

# Spectrum of parameters characterizing the non-Markov behavior of relaxation processes in liquids

V. Yu Shurygin and R. M. Yul'met'ev

*Kazan Pedagogical Institute*

(Submitted 23 November 1991)

Zh. Eksp. Teor. Fiz. **102**, 852–862 (September 1992)

A parameter  $\varepsilon$  indicative of the non-Markov properties of random molecular processes was recently introduced by us [Sov. Phys. JETP **72**, 80 (1991); Phys. Lett. A **143**, 199 (1990)]. We report here further development of the notions of non-Markov properties of relaxation processes in liquids. In particular, we introduce the concepts of the spectrum of this parameter and of the extent to which the relaxation is a Markov process. Actual computations and numerical estimates are made for the vibrational, dielectric, and structural relaxations molecular liquids and in simple classical ones. They show that non-Markov time-dependent effects play a basic role in the kinetics of relaxation processes in liquids.

## 1. INTRODUCTION

The title of this article may mislead the reader. 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. 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, of a system of eigenfunctions, of spectral invariants, of spectral properties of a corresponding group of unitary shift operators, etc. We analyze in the present paper the spectral features of processes such as vibrational and dielectric relaxations and of random density fluctuations that lead to structural relaxation.

Spectral analysis of stationary random processes consists usually of two characteristic tasks.<sup>1-3</sup> The first is the spectral resolution of stationary random processes. In this case a random function (process) is expanded in a series or an integral over a special system of functions, where the coefficients of this expansion take the form of mutually uncorrelated random quantities. In a number of cases this expansion is with respect to some standard and quite simple complete set of functions. The second task is the development of an aggregate of statistical devices that permit the spectral density of a stationary random process to be estimated from data observed in a single realization of this process.

The fundamental role of non-Markovian temporal correlation effects in relaxation processes in liquids has recently been reliably confirmed.<sup>4-9</sup> It is known that processes designated as Markovian are those in which there is no connection between the past and the future, i.e., there is no memory. The science of Markov processes was initiated by Markov's famous paper<sup>10</sup> published in Kazan' in 1906. The properties of Markov processes have been studied in sufficient detail both in mathematics and in physics. The tremendous role of Markov processes, in particular, is attested to by the fact that all the basic equations of the theory of irreversible processes (transport and kinetic phenomena, spin and galvanomagnetic effects, and others) are Markov equations and take no

account whatsoever of the statistical effects of molecular memory.

This status of the theory as reflected the feasibility of experiments in which most observations pertained to relatively slow processes in the long-wave region of space-time processes. The situation was noticeably changed after accumulation of data for the short-wave region of the spectrum and observation of fast processes. The available data on slow-neutron processes, and on dielectric, vibrational, spin and other types of relaxation, attest to the existence of non-Markov effects in relaxation processes in liquids. The situation is such that it is possible to extract from experiments detailed data on the kinetics of non-Markov processes. In contemporary theory of random processes, however, the study of the class of non-Markov processes has been patently insufficient. This raises fundamental difficulties in the physical interpretation of experimental data. It suffices to point, for example, to a specific fact that follows from Refs. 8 and 11, that a process cannot be firmly identified as Markov or non-Markov is not firmly established and its very classification can be gradually varied. The situation is aggravated also by the lack of established concepts and representations of non-Markov random processes. The first attempt to introduce a parameter and criterion for non-Markov behavior is contained in our earlier papers.<sup>8,11</sup>

We introduce here the concept of the "non-Markov" parameter spectrum. The concept is analyzed using as examples structural, dielectric, and vibrational relaxations in various liquids.

## 2. GENERAL THEORY

An extensive class of relaxation processes is presently studied by the method of projection operators, introduced in the Sixties by Zwanzig<sup>4,12</sup> and Mori.<sup>5,13</sup> This method is used to find for a normalized temporal correlation function (TCF)

$$a(t) = \langle \delta A^*(0) \delta A(t) \rangle / \langle |\delta A(0)|^2 \rangle \quad (1)$$

of the fluctuations of a physical quantity  $A(t)$

$$\delta A(t) = A(t) - \langle A(t) \rangle \quad (2)$$

an infinite chain of coupled non-Markov kinetic equations

$$\begin{aligned} \frac{da(t)}{dt} &= -\Omega_1^2 \int_0^t d\tau M_1(t-\tau) a(\tau), \\ \frac{dM_1(t)}{dt} &= -\Omega_2^2 \int_0^t d\tau M_2(t-\tau) M_1(\tau), \\ \frac{dM_2(t)}{dt} &= -\Omega_3^2 \int_0^t d\tau M_3(t-\tau) M_2(\tau), \end{aligned} \quad (3)$$

Here  $M_1(t)$ ,  $M_2(t)$ ,  $M_3(t)$  are memory functions of first, second, and third order, respectively, and  $\Omega_1^2$ ,  $\Omega_2^2$ ,  $\Omega_3^2$  are relaxation parameters having the dimension of frequency squared. Their connection with the even frequency moments of the spectral density of the TCF  $a(t)$  is<sup>11</sup>

$$\begin{aligned} \Omega_1^2 &= I_2, \quad \Omega_2^2 = I_1 I_2^{-1} - I_2, \\ \Omega_3^2 &= (I_6 I_2 - I_4^2) / (I_4 I_2 - I_2^3), \\ I_{2n} &= \int_{-\infty}^{\infty} \omega^{2n} \bar{a}(\omega) d\omega / \int_{-\infty}^{\infty} \bar{a}(\omega) d\omega. \end{aligned} \quad (4)$$

Several different methods have by now been developed to close the equation chain (3). Firstly, a transition to the Markov limit, effected by introducing the so-called slow time  $T = \lambda^{-2} t (\lambda \rightarrow 0)$  (Refs. 12 and 14). Secondly, the interacting-mode approximation.<sup>6,15</sup> Thirdly, the method of slow memory functions, when a memory function of a definite order is approximated by a known model function whose parameters are obtained with the aid of the frequency moments of the corresponding TCF or are established by fitting to the experimental data.

In addition to the foregoing there is one more method based in Bogolyubov's ideas of the abbreviated description and the relaxation-time hierarchy. It was first proposed by one of us to describe magnetic spin relaxation in liquids.<sup>7,16</sup> It was used as a basis for the development of a theory of electron spin relaxation observed in liquids by the method of nonresonant parametric absorption in parallel fields,<sup>17</sup> and of a theory of quadrupole relaxation in liquefied inert gases, liquid metals, and semiconductors.<sup>18</sup> The method was also used to develop a microscopic theory of coherent<sup>19</sup> and incoherent<sup>20</sup> scattering of slow neutrons in simple classical liquids, and to investigate the kinetics of spin-density fluctuations in paramagnetic liquids.<sup>21</sup> Closely similar ideas were used to study vibrational<sup>22</sup> and dielectric relaxations.<sup>9,23</sup> This method used in the present paper to close the equation chain (3).

In our preceding papers<sup>8,11</sup> we introduced a microscopic parameter  $\varepsilon_1^{(1)}$  indicative of the extent to which an arbitrary relaxation process

$$\varepsilon_1^{(1)} = \tau_0 / \tau_1, \quad (5)$$

is non-Markov; here  $\tau_0$  and  $\tau_1$  are the relaxation times of the initial TCF  $a(t)$  and of the first-order memory function  $M_1(t)$ ,

$$\tau_0 = \text{Re} \int_0^{\infty} dt a(t), \quad \tau_1 = \text{Re} \int_0^{\infty} dt M_1(t). \quad (6)$$

In Refs. 8 and 11 we introduced also a more accurate non-Markov parameter  $\varepsilon_1^{(2)}$  analogous to  $\varepsilon_1^{(1)}$ :

$$\varepsilon_1^{(2)} = \tau_{10} / \tau_{11}, \quad (7)$$

where  $\tau_{10}$  is the lifetime of the fluctuation correlations  $\delta A(t)$  and  $\tau_{11}$  is the memory lifetime,

$$\tau_{10} = \left\{ \int_0^{\infty} dt t^n W_0(t) \right\}^{1/n}, \quad \tau_{11} = \left\{ \int_0^{\infty} dt t^n W_1(t) \right\}^{1/n},$$

$$W_0(t) = |a(t)|^2 / \int_0^{\infty} dt |a(t)|^2,$$

$$W_n(t) = |M_n(t)|^2 / \int_0^{\infty} dt |M_n(t)|^2, \quad n=1, 2, 3, \dots \quad (8)$$

It was shown in Refs. 8 and 11 that to obtain a clear enough qualitative picture it suffices to calculate the simpler parameter  $\varepsilon_1^{(1)} = \varepsilon_1$ . In the case when  $\varepsilon_1 \gg 1$  the relaxation time of the initial TCF  $a(t)$  is much longer than the relaxation time of the memory function  $M_1(t)$ , and the process can be regarded as quasi-Markov. It will be a Markov process in the limit as  $\varepsilon_1 \rightarrow \infty$ . If, however,  $\varepsilon_1 \sim 1$ , the times  $\tau_0$  and  $\tau_1$  are of the same order and the process becomes definitely non-Markovian. The spatial dispersion of a parameter serving as a measure of the deviation of the process from a Markovian nature was calculated in Refs. 8 and 11 for a structural-relaxation process responsible for the coherent scattering of slow neutrons in simple liquids. That theory led to a clear identification of regions of Markovian and non-Markovian behavior of the process, and it explained several features of the scattering spectra.

To analyze the non-Markovian properties of relaxation properties at a more profound level, and in more detail, we follow the ideas of Refs. 8 and 11, introducing a sequence of parameter values  $\varepsilon_i$  ( $i = 1, 2, 3, \dots$ ):

$$\varepsilon_1 = \tau_0 / \tau_1, \quad \varepsilon_2 = \tau_1 / \tau_2, \quad \varepsilon_3 = \tau_2 / \tau_3, \dots, \quad (9)$$

where  $\tau_i$  is the relaxation time of the memory function of index  $i$ . We refer to the entire set of parameter values,  $\{\varepsilon\} = \{\varepsilon_1, \varepsilon_2, \varepsilon_3, \dots\}$ , as the "spectrum of the deviation from a Markovian process." Corresponding to each  $i$ th equation of chain of equations (3) is a certain value of  $\varepsilon_i$ . The index  $i$  can be called a "level." In general, the system of equations in (3) is infinite ( $i \rightarrow \infty$ ), so the spectrum  $\{\varepsilon\}$  is also infinite.

The approximation  $M_i(t) \approx M_{i+1}(t)$  was used frequently to close chain of equations (3) in Refs. 7, 9, and 16–23. From the physical standpoint, that approximation means that the time scales over which the memory functions of orders  $i$  and  $i+1$  relax are approximately the same:  $\tau_i \approx \tau_{i+1}$ . In this case we thus have  $\varepsilon_{i+1} \sim 1$ , the  $(i+1)$  st equation of the chain becomes

$$\frac{dM_i(t)}{dt} = -\Omega_{i+1}^2 \int_0^t d\tau M_i(t-\tau) M_i(\tau). \quad (10)$$

Solving (10) by Laplace transforms,

$$\tilde{y}(s) = \int_0^{\infty} dt e^{-st} y(t),$$

we find

$$\bar{M}_i(s) = [-s + (s^2 + 4\Omega_{i+1}^2)^{1/2}] / 2\Omega_{i+1}^2. \quad (11)$$

We obtain then for the relaxation time  $\tau_i$

$$\tau_i = \bar{M}_i(0) = \Omega_{i+1}^{-1}. \quad (12)$$

Taking the Laplace transforms of the remaining equations of the chain and putting  $s = 0$  we obtain the remaining relaxation times:

$$\tau_{i-1} = (\Omega_i^2 \tau_i)^{-1}. \quad (13)$$

Knowing all the times  $\tau_i$  and using (7), we now easily obtain the entire spectrum of the parameter  $\varepsilon$  indicative of deviation from Markov behavior. In the next sections we demonstrate a simplified procedure for finding the spectrum for vibrational, dielectric, and structural relaxation.

### 3. VIBRATIONAL RELAXATION

We begin with considering the TCF  $g(t)$  of the normal coordinate  $q(t)$ :

$$g(t) = \langle q(0)q(t) \rangle / \langle |q(0)|^2 \rangle. \quad (14)$$

Its spectral density

$$I(\omega) = \frac{1}{\pi} \lim_{\epsilon \rightarrow +0} \text{Re} \tilde{g}(i\omega + \epsilon) \quad (15)$$

is the normalized isotropic Raman-scattering intensity. The TCF (14) is frequently investigated using the memory-function formalism. One of the methods listed above is used to close the kinetic-equation chain (3). Thus, for example, a vibrational relaxation theory based on the approximation  $M_3(t) \approx M_2(t)$  was developed in Ref. 22. In this case, using (12) and (13), we obtain for the relaxation time

$$\tau_0 = \frac{\Omega_2^2}{\Omega_1^2 \Omega_3}, \quad \tau_1 = \frac{\Omega_3}{\Omega_2^3}, \quad \tau_2 = \frac{1}{\Omega_3}. \quad (16)$$

For the non-Markov parameters (9) of the first and second levels we have

$$\varepsilon_1 = \frac{\Omega_2^4}{\Omega_1^2 \Omega_3^2}, \quad \varepsilon_2 = \frac{\Omega_3^2}{\Omega_2^2}. \quad (17)$$

We present numerical calculations of the parameters  $\varepsilon_1$  and  $\varepsilon_2$  for  $\text{SiD}_4$  at a temperature  $T = 148$  K and for liquid ethane  $\text{C}_2\text{H}_6$  at  $T = 168$  and  $93$  K. The frequency moments  $I_2$ ,  $I_4$ , and  $I_6$  needed to calculate the relaxation frequencies  $\Omega_1$ ,  $\Omega_2$ , and  $\Omega_3$  were measured in Ref. 24. The values of  $\Omega_i^2$  obtained in this manner are listed in Table I and the numerically calculated parameters  $\varepsilon_i$  are shown in Fig. 1.

It is seen from Fig. 1 that  $\varepsilon_1 \sim 10$ – $20$  in all the considered cases, i.e., vibrational relaxation on the first level is quasi-Markovian. The parameter  $\varepsilon_1$  for  $\text{SiD}_4$ , however, is half that for  $\text{C}_2\text{H}_6$ . One can therefore expect the molecular

memory effects to be more substantial in  $\text{SiD}_4$ . On the other hand, in the general cases the parameter  $\varepsilon_2$  is on the order of unity. The relaxation times of the first- and second-order memory functions are very close. It can therefore be concluded that more complicated processes are inherent in a non-Markov process—processes with non-Markov properties. It should also be noted that Figs. 1b and 1c differ relatively little. This leads to the conclusion that non-Markov peculiarities of vibrational relaxation in  $\text{C}_2\text{H}_6$  apparently depend little on frequency.

### 4. DIELECTRIC RELAXATION

One of the most important quantities determined by studying dielectric relaxation is the absorption coefficient

$$\alpha(\omega) \propto \omega \text{th}(\hbar\omega/2k_B T) I(\omega). \quad (18)$$

Here  $I(\omega)$  is the TCF spectral density

$$\Psi(t) = \langle \mathbf{P}(0)\mathbf{P}(t) \rangle / \langle \mathbf{P}^2(0) \rangle, \quad (19)$$

where  $\mathbf{P}(0)$  is the polarization vector of the dielectric.

A dielectric-relaxation theory was developed in Ref. 9 for liquid  $\text{CH}_3\text{I}$ , based on the Zwanzig–Mori formalism.<sup>4,5,12,13</sup> It was also shown there that the best agreement with experiment is reached by using the approximation  $M_8(t) \approx M_7(t)$  for the memory function. From this approximation and from (10) and (11) we get

$$\tau_7 = \Omega_8^{-1}, \quad \tau_{i-1} = (\Omega_i^2 \tau_i)^{-1}, \quad i=1, 2, \dots, 7. \quad (20)$$

Knowing all the necessary times  $\tau_i$  it is easy to calculate all the parameters  $\varepsilon_i$  [Eq. (9)].

The numerical values of the frequency parameters  $\Omega_i^2$  taken from Ref. 9 are listed in Table II, and the calculated  $\varepsilon_i$  are shown in Fig. 2.

It is seen from Fig. 2 that  $\varepsilon_1 \gg 1$ , i.e., in this case the dielectric relaxation process can be regarded with sufficient accuracy as quasi-Markov. On the other hand, the remaining  $\varepsilon_i$  are much less than  $\varepsilon_1$  and are comparable with unity. Thus, just as in the case of vibrational relaxation, the deeply inherent nature of dielectric relaxation is essentially non-Markov and much more complicated.

### 5. STRUCTURAL RELAXATION

In the discussion of this relaxation we confine ourselves to simple classical fluids. The structural relaxation reduces then to a change of the mutual arrangement of the fluid particles, i.e., to a restructuring of the radial distribution of the particles. The structural relaxation time  $\tau_s$  is defined as the correlation time of the TCF of the fluctuations of the numerical density

TABLE I. Values of the frequency relaxation parameters  $\Omega_i^2$  obtained on the basis of the measured<sup>24</sup> frequency moments  $I_2$ ,  $I_4$ , and  $I_6$ .

Liquid	T, K	$\Omega_i^2, \text{cm}^{-2}$		
		i=1	i=2	i=3
$\text{SiD}_4$	148	4.5	55.94	69.77
$\text{C}_2\text{H}_6$	168	8.5	137.4	93.43
$\text{C}_2\text{H}_6$	93	4.0	59.25	37.965

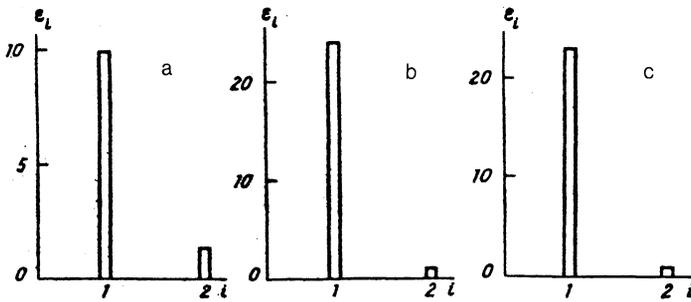


FIG. 1. Numerical values of the parameter  $\varepsilon$  for the first two-level of vibrational relaxation processes: a—SiD<sub>4</sub>,  $T = 148$  K; b—C<sub>2</sub>H<sub>6</sub>,  $T = 168$  K; c—C<sub>2</sub>H<sub>6</sub>,  $T = 93$  K.

$$\tau_s = \tau_0 = \text{Re} \int_0^{\infty} dt \rho(\mathbf{k}, t),$$

$$\rho(\mathbf{k}, t) = \langle \delta \rho_{\mathbf{k}}^*(0) \delta \rho_{\mathbf{k}}(t) \rangle / \langle |\delta \rho_{\mathbf{k}}(0)|^2 \rangle, \quad (21)$$

$$\delta \rho_{\mathbf{k}}(t) = \frac{1}{V} \sum_{j=1}^N \exp(ikr_j) - \delta_{\mathbf{k},0} \frac{N}{V},$$

where  $\delta_{\mathbf{k},0}$  is the Kronecker delta. The TCS Laplace transform  $\rho(\mathbf{k}, t)$  is connected with the dynamic structure factor  $S(\mathbf{k}, \omega)$  of the fluid, determined in experiment from the coherent inelastic scattering of slow neutrons<sup>8</sup>

$$S(\mathbf{k}, \omega) = \frac{S(\mathbf{k})}{\pi} \lim_{\varepsilon \rightarrow +0} \text{Re} \bar{\rho}(\mathbf{k}, i\omega + \varepsilon). \quad (22)$$

Here  $S(\mathbf{k})$  is the static structure factor, while  $\mathbf{k}$  and  $\omega$  are the wave vector and the scattering frequency.

In Ref. 11 we constructed a microscopic coherent neutron scattering theory for liquid Al at  $T = 1056$  K. It was shown that at this temperature there is realized a relaxation regime in which the relaxation times of the second- and third-order memory functions are approximately equal:  $\tau_2 \approx \tau_3$ . Consequently, the chain (3) can be closed by using the approximation  $M_2(\mathbf{k}, t) \approx M_3(\mathbf{k}, t)$ . We obtain then expression (16) for the relaxation time and expressions (17) for the non-Markov parameters  $\varepsilon_1$  and  $\varepsilon_2$ . Note that in this case all these quantities depend substantially on the wave vector  $\mathbf{k}$ . The frequency moments  $I_2, I_4,$  and  $I_6$  needed to find the squared relaxation frequencies  $\Omega_1^2, \Omega_2^2, \Omega_3^2$  were calculated in Ref. 25 for the given state of Al on the basis of the Duesbery–Taylor model potential.<sup>26</sup> The values of  $\Omega_i^2$  at different wave vectors  $\mathbf{k}$  are listed in Table III. Figure 3 shows the calculated spatial dispersion of the non-Markov parameters  $\varepsilon_1$  and  $\varepsilon_2$ .

TABLE II. Frequency parameters  $\Omega_i^2$  for C<sub>3</sub>I at  $T = 294$  K (Ref. 9).

$i$	$\Omega_i^2, 10^{24} \text{ s}^{-2}$	$i$	$\Omega_i^2, 10^{24} \text{ s}^{-2}$
1	10.2	5	753
2	391	6	1023
3	1353	7	827
4	1655	8	955

It is evident from Fig. 3 that both non-Markov potentials (especially  $\varepsilon_1$ ) have a rather strongly pronounced spatial dispersion. The numerical value of  $\varepsilon_1$  for a given process is much less than that of the corresponding values for vibrational or dielectric relaxation and is quite close to unity. Structural relaxation is consequently essentially non-Markovian even on the first level. The only exception is the rather narrow region near the maximum of the static structure factor  $S(\mathbf{k})$  ( $k \approx 2.7 \text{ \AA}^{-1}$ ), where  $\varepsilon_1$  has a sharp peak. It is only here that the structural relaxation is based on quasi-Markov processes. This explains, in particular, why all the existing theories of slow-neutron coherent scattering agree well with experiment in this region, notwithstanding the entirely different memory functions used.

## 6. DISCUSSION OF RESULTS AND CONCLUSION

To estimate the role of the non-Markov temporal effects we had to introduce in our present study the concept of a non-Markov spectrum, which has nothing in common with the customarily employed concept of a spectrum. It reflects the infinite character of the set (3) of coupled equations, i.e.,

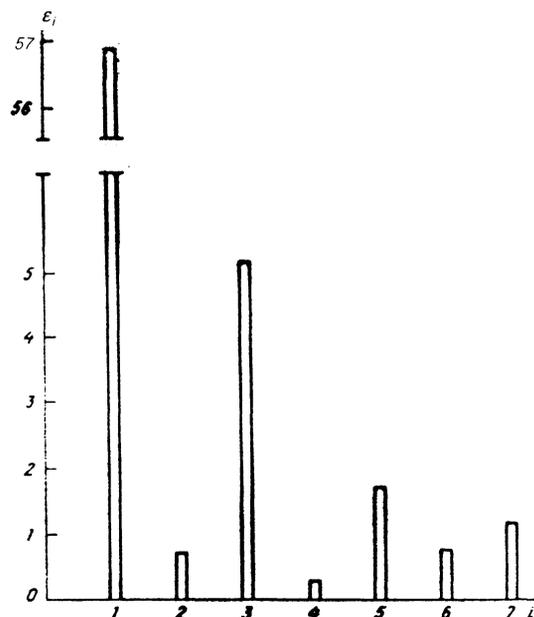


FIG. 2. Spectrum of the parameter  $\varepsilon$  in CH<sub>3</sub>I for the first seven levels.

TABLE III. Frequency parameters  $\Omega_i^2$  for liquid aluminum at  $T = 1056$  K.

$h_i, \text{\AA}^{-1}$	$\Omega_i^2, 10^{20} \text{ s}^{-2}$		
	$i=1$	$i=2$	$i=3$
1.224	9,95	23,08	24,74
1.514	9,44	24,58	31,23
1,83	6,6	22,6	35,6
2,1	3,82	17,7	41,27
2,672	0,96	16,36	46,02
4,006	8,73	29,4	48,91
4,995	6,19	32,3	47,17

the infinite structure and hierarchy properties of an arbitrary relaxation process. The hierarchy of the equation is due to the quasimolecular interactions and to the static properties of the system. The presence of a definite  $i$ th level reflects only the existence of an  $i$ th equation of the chain. Since the number of equations in the chain (3) is infinite, the spectrum of the parameter  $\varepsilon$  is also infinite.

From the physical standpoint, we are interested in the Markov ( $\varepsilon \gg 1$ ) and non-Markov ( $\varepsilon \sim 1$ ) regions of the spectrum. The number of the level at which the change from a Markov to a non-Markov spectrum takes place can be called the depth of the "Markovization." It is seen from Figs. 1 and 2, for example, that the vibrational and dielectric relaxation are Markov processes only on the first level ( $i = 1$ ). (Note that the  $\varepsilon$  spectrum for dielectric relaxation of  $\text{CH}_3\text{I}$  molecules is subject to strongly pronounced damped oscillations.) As the number of the level increases, for example at  $i = 7$ , the non-Markov character of the relaxation becomes obvious and fixed. It is quite possible that a similar picture can be observed also for vibrational relaxations. Non-Markov effects ( $\varepsilon_i \sim 1$ ) become clearly noticeable starting with the second level ( $i = 2$ ). The depth of the "Markovization" for these two cases is therefore  $h_M = 1$ .

The situation is different for structural relaxation. Figure 3 reveals two characteristic peculiarities. First, the process is essentially non-Markov starting already with the first level, i.e.,  $h_M = 0$ . Second, the very concepts of a Markov and non-Markov relaxation become relatively arbitrary. The reason is the existence of a strongly pronounced spatial dispersion of  $\varepsilon_1(\mathbf{k})$  and  $\varepsilon_2(\mathbf{k})$  in the region of the first maxi-

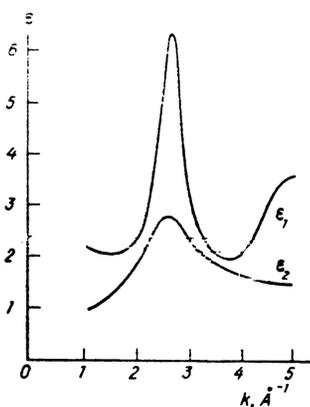


FIG. 3. Spatial dispersion of the parameters  $\varepsilon_1$  and  $\varepsilon_2$  of the first and second levels of structural relaxation of liquid Al at  $T = 1056$  K.

um of the static structural factor  $S(\mathbf{k})$  of liquid aluminum. In the range of  $k$  from 1 to  $5 \text{ \AA}^{-1}$  the relaxation changes smoothly from the non-Markov to the Markov regime and back.

It is noteworthy that for quasi-Markov ( $\varepsilon_i \gg 1$ ) and purely Markov ( $\varepsilon_i \rightarrow \infty$ ) processes the initial TCF  $a(t)$  cannot be determined from the first equation of the chain (3). The point is that the presence of non-Markov behavior at deep levels plays an essential role in the behavior of the experimentally observed physical quantities in the case of quasi-Markov and Markov processes on the first level. By way of example we refer to spin relaxation in liquids,<sup>7,17,18</sup> where the spin relaxation itself is a Markov process. However, the presence of non-Markov behavior in molecular processes ( $\varepsilon_2 \sim 1$  at the second 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 ( $\varepsilon_2 \rightarrow \infty$ ). The temperature dependences of  $T_1$  and  $T_2$  become of the traditional activation type.

It becomes obvious from the foregoing that the concept of molecular memory effects and of non-Markov temporal correlation effects become fundamental in statistical physics. It was suggested repeatedly in the literature that any non-Markov process can be reduced by some definite procedure to a Markov process. It seems that in principle this is impossible. The point is that the molecular memory or statistical inertia effects cannot be reduced fully, in our opinion, to molecular stochastic effects of the Markov type.

The role of Markov effects is also seen from a new viewpoint. A process initially of Markov type on a definite level and at a definite "Markovization" type ( $h_M$ ) can be transformed into a non-Markov process. It follows hence that known equations of irreversible processes, such as the diffusion, viscosity, heat-conduction, Bloch, Redfield equations and others, should correspond to their non-Markov analog in the theory of high-speed magnetic-resonance processes.

It seems that a non-Markov process corresponds to each known Markov random process in physics at some definite depth of "Markovization."

Our numerical estimates show that non-Markov effects are not the result of the procedure chosen to close the infinite chain of coupled equations. They reflect the profound physical nature of the statistical processes occurring in liquids. Everything stated above offers evidence that non-Markov random processes play a tremendous role in kinetic phenomena in liquids. A detailed study of the structure, properties, and parameters of non-Markov processes extends noticeably

the existing notions concerning the properties of condensed media.

The authors are grateful to R. Bittl (Free University, Berlin) for a helpful discussion of non-Markov properties of statistical systems.

- <sup>1</sup>S. M. Rytov *et al.*, *Principles of Statistical Radiophysics*, Vol. 1, Springer, 1987.
- <sup>2</sup>M. I. Yadrenko, *Spectral Theory of Random Fields* [in Russian], Nauk. Dumka, Kiev, 1980.
- <sup>3</sup>Yu. A. Rozanov, *Stationary Random Processes* [in Russian], Fizmatgiz, Moscow (1963).
- <sup>4</sup>R. Zwanzig, *J. Chem. Phys.* **33**, 1338 (1960).
- <sup>5</sup>H. Mori, *Progr. Theor. Phys.* **34**, 765 (1965).
- <sup>6</sup>K. Kawasaki, *Phys. Rev.* **150**, 291 (1966).
- <sup>7</sup>R. M. Yul'met'ev, *Teor. Mat. Fiz.* **30**, 265 (1977).
- <sup>8</sup>V. Yu. Shurygin and R. M. Yulmet'ev, *Zh. Eksp. Teor. Fiz.* **99**, 144 (1991) [*Sov. Phys. JETP* **72**, 80 (1991)].
- <sup>9</sup>K. Pasterny and A. Kocot, *Chem. Phys. Lett.* **139**, 295 (1987).
- <sup>10</sup>A. A. Markov, *Izv. fiz.-mat. obshch. Kaz. un-ta* **15**, 135 (1906).
- <sup>11</sup>V. Yu. Shurygin, R. M. Yulmetyev, and V. V. Vorobjev, *Phys. Lett. A* **143**, 199 (1990).
- <sup>12</sup>R. Zwanzig, *Phys. Rev.* **124**, 983 (1961).
- <sup>13</sup>H. Mori, *Progr. Theor. Phys.* **33**, 423 (1965).
- <sup>14</sup>R. Zwanzig, *Lect. Theor. Phys.* **3**, 106 (1960).
- <sup>15</sup>K. Kawasaki, *Ann. Rev.* **61**, 1 (1970).
- <sup>16</sup>R. M. Yulmetyev, *Phys. Stat. Sol. B* **59**, 667 (1973).
- <sup>17</sup>R. M. Yul'met'ev, *Ukr. Fiz. Zh.* **25**, 1872 (1960).
- <sup>18</sup>R. M. Yul'met'ev, *Acta Phys. Pol. A* **65**, 25 (1984).
- <sup>19</sup>V. Yu. Shurygin and R. M. Yul'met'ev, *Zh. Eksp. Teor. Fiz.* **96**, 938 (1989) [*Sov. Phys. JETP* **69**, 532 (1989)].
- <sup>20</sup>V. Yu. Shurygin and R. M. Yul'met'ev, *TMF* **83**, 222 (1990).
- <sup>21</sup>V. Yu. Shurygin and R. M. Yulmetyev, *Phys. Lett. A* **135**, 311 (1989); **14**, 196 (1989).
- <sup>22</sup>Z. Gburski, *Chem. Phys. Lett.* **115**, 236 (1985).
- <sup>23</sup>V. I. Arkhipov, *Pis'ma Zh. Eksp. Teor. Fiz.* **53**, 608 (1991) [*JETP Lett.* **53**, 631 (1991)].
- <sup>24</sup>R. E. Wilde, *J. Chem. Phys.* **75**, 5883 (1981); **78**, 4334 (1984).
- <sup>25</sup>I. Ebbsio, T. Kinell, and I. Waller, *J. Phys. C* **13**, 1865 (1980).
- <sup>26</sup>M. S. Duesbery and R. Taylor, *Phys. Rev. B* **7**, 2070 (1973).

Translated by J. G. Adashko