Space dispersion of structural relaxation in simple liquids

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The concept of a reduced description is used to study the space dispersion of the structural relaxation in simple classical liquids. Microscopic expressions are derived. Dispersion curves are found for the half-width at half-maximum of a dynamic structure factor and also for four other parameters of the structural relaxation: the relaxation time τ_s, the structure lifetime τ_{ls}, the memory lifetime τ_{lm}, and the parameter $\varepsilon = \tau_{ls}/\tau_{lm}$. The latter parameter characterizes the relative "speeding up" or "slowing down" of the molecular memory. A comparison of the theoretical results with experimental data on liquid rubidium, krypton, and argon reveals both the dispersion of this set of five relaxation parameters (τ_s, $\Delta\omega_{1/2}$, τ_{ls}, τ_{lm}, and ε) and the dispersion of the non-Markovian behavior of the structural relaxation and its transition to a quasi-Markov regime at small wave vectors, near the de Gennes narrowing and the maximum of the static structure factor.

1. INTRODUCTION

Among the basic relaxation processes in liquids, such as vibrational relaxation, rotation-isomer relaxation, intramolecular conversions, acoustic relaxation, and chemical relaxation, an important role is played by structural relaxation processes. Included in this category are the nonequilibrium changes which occur in the stable and ordered bonds between physical elements of the liquid. Specifically, these changes consist of variations in the relative positions and orientations of molecules. The following processes are usually included in this group.

1) Fluctuations of the order in the relative positions of particles. These fluctuations can be characterized by a change in the concentration of defects and holes and a restructuring of the radial (binary) distribution of particles, the ternary distribution, and the distributions of higher orders.

2) A randomization of a quasicrystalline structure. Examples are transitions from an icelike periodic lattice to a close-packed structure.

3) The ionization and dissociation of molecules, chemical reactions, quasichemical polymerization processes, a formation and decay of dimers, trimers, etc.[1-4]

In simple liquids, of course, only the first of these relaxation mechanisms operates.

A variety of spectroscopic methods are used to study structural relaxation in liquids: ultrasound, hypersound, molecular scattering of light, laser spectroscopy, and dielectric spectroscopy. These methods can be used to study fast relaxation processes over times as short as 10^{-8}–10^{-12} s for dielectric absorption, 10^{-11}–10^{-12} s in acoustics, 10^{-12}–10^{-13} s for the scattering of light, and 10^{-15} s in laser spectroscopy.[1-4] All these methods, however, are afflicted by a fundamental shortcoming: It is difficult (in practice, even impossible) to observe the dispersion associated with the scattering wave vector. The reason is that the wavelengths of sound and light waves are far greater than the dimensions of those microscopic regions in liquids in which the spatial inhomogeneity of the system is manifested significantly.

To the list of research methods given above we should add one more: the spectroscopy of slow-neutron scattering. A distinctive feature of this method, and an indisputable advantage, is that the structural relaxation time depends on the wave vector **k**, and it can easily be varied. A particularly interesting situation is that in which the wave vectors involved in the neutron scattering are on the order of a few reciprocal angstroms, while the wavelengths are on the order of interatomic distances. In this case it becomes possible to study relaxation structural phenomena which play out over short distances, on the order of $2\pi/k$, in microscopic volumes of the substance on the order of $(2\pi/k)^3$ in size. Our purpose in the present paper is to study the space dispersion of structural relaxation in simple classical liquids in the picosecond region on the basis of data on the inelastic scattering of slow neutrons. None of the other spectroscopic methods listed above can provide such information.

2. DETERMINATION AND CALCULATION OF THE TIME SCALE AND SPECTRAL HALF-WIDTH OF STRUCTURAL RELAXATION

The time scale of structural relaxation can be found from the spectra of the coherent scattering of slow neutrons in liquids in the following way:

$$\tau_s(\mathbf{k}) = \lim_{\omega\to 0} \operatorname{Re}\int_0^\infty dt\, \rho(\mathbf{k},t) e^{i\omega t} = \frac{\pi}{S(\mathbf{k})} \lim_{\omega\to 0} S(\mathbf{k},\omega). \qquad (1)$$

Here $\rho(\mathbf{k}, t)$ is a normalized temporal correlation function of the fluctuations in the local number density of particles, $S(\mathbf{k})$ is a static structure factor, and $S(\mathbf{k}, \omega)$ is a dynamic structure factor, which can be measured directly in a neutron experiment with transfer of a momentum $\hbar\mathbf{k}$ and an energy $\hbar\omega$ from a neutron to a particle of the liquid.

The method most widely used today to calculate $S(\mathbf{k}, \omega)$ is Mori's method of kinetic equations with memory,[5,6] which uses a projection-operator technique. The infinite chain of coupled kinetic equations for the temporal correlation function $\rho(\mathbf{k}, t)$ generated by this method, however, is usually closed on the basis of phenomenological assumptions regarding the time evolution of the memory functions.

In Ref. 7, for example, the unknown part of the second-

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order memory function was modeled by a Gaussian function, whose parameters were determined with the help of adjustable parameters which were themselves found through a comparison with experimental data at a zero frequency. A sum of several Gaussian functions was used in Ref. 8, while in Ref. 9 a memory function was approximated by a hyperbolic secant. None of these rather important approximations for the memory functions in Refs. 7–9 were put on a solid foundation. In addition, the presence of adjustable parameters in a theory rules out the use of the most general definition, in (1), for a microscopic calculation of the structural relaxation time. For this reason, a determination of $\tau_s(\mathbf{k})$ was carried out in Refs. 10 and 11 through the use of $\Delta\omega_{1/2}(\mathbf{k})$, the half-width at half-maximum of the dynamic structure factor $S(\mathbf{k},\omega)$. Generally speaking, that approach is valid only if the spectrum is Lorentzian.

A theory was derived for $S(\mathbf{k},\omega)$ in Ref. 12 on the basis of the concept of a reduced description. In the correlation approximation, which was first used in Ref. 13 to describe magnetic relaxation in condensed media, we found the following result in Ref. 12:

$$S(\mathbf{k},\omega)=\frac{S(\mathbf{k})}{\pi}\frac{(\omega_\rho^2/2\omega_M^2)(4\omega_M^2-\omega^2)^{1/2}}{\omega^2(1-\omega_\rho^2/2\omega_M^2)+\omega_\rho^4(4\omega_M^2-\omega^2)/4\omega_M^4} \tag{2a}$$

with the frequency relaxation parameters

$$\begin{gathered}\omega_\rho^2(\mathbf{k})=\frac{k_BT}{m}k^2S^{-1}(\mathbf{k}),\\ \omega_M^2(\mathbf{k})=\frac{3k_BT}{m}k^2+\frac{N}{mV}\int d\mathbf{r}\,g(\mathbf{r})\,[1-\cos(\mathbf{kr})]\,\nabla_z^2u(\mathbf{r}),\end{gathered} \tag{2b}$$

where $g(\mathbf{r})$ is the radial distribution function of the particles in the liquid, $u(\mathbf{r})$ is the binary interparticle interaction potential, and the z axis is chosen along the direction of the wave vector $\mathbf{k}$. The microscopic theory of Ref. 12 agrees well with experimental data on several liquids.

Substituting (2) into definition (1), we find the following expression for the structural relaxation time $\tau_s(\mathbf{k})$:

$$\tau_s(\mathbf{k})=\frac{mS(\mathbf{k})}{k_BTk^2}\left\{\frac{3k_BT}{m}k^2+\frac{N}{mV}\int d\mathbf{r}\,g(\mathbf{r})\,[1-\cos(\mathbf{kr})]\,\nabla_z^2u(\mathbf{r})\right\}^{1/2}. \tag{3}$$

The space dispersion of the structural relaxation time is thus determined entirely by the thermal energy (k_BT) of the liquid particles, by the radial distribution function, by the static structure factor, and by the interparticle interaction potential. It is not difficult to see that in the limit of large k, $k\to\infty$, the relaxation time vanishes: $\tau_s(\mathbf{k})\to0$. In the long-wavelength limit, as $k\to0$, in contrast, the behavior of $\tau_s(\mathbf{k})$ is largely determined by the particular features of the static structure factor $S(\mathbf{k})$ at small values $k\to0$.

Research on structural relaxation phenomena frequently makes use of yet another important characteristic of a spectrum: $\Delta\omega_{1/2}(\mathbf{k})$, the half-width at half-maximum of the dynamic structure factor. The following expression was derived for the half-width in Refs. 14 and 15, for example, on the basis of a diffusion model of a liquid of particles modeled by hard spheres:

$$\begin{gathered}\Delta\omega_{1/2}(\mathbf{k})=[Dk^2/S(\mathbf{k})]\,d(\mathbf{k}),\\ d(\mathbf{k})\approx[1-j_0(k\sigma)+2j_2(k\sigma)]^{-1}.\end{gathered} \tag{4}$$

Here D is the self-diffusion coefficient in the Enskog hard-sphere theory,[16] σ is the diameter of the hard sphere, and $j_0(x)$ and $j_2(x)$ are Bessel functions of index zero and two, respectively. Expression (3) was used in Ref. 14 to study a wide range of simple liquids, but its validity is restricted to a narrow region $k\sigma\approx1$. In practice, it is valid only in the immediate neighborhood of the minimum of $\Delta\omega_{1/2}(\mathbf{k})$, which was first predicted by de Gennes.[17]

On the other hand, an expression for the half-width $\Delta\omega_{1/2}(\mathbf{k})$ can easily be derived from the known form of $S(\mathbf{k},\omega)$. Using (2) and the simple equality $S(\mathbf{k},0)=2S(\mathbf{k},\Delta\omega_{1/2})$, we find the following biquadratic equation for the half-width at half-maximum $\Delta\omega_{1/2}(\mathbf{k})$:

$$A\Delta\omega_{1/2}^4(\mathbf{k})+B\Delta\omega_{1/2}^2(\mathbf{k})+C=0, \tag{5a}$$

The coefficients A, B, and C are given by

$$\begin{gathered}A=\frac{\pi^2}{4}S^2(\mathbf{k},0)\{(1-\omega_\rho^2/2\omega_M^2)^4+\omega_\rho^8/16\omega_M^8\\ -(\omega_\rho^4/2\omega_M^4)(1-\omega_\rho^2/2\omega_M^2)^2\}.\end{gathered} \tag{5b}$$

$$\begin{gathered}B=\frac{\pi^2}{4}S^2(\mathbf{k},0)(1-\omega_\rho^2/2\omega_M^2)^2\omega_\rho^4/\omega_M^2+S^2(\mathbf{k})\,\omega_\rho^4/4\omega_M^4\\ -\pi^2S^2(\mathbf{k},0)\,\omega_\rho^8/8\omega_M^6,\\ C=\frac{\pi^2}{4}S^2(\mathbf{k},0)\,\omega_\rho^8/\omega_M^4-S^2(\mathbf{k})\,\omega_\rho^4/\omega_M^2.\end{gathered}$$

It can be seen from (5) that in this case, in contrast with the result in (4) (Refs. 14 and 15), the half-width $\Delta\omega_{1/2}(\mathbf{k})$ [like the structural relaxation time $\tau_s(\mathbf{k})$] is independent of the self-diffusion coefficient in the hard-sphere model, being determined exclusively by static structural effects in the distribution of particles.

3. STRUCTURAL LIFETIME AND MEMORY LIFETIME

For a more detailed analysis of structural relaxation and of its non-Markov nature, we introduce along with the relaxation time $\tau_s(\mathbf{k})$ the structural lifetime $\tau_{ls}(\mathbf{k})$, the memory lifetime $\tau_{lm}(\mathbf{k})$, and their ratio $\varepsilon(\mathbf{k})=\tau_{ls}(\mathbf{k})/\tau_{lm}(\mathbf{k})$. We will show how these three quantities can be utilized to find detailed information about the space dispersion and the non-Markov nature of relaxation processes which result in a change in structure. To determine them, we work from two normalized temporal correlation functions: $\rho(\mathbf{k},t)$, for density fluctuations, and $M_0(\mathbf{k},t)$, the memory function.[12] In contrast with Refs. 18 and 19, we use the definitions

$$\tau_{ls}(\mathbf{k})=\frac{\operatorname{Re}\int_0^\infty dt\,t\rho(\mathbf{k},t)}{\operatorname{Re}\int_0^\infty dt\,\rho(\mathbf{k},t)},\qquad \tau_{lm}(\mathbf{k})=\frac{\operatorname{Re}\int_0^\infty dt\,tM_0(\mathbf{k},t)}{\operatorname{Re}\int_0^\infty dt\,M_0(\mathbf{k},t)},$$

$$\varepsilon(\mathbf{k})=\frac{\tau_{ls}(\mathbf{k})}{\tau_{lm}(\mathbf{k})}=\frac{\operatorname{Re}\int_0^\infty dt\, t\rho(\mathbf{k},t)\cdot\operatorname{Re}\int_0^\infty M_0(\mathbf{k},t)\,dt}{\operatorname{Re}\int_0^\infty dt\, tM_0(\mathbf{k},t)\cdot\operatorname{Re}\int_0^\infty \rho(\mathbf{k},t)\,dt}. \tag{6}$$

The quantity $\varepsilon(\mathbf{k})$ characterizes the time over which the microscopic structure exists with respect to the memory lifetime. The specific numerical value of this quantity indicates memory effects and non-Markov aspects of the process. Large values $\varepsilon(\mathbf{k})\gg 1$ imply the condition $\tau_{ls}(\mathbf{k})\gg\tau_{lm}(\mathbf{k})$, which corresponds to a relatively rapid decay of the memory. In this case the relaxation process has a very short memory, and the process can be regarded as quasi-Markov. A decrease in $\varepsilon(\mathbf{k})$ to values on the order of unity implies a significant "slowing down" of the memory and an increase in the effectiveness of non-Markov processes in the structural relaxation.

Using (2), along with expression (27) from Ref. 12, we find the following expressions for the times $\tau_{ls}(\mathbf{k})$ and $\tau_{lm}(\mathbf{k})$ and their ratio $\varepsilon(\mathbf{k})$:

$$\tau_{ls}(\mathbf{k})=\frac{\omega_M(\mathbf{k})}{\omega_\rho^2(\mathbf{k})}\left[1-(\omega_\rho^2(\mathbf{k})/2\omega_M^2(\mathbf{k}))\right],$$

$$\tau_{lm}(\mathbf{k})=1/2\omega_M(\mathbf{k}),$$

$$\varepsilon(\mathbf{k})=2\omega_M^2(\mathbf{k})/\omega_\rho^2(\mathbf{k})-1. \tag{7}$$

Substituting (2b) into (7), we finally find the following microscopic expressions for these three quantities:

$$\tau_{ls}(\mathbf{k})=\frac{mS(\mathbf{k})}{k_BTk^2}\left\{3k_BTk^2m^{-1}+N(mV)^{-1}\times\int d\mathbf{r}\, g(\mathbf{r})\left[1-\cos(\mathbf{kr})\right]\nabla_z^2u(\mathbf{r})\right\}^{1/2}\cdot$$

$$\times\left\{1-\frac{k_BTk^2}{2mS(\mathbf{k})}\left[3k_BTk^2m^{-1}+N(mV)^{-1}\times\int d\mathbf{r}\, g(\mathbf{r})\left[1-\cos(\mathbf{kr})\right]\nabla_z^2u(\mathbf{r})\right]^{-1}\right\}, \tag{8a}$$

$$\tau_{lm}(\mathbf{k})=\frac{1}{2}\left\{\frac{3k_BTk^2}{m}+\frac{N}{mV}\int d\mathbf{r}\, g(\mathbf{r})\left[1-\cos(\mathbf{kr})\right]\nabla_z^2u(\mathbf{r})\right\}^{-1/2}, \tag{8b}$$

$$\varepsilon(\mathbf{k})=\frac{2mS(\mathbf{k})}{k_BTk^2}\left\{\frac{3k_BT}{m}k^2+\frac{N}{mV}\int d\mathbf{r}\, g(\mathbf{r})\left[1-\cos(\mathbf{kr})\right]\nabla_z^2u(\mathbf{r})\right\}-1. \tag{8c}$$

Equations (3), (5), and (8) make it possible to construct a detailed microscopic description of non-Markov relaxation effects in the structural relaxation of particles in liquids.

4. COMPARISON WITH EXPERIMENTAL DATA AND DISCUSSION OF RESULTS

We have carried out numerical calculations on the space dispersion of the half-width $\Delta\omega_{1/2}(\mathbf{k})$; the times $\tau_s(\mathbf{k})$, $\tau_{ls}(\mathbf{k})$, and $\tau_{lm}(\mathbf{k})$; and the quantity $\varepsilon(\mathbf{k})$ on the basis of Eqs. (3), (5), and (8) for liquid rubidium, krypton, and argon. For these substances, reliable experimental data on slow-neutron scattering are available.[20-23] The data required on the static structure factor $S(\mathbf{k})$ were taken from Refs. 24–27. The relaxation regime corresponding to Eqs. (3), (5), and (8) was chosen on the basis of our numerical estimates of the relaxation times τ_{M_0} and τ_{K_0}. To estimate the relaxation time of the first-order memory function, τ_{M_0}, we follow Refs. 2 and 3 and use the known expression

$$\tau_{M_0}=\frac{mD_s}{k_BT}.$$

According to Refs. 26 and 28–31, the self-diffusion coefficients D_s of these liquids lie in the interval $(1.837–2.43)\cdot 10^{-5}$ cm^2/s for the given temperatures and densities. For the time τ_{M_0} we then find the interval $(0.599–1.37)\cdot 10^{-13}$ s. The relaxation time of the longitudinal-motion energy, τ_{K_0}, for simple classical liquids can be estimated under these conditions from the data in Ref. 2: $\tau_{K_0}\approx 1.2\cdot 10^{-13}$ s. It can thus be concluded that for all the

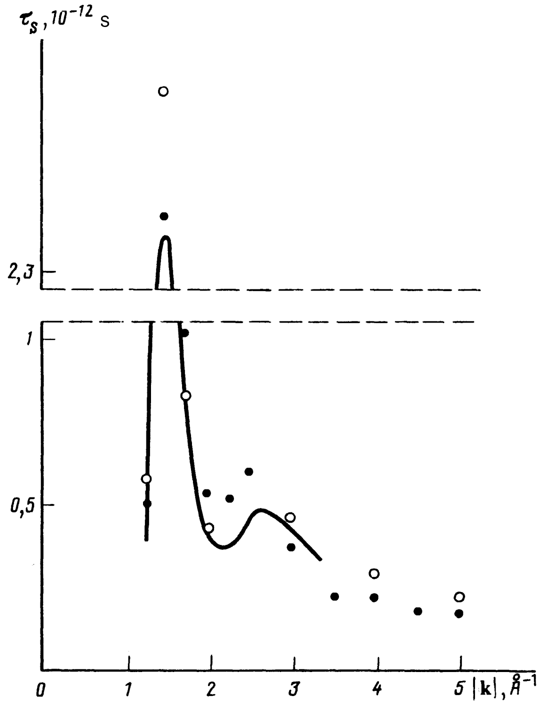

FIG. 1. Dispersion of the structural relaxation time $\tau_s(\mathbf{k})$ for liquid rubidium at $T = 315$ K and $n = 10.6\cdot 10^{21}$ cm^{-3} according to definition (1). ○—Theory of the present paper, (3), with a Lennard-Jones potential; solid line—also from (3), but with effective potential (9); ●—experimental data.[20]

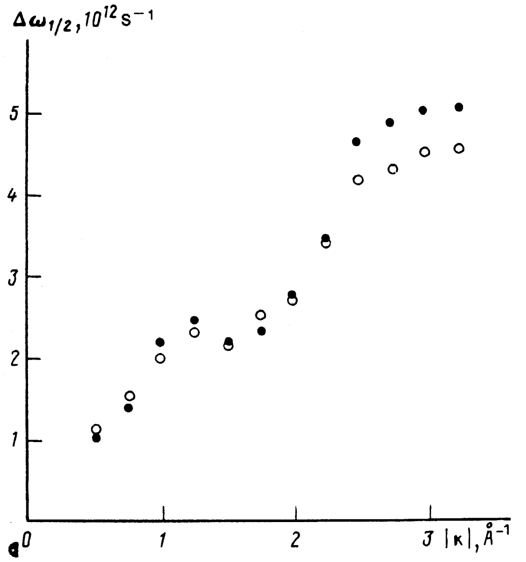

FIG. 2. Dispersion of $\Delta\omega_{1/2}(\mathbf{k})$, the half-width at half-maximum of the dynamic structure factor, for dense gaseous krypton at $T = 297$ K and $n = 10.6\cdot 10^{21}$ cm^{-3}. ○—Theory of the present paper, (5); ●—experimental data.[21]

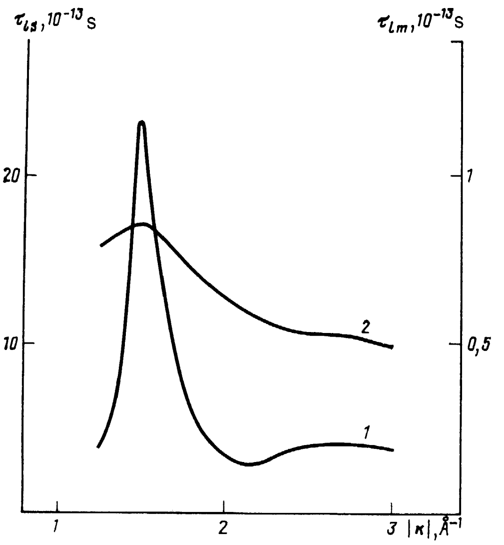

FIG. 4. Dispersion of the structural lifetime $\tau_{ls}(\mathbf{k})$ (line 1) and of the memory lifetime $\tau_{lm}(\mathbf{k})$ (line 2) for liquid rubidium according to calculations from (8a) and (8b).

liquids considered here there is, more or less, a relaxation regime with $\tau_{M_0} \approx \tau_{K_0}$. In other words, the correlation approximation $M_0(\mathbf{k}, t) \approx K_0(\mathbf{k}, t)$ is valid in this case, and we can use expression (2a) for the dynamic structure factor.

Numerical calculations show that the agreement with experiment is best for Rb and Kr. Some of the calculated results are shown in Figs. 1–5.

Figure 1 shows the dispersion of the structural relaxation time $\tau_s(\mathbf{k})$ for liquid rubidium at $T = 315$ K according to a calculation from Eq. (3). In the calculation of the equilibrium integral in (3), use was made of numerical results from Refs. 7 and 28, where this integral was calculated as a function of the wave vector **k** on the basis of a Lennard-Jones interparticle interaction potential[7] and an effective potential of the following type:[28]

$$u(\mathbf{r}) = \frac{2Z^2}{r} + \sum_{\mathbf{q}} \frac{q^2}{8\pi V} [\varepsilon^{-1}(\mathbf{q}) - 1] |v_i(\mathbf{q})|^2 e^{i\mathbf{qr}}. \qquad (9)$$

Here Z is the valence, $\varepsilon(\mathbf{q})$ is the electric constant, which depends on the wave vector **q**, and $v_i(\mathbf{q})$ is the electron-ion interaction potential.[28] We see from Fig. 1 that the solid line agrees considerably better with the experimental data. Consequently, potential (9) leads to a better agreement with experiment than is found with a Lennard-Jones potential in the case of liquid rubidium. The clearly defined damped oscillations in the dispersion of the time $\tau_s(\mathbf{k})$ correspond precisely to oscillations of the static structure factor of the liquid metal.

Figure 2 shows results calculated on the dispersion of $\Delta\omega_{1/2}(\mathbf{k})$, the half-width at half-maximum of $S(\mathbf{k}, \omega)$, for

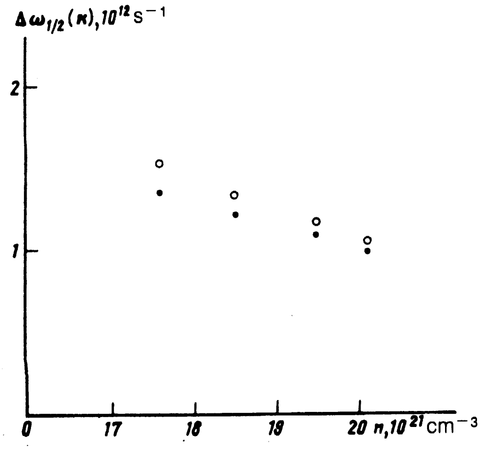

FIG. 3. The half-width $\Delta\omega_{1/2}$ versus the number density of particles for liquid argon at $T = 120$ K and at a wave-vector value $|\mathbf{k}| = 1.92$ Å^{-1}. ○—Theory of the present paper, (5); ●—experimental data.[23]

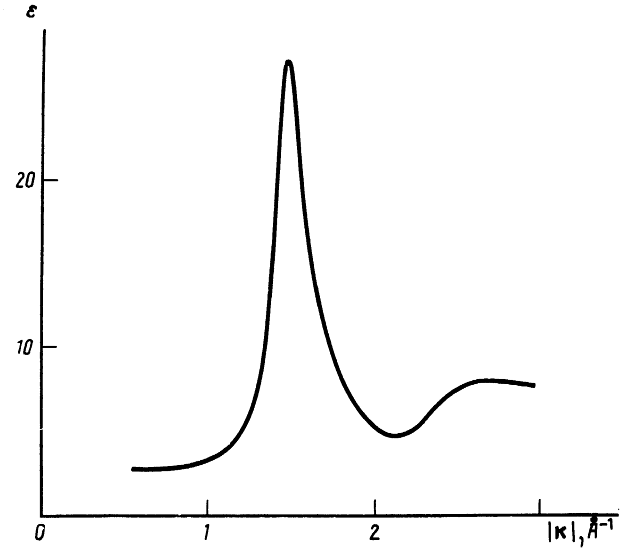

FIG. 5. Space dispersion of the quantity $\varepsilon = \tau_{ls}/\tau_{lm}$ for liquid rubidium [Eq. (8c)].

dense gaseous krypton at $T = 297$ K and at a density $n = 10.6 \cdot 10^{21}$ cm^{-3}. These results were found through a numerical solution of Eq. (5). We see a good agreement with experimental data[21] over a broad range of the wave vector **k**. Similar results were found for liquid rubidium and argon. Interestingly, Eq. (5) gives a qualitatively correct description of the behavior of the half-width $\Delta\omega_{1/2}(\mathbf{k})$ as a function of the density at an arbitrary value of the wave vector **k** in the case of argon. It turns out that this dependence is essentially linear. At small values of k the half-width increases linearly, while at large k it falls off linearly with increasing density. The situation is illustrated in Fig. 3 for a wave vector $k = 1.92$ Å^{-1}. There is also a certain value of k, approximately 1.3 Å^{-1}, at which the half-width of the spectrum is independent of the number density of particles.

Figure 4 shows the dispersion of the structural lifetime $\tau_{ls}(\mathbf{k})$ and of the memory lifetime $\tau_{lm}(\mathbf{k})$ for liquid rubidium as found from Eqs. (8a) and (8b) with the help of effective potential (9). It can be seen from Fig. 4 that the space dispersion of the memory lifetime $\tau_{lm}(\mathbf{k})$ is weaker than that of the structural lifetime $\tau_{ls}(\mathbf{k})$. The explanation here is that expression (8b) for $\tau_{lm}(\mathbf{k})$ does not have a dependence on the static structure factor $S(\mathbf{k})$.

We find the data in Fig. 5 particularly interesting. Shown here is the space dispersion of the parameter $\varepsilon(\mathbf{k})$, which is the ratio of the times $\tau_{ls}(\mathbf{k})$ and $\tau_{lm}(\mathbf{k})$. As was mentioned earlier, one can draw conclusions about the extent to which the relaxation process is non-Markov on the basis of this ratio. Near the maximum of the static structure factor $S(\mathbf{k})$ (the value is $k \approx 1.54$ Å^{-1} for rubidium), for example, this ratio is at a maximum. In other words, the memory lifetime is much shorter (by a factor of about 27) than the structural lifetime. In this case the relaxation process can be regarded as quasi-Markovian. The particular form of the memory function becomes irrelevant in this case. We believe that this situation explains why all the existing theories for the dynamic structure factor (see, for example, Refs. 7–9 and 12) agree identically well with experimental data near the de Gennes maximum (despite the fact that these theories use totally different forms of the memory function).

For other values of the wave vector **k**, the ratio $\varepsilon(\mathbf{k})$ is considerably smaller than the maximum value, but still greater than unity. Consequently, over all the rest of the **k** region the memory lifetime is comparable to the structural lifetime, and relaxation processes become very non-Markovian. The particular form of the memory function becomes important for finding a description of the relaxation; different functions lead to quite different results.[7–9,12] The smallest value of the parameter $\varepsilon(\mathbf{k})$ is reached in the case of liquid rubidium at $k < 1$ Å^{-1} (this effect is not seen in the cases of Ar and Kr). In this region, structural relaxation processes are of a more complex non-Markovian nature. It may be that these effects are responsible for the clearly defined peaks of collective excitations in the dynamic structure factor of liquid rubidium in the high-frequency region.[20] These peaks have eluded theoretical explanation on the basis of hydrodynamic models of the liquid.

5. CONCLUSION

The theory presented here gives a detailed description of structural relaxation in liquids. We feel it is particularly important to introduce and use three relaxation parameters: the relaxation time $\tau_s(\mathbf{k})$, the structural lifetime $\tau_{ls}(\mathbf{k})$, and the memory lifetime $\tau_{lm}(\mathbf{k})$. Adding a fourth (relative) parameter $\varepsilon(\mathbf{k}) = \tau_{ls}(\mathbf{k})/\tau_{lm}(\mathbf{k})$, we obtain a set which gives a complete microscopic description of the space dispersion of the structural relaxation associated with the inhomogeneity of a medium.

A distinctive feature of the structural relaxation process in a liquid is its non-Markov behavior in the case in which the process is characterized by a memory with a molecular lifetime on the order of 0.1 ps. Here again we can clearly see a distinctive dispersion: Over the entire wave-vector region there are small regions near the maximum of the static structure factor for which memory effects become relatively weak, while the relaxation process itself becomes quasi-Markovian.

The fact that the space dispersion of all the parameters which we have considered is determined to a large extent by the static structure factor $S(\mathbf{k})$ in this case deserves a separate discussion.

This situation is found only in the region of wave-vector values which we have been discussing. It can be seen from (3), (5), and (8) that the dispersion is determined by the behavior of both the structure factor of the liquid and the equilibrium integral, which contains an intermolecular potential, a radial distribution function, and the wave function of the neutron. These two contributions are of the same nature and are governed entirely by the microscopic inhomogeneity of the medium. In this interval of **k** values, however, the space dispersion of the equilibrium integral is weak in comparison with the clearly expressed dispersion of $S(\mathbf{k})$ (see, for example, Refs. 7 and 28). The characteristic oscillations of the static structure factor thus play a determining role here. For other values of the wave vector **k**, the picture may be quite different.

In light of this discussion, we should look at the results of this paper in a broader context. We would expect that rapid molecular processes in liquids should have a strong space dispersion and should be very non-Markovian, with a memory time ranging from tens of picoseconds to a few picoseconds. The non-Markovian nature itself should have a specific dispersion: For example, near the maximum of the static structure factor $S(\mathbf{k})$ there should be a relative "speeding up" of the memory, while the relaxation process itself may become quasi-Markovian (with a short-range memory). This conclusion is of general applicability and should be taken into consideration in the construction of microscopic models for relaxation processes in condensed media.

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