_n \to \infty$ for point n of the spectrum. We found the connection of parameter ε_n with the so-called "slow-time" van Hove approximation. However, the last approximation is inconvenient for joint analysis the Markovian effects in all kinetic equations of infinite hierarchy for TCF.

The spectrum of non-Markovian parameter ε_n gives a background for analysis of statistical memory phenomena. In particular, our analysis has shown that both approaches namely, the van Hove approximation and the spectrum $\{\varepsilon_n\}$ in the Markovian limit lead to simple, exponential form of TCF. However, the exponential form itself does not provide yet the Markovian regime of relaxation. The simulation of two higher memory's functions by using delta-like functions show that the transformation in the Markov regime leads to $\varepsilon_n \to \infty$.

The notion of the spectrum of non-Markovity parameter $\{\varepsilon_n\}$ reveals itself in the statistical memory. On the example of NMR spin relaxation in liquids, we have shown that transition to the non-Markovian scenario of relaxation of molecular variables from the Markovian one gives significant physical consequences. The dependence of NMR relaxation rate on the temperature is changed from conventional activation type to square root form. The last dependence has been experimentally established in the series of physical systems such as liquid metals and semiconductors, liquefied inert gases, *etc.*

Furthermore, the spectrum $\{\varepsilon_n\}$ allows to avoid the obstacles which are connected with traditional perturbation procedure over power of interaction. The strength of interaction, in principle, does not play a noticeable role. The non-Markovity parameter permits to investigate wide scope of problems which are coupled with temporal kinetics of macroscopic systems.

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REFERENCES

[1] R. Zwanzig, *Phys. Rev.* **124**, 1338 (1961).

[2] H. Mori, *Prog. Theor. Phys.* **33**, 423 (1965); **34**, 399 (1965).

[3] A.A. Markov, *Proc. Phys. Math. Soc. Kazan Univ.* **15**, 135 (1906).

[4] P. Résibois, M. De Leener, *Classical Kinetic Theory of Fluids*, Wiley, New York 1977.

[5] L.D. Landau, G. Plaszek, *Phys. Zs. Sowjetun.* **5**, 172 (1934).

[6] W. Coffey , M. Evans, P. Grigolini, *Molecular Diffusion and Spectra*, A. Wiley Int. Publ., John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore, 1984.

[7] I. Prigogine, *Non-Equilibrium Statistical Mechanics*, Interscience, New York/London 1964.

[8] L. van Hove, *Physica*, **21**, 901 (1955); **22**, 343 (1956); **23**, 441 (1957).

[9] S.A. Rice, P. Gray, *The Statistical Mechanics of Simple Liquids*, N.Y. Intersc. Publ., 1965.

[10] N.N. Bogolyubov, N.N. Bogolyubov Jr., *Introduction to Quantum Statistical Mechanics*, Nauka, Moscow 1984.

[11] Statistical Mechanics : New Concepts, New Problems, New Application. Proc. VIth IUPAP Conf. Stat. Mechanics, Ed. Rice S.A., Freed H.F., Light J.C., Chicago : Univ. of Chicago Press, 1972.

[12] V.Yu. Shurygin, R.M. Yulmetyev, V.V. Vorobjev, *Phys. Lett.* **A148**, 199 (1990).

[13] V.Yu. Shurygin, R.M. Yulmetyev, *Zh. Eksp. Teor. Fiz.* **99**, 144 (1991).

[14] V.Yu. Shurygin, R.M. Yulmetyev, *Zh. Eksp. Teor. Fiz.* **102**, 852 (1992).

[15] V.Yu. Shurygin, R.M. Yulmetyev, *Phys. Lett.* **A174**, 433 (1993).

[16] M.W. Evans, P. Grigolini, G.P. Parravicini (Editors), *Memory Function Approaches to Stochastic Problems in Condensed Matter*, *Adv. Chem. Phys.* **LXII**, 542 (1985).

[17] V.Yu. Shurygin, R.M. Yulmetyev, *Phys. Lett.* **A135**, 311 (1989); 141 (1989).

[18] V.I. Arkhipov, *Pis'ma v ZETF* **53**, 608 (1991) [*Sov. Phys. JETP Lett.* **53**, 631 (1991)].

[19] R.M. Yulmetyev, R.I. Galeev, V.Yu. Shurygin, *Phys. Lett.* **A202**, 258 (1995).

[20] R.I. Galeev, V.Yu. Shurygin, R.M. Yulmetyev, *Ukr. Fiz. Zh.* **36**, 396 (1991).

[21] R.M. Yulmetyev, N.R. Khusnutdinov, *J. Phys.* **A27**, 5363 (1994).

[22] R.M. Yulmetyev, R.I. Galeev, T.R. Yulmetyev, *Physica*, **A212**, 26 (1994).

[23] A. Fulinski, *Acta Phys. Pol.* **B26**, 1131 (1995); **B27**, 767 (1996).

[24] A. Fulinski, *Phys. Rev.* **E50**, 2668 (1994); **E52**, 4523 (1995).

[25] V.A. Ditkin, A.P. Prudnikov, *Operation Calculations*, Higher School, Moscow 1975; A.I. Markushevich, *Teoriya Analiticheskikh Funkzii*, Moscow–Leningrad 1950) (in Russian).

[26] R.M. Yulmetyev, *Teor. Mat. Fiz.*, **30**, 265 (1977) (in Russian).

[27] R.M. Yulmetyev, *Acta Phys. Pol.* **A65**, 25, 33 (1984).

[28] A. Abragam, *The Principles of Nuclear Magnetism*, University Press, Oxford/London 1961.

[29] R. Kubo, K. Tomita, *J. Phys. Soc. Japan*, **9**, 888 (1954).

[30] I.S. Gradstein, I.M. Ryzik, *The Tables of the Integrals, Summs, Series and Multiplications*, GIFML Publ., Moscow 1962 (in Russian).