Calculation of the dynamic structure factor of a liquid by the reduced description method

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The kinetics of the local particle-number density fluctuations in a classical liquid are investigated on the basis of the reduced description and the hierarchy of the relaxation times in a many-particle system, as postulated by Bogoluybov. The projection-operators method is used to formulate, and solve in the long-time approximation, kinetic equations for the temporal correlation function of the density fluctuations and for the memory functions. Methods of calculating the structure factor $S(\mathbf{k},\omega)$ of the liquid in the low-frequency region are proposed, on the basis of the solutions, for several molecular-relaxation regimes. Numerical computations are carried out for liquid rubidium at $T = 315$ K and at a wave vector ranging from 1.25 to 3 Å^{-1}. The theory agrees well with experiment on inelastic scattering of neutrons and with the molecular-dynamics data.

1. An important role in molecular and statistical physics of liquids is played by the dynamic structure factor $S(\mathbf{k},\omega)$, which is measured by using inelastic scattering of slow neutrons[1-3] or by the molecular-dynamics method.[4] Several different theories for the determination of $S(\mathbf{k},\omega)$ have by now been developed (see, e.g., Refs. 5–14 and the citations therein). Some of them agree with the experimental data, but cannot be regarded as fully satisfactory. The point is that most theoretical studies are based on assumed time dependences of unknown functions and employ a large number of fitting parameters. In Refs. 10–12, for example, the time dependence of the second-order memory function was phenomenologically represented either as a Gaussian function or in the form of a sum of two Gaussian functions. A sum of several Gaussian functions is used also in Refs. 5 and 6. Such approximations, however, are not physically justified, notwithstanding the importance of the assumptions employed. At the same time, an exceptionally fruitful approach in the theory of condensed and dense media was found to be one based on the reduced description and on the idea of the relaxation-times hierarchy in a multiparticle system. We propose here on this basis a method of describing inelastic coherent scattering of slow neutrons and of calculating $S(\mathbf{k},\omega)$ in the low-frequency region. The final expressions for $S(\mathbf{k},\omega)$ depend essentially on the molecular-relaxation regime and on the relation between the relaxation times of the molecular variables of the liquid. This attests to the importance of the relation between the relaxation times of the molecular variables for the determination of the dynamic behavior of the structure factor $S(\mathbf{k},\omega)$ of the liquid.

The theory developed is applied in the last section of the paper to liquid rubidium, and the results are compared in detail with the experimental data on inelastic neutron scattering[2] and on molecular dynamics.[4]

2. Consider a classical liquid consisting of particles of mass m. We choose for the dynamic variables the Fourier components of the local particle-number density:

$$\rho_{\mathbf{k}}(t)=\frac{1}{V}\sum_{j=1}^{N}e^{i\mathbf{k}\mathbf{r}_j(t)}. \tag{1}$$

The Fourier components $\rho_{\mathbf{k}}$ are connected with the local-density fluctuations about the mean value

$$\rho_0=\langle\rho(\mathbf{r},\,t)\rangle, \tag{2}$$

where the angle brackets $\langle ... \rangle$ denote statistical averaging with the distribution function described by a Gibbs canonical ensemble of the entire system. In an equilibrium liquid we have $\rho_0 = N/V$.

We introduce the normalized temporal correlation function (TCF) of the fluctuations:

$$\rho(\mathbf{k},t)=\frac{\langle\delta\rho_{\mathbf{k}}^*(0)\,\delta\rho_{\mathbf{k}}(t)\rangle}{\langle\delta\rho_{\mathbf{k}}^*(0)\,\delta\rho_{\mathbf{k}}(0)\rangle},\qquad \delta\rho_{\mathbf{k}}(t)=\rho_{\mathbf{k}}(t)-\delta_{\mathbf{k},0}\rho_0, \tag{3}$$

where $\delta_{\mathbf{k},0}$ is the Kronecker symbol. We analyze $\rho(\mathbf{k},t)$ by the Mori projection-operators method[15,16] in the form employed in Refs. 17–19.

The fluctuations $\delta\rho_{\mathbf{k}}(t)$ obey the equation of motion

$$d\delta\rho_{\mathbf{k}}(t)/dt=i\hat{\mathscr{L}}_F\delta\rho_{\mathbf{k}}(t),\quad \hat{\mathscr{L}}_F=-i\hat{L}_F, \tag{4}$$

where $\hat{L}_F$ is the usual Liouville self-adjoint operator for the liquid:

$$\hat{L}_F=\sum_{j=1}^{N}\frac{\mathbf{p}_j\nabla_j}{m}-\sum_{i>j=1}^{N}\nabla_j u(j,i)\,(\nabla_{\mathbf{p}_j}-\nabla_{\mathbf{p}_i}), \tag{5}$$

$u(j,i)$ is the pair interaction potential of particles numbered j and i, and $\mathbf{p}_j$ is the momentum of the jth particle.

In accordance with the form of $\rho(\mathbf{k},\,t)$ we introduce, following Refs. 17–19, two mutually complementary projectors:

$$\Pi_\rho=\frac{\delta\rho_{\mathbf{k}}(0)\rangle\langle\delta\rho_{\mathbf{k}}^*(0)}{\langle\delta\rho_{\mathbf{k}}^*(0)\,\delta\rho_{\mathbf{k}}(0)\rangle},\qquad P_\rho=1-\Pi_\rho. \tag{6}$$

The main property of the projector Π_ρ is that it separates the sought TCF $\rho(\mathbf{k},\,t)$ from the total evolution of the local-density fluctuations:

$$\Pi_\rho\delta\rho_{\mathbf{k}}(t)=\delta\rho_{\mathbf{k}}(0)\,\rho(\mathbf{k},\;t). \tag{7}$$

Acting on the equation of motion (4) in succession by the operators Π_ρ and P_ρ, we get

$$\begin{aligned}d\delta\rho_{\mathbf{k}}'(t)/dt&=i\mathscr{L}_{11}\delta\rho_{\mathbf{k}}'(t)+i\mathscr{L}_{12}\delta\rho_{\mathbf{k}}''(t),\\ d\delta\rho_{\mathbf{k}}''(t)/dt&=i\mathscr{L}_{21}\delta\rho_{\mathbf{k}}'(t)+i\mathscr{L}_{22}\delta\rho_{\mathbf{k}}''(t),\end{aligned} \tag{8}$$

where we have introduced the irreducible and reducible parts of the density, respectively:

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$$\delta\rho_{\mathbf{k}}'(t)=\Pi_\rho\delta\rho_{\mathbf{k}}(t), \quad \delta\rho_{\mathbf{k}}''(t)=P_\rho\delta\rho_{\mathbf{k}}(t), \tag{9}$$

and we represent the Liouville operator in matrix form[20]

$$\hat{\mathscr{L}}_F=\begin{pmatrix}\mathscr{L}_{11} & \mathscr{L}_{12}\\ \mathscr{L}_{21} & \mathscr{L}_{22}\end{pmatrix},$$

$$\mathscr{L}_{11}=\Pi_\rho\hat{\mathscr{L}}_F\Pi_\rho, \quad \mathscr{L}_{12}=\Pi_\rho\hat{\mathscr{L}}_F P_\rho=\Pi_\rho\hat{\mathscr{L}}_F-\mathscr{L}_{11}, \tag{10}$$
$$\mathscr{L}_{21}=P_\rho\hat{\mathscr{L}}_F\Pi_\rho=\hat{\mathscr{L}}_F\Pi_\rho-\mathscr{L}_{11},$$
$$\mathscr{L}_{22}=P_\rho\hat{\mathscr{L}}_F P_\rho=\hat{\mathscr{L}}_F-\Pi_\rho\hat{\mathscr{L}}_F-\hat{\mathscr{L}}_F\Pi_\rho+\mathscr{L}_{11}.$$

The solution of the second equation of (8) is

$$\delta\rho_{\mathbf{k}}''(t)=\exp(i\mathscr{L}_{22}t)\,\delta\rho_{\mathbf{k}}''(0)+i\int_0^t d\tau\,\exp(i\mathscr{L}_{22}\tau)\mathscr{L}_{21}\delta\rho_{\mathbf{k}}'(t-\tau). \tag{11}$$

Substituting (11) in the first equation of (8) and recognizing that $\delta\rho_{\mathbf{k}}''(0)=0$, we obtain a closed equation for $\delta\rho_{\mathbf{k}}'(t)$:

$$\frac{d\delta\rho_{\mathbf{k}}'(t)}{dt}=i\mathscr{L}_{11}\delta\rho_{\mathbf{k}}'(t)-\int_0^t d\tau\mathscr{L}_{12}\exp(i\mathscr{L}_{22}\tau)\mathscr{L}_{21}\,\delta\rho_{\mathbf{k}}'(t-\tau). \tag{12}$$

Note that in this case

$$\mathscr{L}_{11}=\frac{\delta\rho_{\mathbf{k}}(0)\rangle\langle\delta\rho_{\mathbf{k}}^*(0)\hat{\mathscr{L}}_F\delta\rho_{\mathbf{k}}(0)\rangle\langle\delta\rho_{\mathbf{k}}^*(0)}{\langle\delta\rho_{\mathbf{k}}^*(0)\,\delta\rho_{\mathbf{k}}(0)\rangle}=0.$$

We represent the projector Π_ρ in the form

$$\Pi_\rho=RS, \quad R=\delta\rho_{\mathbf{k}}(0)\rangle, \quad S=\frac{\langle\delta\rho_{\mathbf{k}}^*(0)}{\langle\delta\rho_{\mathbf{k}}^*(0)\,\delta\rho_{\mathbf{k}}(0)\rangle}, \tag{13}$$

where S is the integral of averaging in the function space of the molecular variables. Acting with the operator S on (12), we obtain for $\rho(\mathbf{k},t)$ the equation

$$\frac{d\rho(\mathbf{k},t)}{dt}=-\int_0^t d\tau S\hat{\mathscr{L}}_F(1-\Pi_\rho)\exp(i\mathscr{L}_{22}\tau)$$
$$\times(1-\Pi_\rho)\hat{\mathscr{L}}_F R\rho(\mathbf{k},t-\tau). \tag{13a}$$

Taking into account the explicit forms of the Liouville operator $\hat{\mathscr{L}}_F$ and of the operators Π_ρ, R, and S we obtain ultimately an exact kinetic equation for $\rho(\mathbf{k},t)$:

$$\frac{d\rho(\mathbf{k},t)}{dt}=-\int_0^t d\tau M(\mathbf{k},\tau)\rho(\mathbf{k},t-\tau) \tag{14}$$

with a memory function

$$M(\mathbf{k},\tau)=\frac{\langle T^*(\mathbf{k},0)\exp(i\mathscr{L}_{22}\tau)T(\mathbf{k},0)\rangle}{\langle\delta\rho_{\mathbf{k}}^*(0)\,\delta\rho_{\mathbf{k}}(0)\rangle}$$
$$T(\mathbf{k},t)=\frac{1}{V}\sum_{j=1}^{N}\frac{(\mathbf{p}_j\mathbf{k})}{m}e^{i\mathbf{k}\mathbf{r}_j(t)}.$$

Note that in the overwhelming majority of papers, starting with Mori's,[15,16] the temporal evolution of the memory function is described incorrectly. In particular, as follows from (10), (13), and (14), the generator of the evolution operator in the memory function is equal to $\mathscr{L}_{22}=\hat{\mathscr{L}}_F-\Pi_\rho\hat{\mathscr{L}}_F-\hat{\mathscr{L}}_F\Pi_\rho+\mathscr{L}_{11}$, and not to $\hat{\mathscr{L}}_F-\Pi_\rho\hat{\mathscr{L}}_F+\mathscr{L}_{11}$ as in Refs. 15 and 16. This leads to inaccuracies in the description of the temporal evolution of the system.

To calculate the temporal evolution operator $\mathscr{L}_{22}$ in (13a) we use the known Kubo identity for arbitrary operators $\hat{A}$ and $\hat{B}$:

$$e^{\alpha(\hat{A}+\hat{B})}=e^{\alpha\hat{A}}+\hat{T}\int_0^\alpha d\beta e^{(\alpha-\beta)\hat{A}}\hat{B}e^{\beta(\hat{A}+\hat{B})}, \tag{15}$$

where $\hat{T}$ is the chronological-ordering operator of the Dyson evolution operators. Putting $\hat{A}=i\hat{\mathscr{L}}_F$, $\hat{B}=i\mathscr{L}_{22}-i\hat{\mathscr{L}}_F$, we obtain for the memory function $M(\mathbf{k},\tau)$ the expansion

$$M(\mathbf{k},\tau)=\omega_\rho^2M_0(\mathbf{k},\tau)$$
$$+\sum_{n=1}^{\infty}(-1)^n\int_0^\tau d\tau_1\int_0^{\tau_1}d\tau_2\ldots\int_0^{\tau_{n-1}}d\tau_n\rho'(\mathbf{k},\tau-\tau_1)$$
$$\times\rho'(\mathbf{k},\tau_1-\tau_2)\ldots\rho'(\mathbf{k},\tau_{n-1}-\tau_n)\rho''(\mathbf{k},\tau_n), \tag{16}$$

$$M_0(\mathbf{k},\tau)=\frac{\langle T^*(\mathbf{k},0)\exp(i\hat{\mathscr{L}}_F\tau)T(\mathbf{k},0)\rangle}{\langle T^*(\mathbf{k},0)T(\mathbf{k},0)\rangle},$$
$$\omega_\rho^2=\langle T^*(\mathbf{k},0)T(\mathbf{k},0)\rangle/\langle\delta\rho_{\mathbf{k}}^*(0)\delta\rho_{\mathbf{k}}(0)\rangle,$$

where the prime denotes the first derivative with respect to time, and $M_0(\mathbf{k},\tau)$ is the memory function calculated with the Liouville operator $\hat{\mathscr{L}}_F$. Taking the Laplace transform of the series (16), we get

$$\tilde{M}(\mathbf{k},s)=\omega_\rho^2\tilde{M}_0(\mathbf{k},s)+s\sum_{n=1}^{\infty}\{1-s\tilde{\rho}(\mathbf{k},s)\}^{n+1},$$
$$\tilde{M}(\mathbf{k},s)=\int_0^\infty d\tau e^{-s\tau}M(\mathbf{k},\tau), \quad \tilde{\rho}(\mathbf{k},s)=\int_0^\infty d\tau e^{-s\tau}\rho(\mathbf{k},\tau). \tag{17}$$

We confine ourselves now to the case of small $s\to0$, when we can retain only the first term in the right-hand side of the memory function (17) and hence also in (16). In the long-time approximation we obtain then in lieu of (14) a kinetic equation for the TCF of the density fluctuations

$$\frac{d\rho(\mathbf{k},t)}{dt}=-\omega_\rho^2\int_0^t d\tau M_0(\mathbf{k},\tau)\rho(\mathbf{k},t-\tau). \tag{18}$$

Assume that the temporal correlations of the spatial variables and momenta contained in $M_0(\mathbf{k},\tau)$ occur on substantially different time scales τ_q and τ_p. Then, following Bogolyubov's idea of the relaxation-times hierarchy, we can carry out partial decoupling in the memory function $M_0(\mathbf{k},\tau)$. Neglecting the correlation of the momenta of the different molecules (this is correct for a quiescent liquid) we obtain in place of (8)

$$\frac{d\rho(\mathbf{k},t)}{dt}=-\omega_\rho^2\int_0^t d\tau\pi(\mathbf{k},\tau)\rho(\mathbf{k},\tau)\rho(\mathbf{k},t-\tau), \tag{19}$$

where $\pi(\mathbf{k},\tau)$ is the normalized TCF of the longitudinal momentum component of an individual particle of the liquid:

$$\pi(\mathbf{k},\tau)=\langle(\mathbf{kp}(0))(\mathbf{kp}(\tau))\rangle/\langle(\mathbf{kp}(0))^2\rangle. \tag{20}$$

On the basis of the relaxation-times hierarchy in the molecular system, we consider the problem for different relations between the relaxation times τ_q and τ_p.

1) $\tau_p \ll \tau_q$—fast relaxation of the molecule momenta (called the impulse or diffusion approximation). In this case the relaxation of the coordinate part of the TCF of $M_0(\mathbf{k},\tau)$ is much slower than the relaxation of its momentum part. We can therefore put $M_0(\mathbf{k},\tau)\approx\pi(\mathbf{k},\tau)$. Then, solving (18) by the Laplace-transform method, we get

$$\tilde\rho(\mathbf{k},s)=[s+\omega_\rho^2\tilde\pi(\mathbf{k},s)]^{-1},\qquad \tilde\pi(\mathbf{k},s)=\int_0^\infty d\tau e^{-s\tau}\pi(\mathbf{k},\tau). \tag{21}$$

2) $\tau_p \gg \tau_q$—the correlation approximation (see Refs. 17 and 18). In this case the time dependence of $M_0(\mathbf{k},\tau)$ is determined only by the spatiotemporal correlations of the particles. We can therefore put with sufficient accuracy $M_0(\mathbf{k},\tau)\approx\rho(\mathbf{k},\tau)$. We obtain then in place of (18) the following nonlinear integrodifferential equation:

$$\frac{d\rho(\mathbf{k},t)}{dt}=-\omega_\rho^2\int_0^t d\tau\rho(\mathbf{k},\tau)\rho(\mathbf{k},t-\tau). \tag{22}$$

Solving (22) by Laplace transformation and following Ref. 18, we easily obtain the solution

$$\tilde\rho(\mathbf{k},s)=[-s\pm(s^2+4\omega_\rho^2)^{1/2}]/2\omega_\rho^2. \tag{23}$$

3) Case of close relaxation times $\tau_p\sim\tau_q$. In this case the relaxation of both the momentum and the coordinate parts of $M_0(\mathbf{k},\tau)$ takes place on one time interval. To analyze directly the memory function of $M_0(\mathbf{k},\tau)$ itself, we use again the method of projection operators. In accordance with the actual form of the function $M_0(\mathbf{k},\tau)$ we choose the projectors in (18) in the form

$$\Pi_M=T(\mathbf{k},0)\rangle\langle T^*(\mathbf{k},0)/\langle T^*(\mathbf{k},0)T(\mathbf{k},0)\rangle,\qquad P_M=1-\Pi_M. \tag{24}$$

Following a known procedure,[15-19] we obtain for the memory function $M_0(\mathbf{k},\tau)$ the exact kinetic equation

$$\frac{dM_0(\mathbf{k},t)}{dt}=-\int_0^t d\tau K(\mathbf{k},\tau)M_0(\mathbf{k},t-\tau), \tag{25}$$

where we have introduced a new memory function

$$K(\mathbf{k},\tau)=\langle B^*(\mathbf{k},0)U_1(\tau)B(\mathbf{k},0)\rangle/\langle T^*(\mathbf{k},0)T(\mathbf{k},0)\rangle,$$

a new dynamic variable

$$B(\mathbf{k},t)=i\sum_{j=1}^N\frac{(\mathbf{p}_j\mathbf{k})^2}{m^2}-\sum_{i>j=1}^N\frac{(\nabla_j\mathbf{k})}{m}u(j,i)\,(e^{i\mathbf{kr}_j}-e^{i\mathbf{kr}_i})$$

and a new evolution operator

$$U_1(\tau)=\exp\left\{i\left[\hat{\mathscr{L}}_F+\frac{T(\mathbf{k},0)\rangle\langle T^*(\mathbf{k},0)\hat{\mathscr{L}}_F}{\langle T^*(\mathbf{k},0)T(\mathbf{k},0)\rangle}\right]\tau\right\}.$$

Confining ourselves to small s (the long-time approximation) we can rewrite (25) in a form similar to (18):

$$\frac{dM_0(\mathbf{k},t)}{dt}=-\omega_M^2\int_0^t d\tau K_0(\mathbf{k},\tau)M_0(\mathbf{k},t-\tau),$$

$$K_0(\mathbf{k},\tau)=\langle B^*(\mathbf{k},0)\exp(i\mathscr{L}_F\tau)B(\mathbf{k},0)\rangle/\langle B^*(\mathbf{k},0)B(\mathbf{k},0)\rangle,$$

$$\omega_M^2=\langle B^*(\mathbf{k},0)B(\mathbf{k},0)\rangle/\langle T^*(\mathbf{k},0)T(\mathbf{k},0)\rangle. \tag{26}$$

Since we are considering relaxation times of the same order, $\tau_p\sim\tau_q$, two simple methods of closing the system of Eqs. (18) and (26) are natural: $K_0(\mathbf{k},\tau)=M_0(\mathbf{k},\tau)$ and b) $K_0(\mathbf{k},\tau)=\rho(\mathbf{k},\tau)$. In the case a) the characteristic molecular relaxation times τ_{K_0} and τ_{M_0} are of the same order. We obtain then for $M_0(\mathbf{k},\tau)$ an integrodifferential equation similar to (22). Solving it by a Laplace transformation, we get

$$\tilde M_0(\mathbf{k},s)=[-s\pm(s^2+4\omega_M^2)^{1/2}]/2\omega_M^2. \tag{27}$$

Recognizing that the following general relation holds in the low-frequency limit

$$\tilde\rho(\mathbf{k},s)=[s+\omega_\rho^2\tilde M_0(\mathbf{k},s)]^{-1}, \tag{28}$$

we get

$$\tilde\rho(\mathbf{k},s)=[s(1-\omega_\rho^2/2\omega_M^2)\pm(\omega_\rho^2/2\omega_M^2)(s^2+4\omega_M^2)^{1/2}]^{-1}. \tag{29}$$

Note that approximations similar to those used by us but for memory functions of higher order were used earlier in Refs. 21 and 22. However, the approximations used in Refs. 21 and 22 were chosen only from formal considerations and used only to describe vibrational relaxation of intramolecular modes and of reorientational motion of liquid molecules.

In case b) the three molecular reaction times τ_p, τ_{M_0}, and τ_{K_0} are actually of the same order. Equation (26) takes then the form

$$\tilde M_0(\mathbf{k},s)=[s+\omega_M^2\tilde\rho(\mathbf{k},s)]^{-1}. \tag{30}$$

Substituting (30) in (28) we get

$$\tilde\rho(\mathbf{k},s)=\frac{1}{2s\omega_M^2}\{-(s^2+\omega_\rho^2-\omega_M^2)$$
$$\pm[(s^2+\omega_\rho^2-\omega_M^2)^2+4s^2\omega_M^2]^{1/2}\}. \tag{31}$$

3. Using expressions (21), (23), (29), and (31) for $\tilde\rho(\mathbf{k},s)$ we can now find the dynamic structure factor $S(\mathbf{k},\omega)$ of the liquid. According to Refs. 10 and 11,

$$S(\mathbf{k},\omega)=[S(\mathbf{k})/\pi]\lim_{\varepsilon\to+0}\operatorname{Re}\tilde\rho(\mathbf{k},i\omega+\varepsilon), \tag{32}$$

where $S(\mathbf{k})$ is the static structure factor

$$S(\mathbf{k})=\frac{V^2}{N}\langle\delta\rho_{\mathbf{k}}^*(0)\delta\rho_{\mathbf{k}}(0)\rangle=1+\frac{N}{V}\int d\mathbf{r}(g(r)-1)e^{i\mathbf{kr}}, \tag{33}$$

and $g(r)$ is the radial distribution function of the particles in the liquid. Substituting (21), (23), (29), and (31) in (32) we obtain for the dynamic structure factor, in the four molecular-relaxation regimes indicated in (21), (23), (29), and (31), respectively, the expressions

$$S(\mathbf{k},\omega)=\frac{S(\mathbf{k})}{\pi}\operatorname{Re}\frac{\omega_\rho^2\tilde\pi(\mathbf{k},i\omega)}{\omega^2+\omega_\rho^4\tilde\pi^2(\mathbf{k},i\omega)}, \tag{34}$$

$$S(\mathbf{k},\omega)=\frac{S(\mathbf{k})}{2\pi\omega_\rho^2}(4\omega_\rho^2-\omega^2)^{1/2}, \tag{35}$$

$$S(\mathbf{k},\omega)=\frac{S(\mathbf{k})}{\pi}\frac{(4\omega_M^2-\omega^2)^{1/2}\omega_\rho^2/2\omega_M^2}{\omega^2(1-\omega_\rho^2/2\omega_M^2)^2+(4\omega_M^2-\omega^2)\omega_\rho^4/4\omega_M^4} \tag{36}$$

$$S(\mathbf{k},\omega)=\frac{S(\mathbf{k})}{\pi}\operatorname{Re}\left\{\frac{1}{2i\omega\omega_M^2}[(\omega_\rho^2-\omega_M^2-\omega^2)^2-4\omega^2\omega_M^2]^{1/2}\right\}. \tag{37}$$

The main feature of the solutions (34)–(37) is that the behavior of $S(\mathbf{k},\omega)$ depends substantially on the actual regime of molecular relaxation. In turn, the regions where the regimes are different depend on the temperature, on the features of the internuclear interaction potential of the particles, on the relations between molecular states with the scales, on the values of the considered neutron momentum and energy, and others. In some cases a transition from one regime to another can be observed. The presence of different relaxation regimes in the liquid was convincingly established in experiment from the electron-spin-relaxation data[24] and confirmed theoretically (see, e.g., Refs. 19 and 25).

The molecular frequency parameters ω_ρ and ω_M in (34)–(37) were defined initially in Eqs. (16) and (26). After the necessary statistical averaging, they take the form

$$\omega_\rho^2=(K_BT/m)k^2S^{-1}(\mathbf{k}),\quad \omega_M^2=3\omega_\rho^2S(\mathbf{k})+\omega_l^2,$$
$$\omega_l^2=\frac{N}{mV}\int d\mathbf{r}\,g(r)\,(1-\cos(\mathbf{kr}))\,\nabla_z^2u(r), \tag{38}$$

where K_BT is the thermal energy, with the z axis chosen along the direction of the wave vector $\mathbf{k}$.

4. We apply now the theory developed in the preceding section to calculation of the dynamic structure factor, at $T=315$ K, of liquid rubidium for which are available experimental data on coherent inelastic scattering of slow neutrons,[2] and also data observed by molecular-dynamics investigations.[4] It must be ascertained first which molecular-relaxation regime is realized in the present case. We estimate the relaxation time τ_{M_0} of the first-order memory by using in (14) and (16) the formula

$$\tau_{M_0}=\frac{mD_s}{K_BT}. \tag{39}$$

We calculate the self-diffusion coefficient D_s of liquid rubidium using the phenomenological equation obtained in Ref. 26 for Lennard-Jones liquids:

$$D_s=\left[0.006423\frac{K_BT}{\varepsilon\rho^2\sigma^6}+0.0222-0.028\rho\sigma^3\right]\sigma\left(\frac{48\varepsilon}{m}\right)^{1/2}, \tag{40}$$

where $m=141.917\cdot10^{-27}$ kg is the rubidium-atom mass, $\rho=1.058\cdot10^{22}$ cm^{-3} is the particle-number density, and $\varepsilon=555.89\cdot10^{-23}$ J and $\sigma=4.4048$ Å are the parameters of the Lennard-Jones potential for rubidium.[4] The calculation yields $D_s=1.837\cdot10^{-5}$ cm$^2\cdot$s^{-1}. We have then in accordance with (39) a relaxation time $\tau_{M_0}=0.599\cdot10^{-13}$ s. According to Ref. 27 the relaxation time of the longitudinal motion under these conditions can be estimated at $\tau_{K_0}\approx1.2\cdot10^{-13}$ s. We can conclude thus that in liquid rubidium at $T=315$ K there is realized a relaxation regime in which τ_{M_0} and τ_{K_0} are of the same order: $\tau_{M_0}\sim\tau_{K_0}$. To calculate the dynamic structure factor $S(\mathbf{k},\omega)$ it is therefore necessary to use Eq. (36), which contains the two frequency-relaxation parameters ω_ρ and ω_M defined in (38).

The calculated parameters ω_ρ for values of the wave vector k from 1.25 to 3 Å^{-1} are listed in Table I (for the static structure factor of liquid rubidium at $T=315$ K of liquid rubidium we used the results of Ref. 4).

An accurate calculation of the parameter ω_M is made difficult by the presence in it of the potential contribution ω_l [see (38)]. For an approximate estimate of ω_M we use the results of Ref. 10, where the frequency ω_l for liquid rubidium at the same temperature was calculated with the aid of a model Lennard-Jones model potential. The numerical values of the parameter ω_M calculated by this method are also listed in Table I (the $\tilde\omega_M$ line). In addition, the frequency parameter ω_M can be determined by comparing the developed theory with experiment at the initial point $\omega=0$. Using (36), we get

$$\omega_M=\pi S(\mathbf{k},0)\omega_\rho^2S^{-1}(\mathbf{k}). \tag{41}$$

The values of the parameter ω_M calculated with the aid of (41) are contained in the ω_M^* line of the table.

The values of $S(\mathbf{k},\omega)$ calculated for two values of the relaxation parameter ω_M ($\tilde\omega_M$ and ω_M^*) are shown in Fig. 1.

It is seen from the figure that the use of $\tilde\omega_M$ for the relaxation parameter ω_M leads to somewhat worse agreement with experiment than the use of ω_M^*, particularly in the low-frequency region. The reason is that the potential of the interaction between the particles in liquid rubidium at $T=315$ K differs from the Lennard-Jones potential used by us to calculate ω_M on the basis of the data of Ref. 10. The main conclusion, however, is that the frequency spectrum given by (36) represents correctly for the main features of the experimental scattering spectrum.

It follows also from the figure that the correlation approximation (36) for the second-order memory function leads to best agreement with experiment[2,4] at wave-vector values $k=1.5$ Å^{-1}, i.e., in the region of the first maximum of the static structure factor $S(\mathbf{k})$ ($k=1.54$ Å^{-1}, Refs. 1

TABLE I. Numerical values of the static structure factor $S(\mathbf{k})$ and of the frequency parameters ω_ρ, ω_M, and ω_M^* for $S(\mathbf{k},\omega)$ shown in Fig. 1.

k, Å^{-1}	1.25	1,5	1.75	2,0	3,0
$S(\mathbf{k})$	0,36	2,84	1,08	0.64	1,18
ω_ρ, 10^{13} s^{-1}	0,3647	0,1558	0.2948	0,4376	0.4834
$\tilde\omega_M$, 10^{13} s^{-1}	0,7698	0,6910	0.7122	0.9460	0.9333
ω_M^*, 10^{13} s^{-1}	0.6835	0.6072	0.8492	1.0181	0.8221

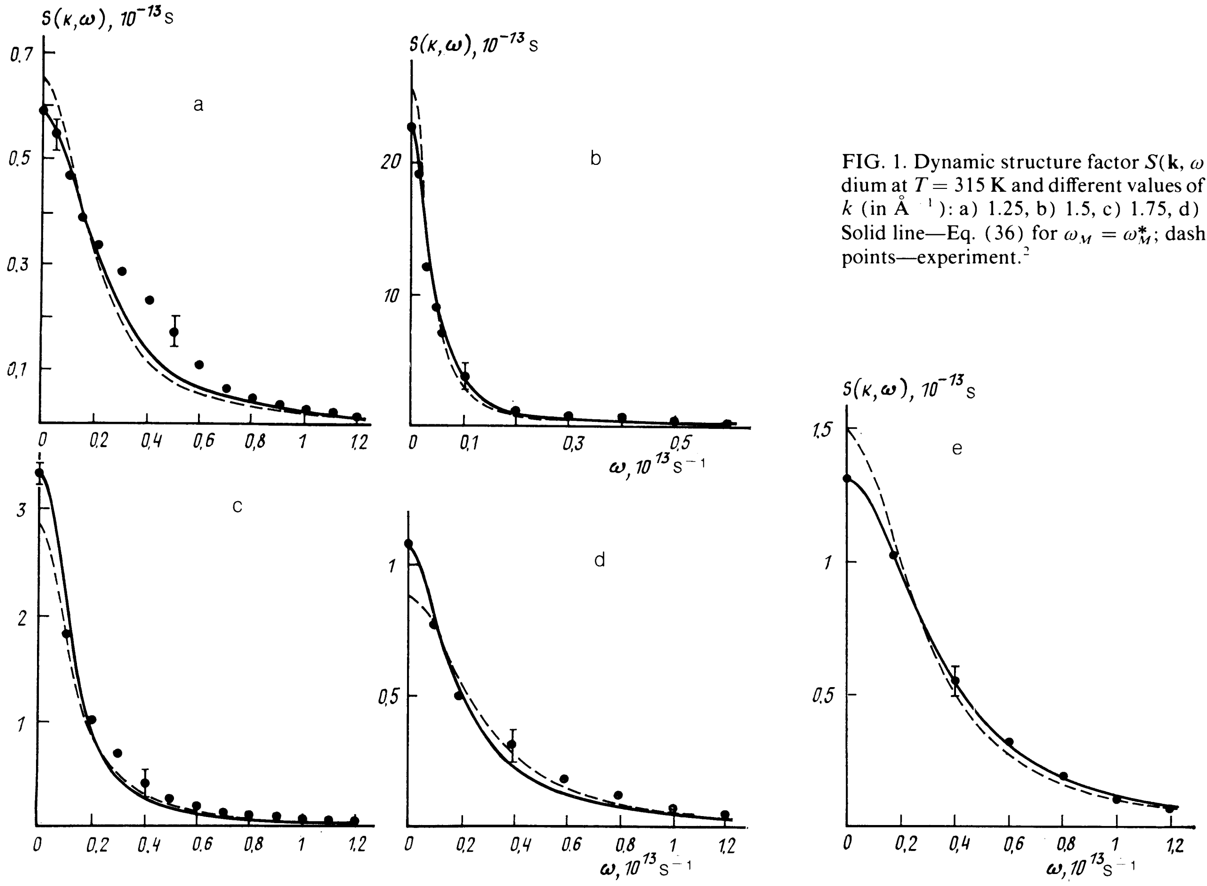

FIG. 1. Dynamic structure factor $S(\mathbf{k}, \omega)$ of liquid rubidium at $T = 315$ K and different values of the wave vector k (in Å^{-1}): a) 1.25, b) 1.5, c) 1.75, d) 2.0, and e) 3.0. Solid line—Eq. (36) for $\omega_M = \omega_M^*$; dashed—$\omega_M = \tilde{\omega}_M$; points—experiment.[2]

and 4), and also at $k = 3$ Å^{-1}. The theory developed describes the experimental data better than the theory proposed in Ref. 10, where the time dependence of the second memory function was approximated by a Gaussian whose parameters were obtained by comparison with experiment. Some discrepancy between theory and experiment at wave vector values $k = 1.25$ Å^{-1} in the intermediate-frequency region $(0.2–0.8) \cdot 10^{13}$ s^{-1} is due to the appearance of collective modes that are particularly strongly pronounced in liquid rubidium at values $k = 0.3–1$ Å^{-1} (Refs. 1 and 2). We note also that the deviation from experiment is even larger in Ref. 10. We did not consider here the problem of describing the existence and features of the collective modes. The theory developed takes into account the most important features of the relaxation processes in liquids: the non-Markov character of the relaxation kinetics, and the complex effects of molecular memory which are reflected in the first- and second-order memory functions.

Another feature of our equations is the following. All the results obtained here for $S(\mathbf{k}, \omega)$ are valid, strictly speaking, only in the long-time (low-frequency) approximation. However, the use of the time-scale hierarchy of molecular relaxation and the proposed methods of nuclear decoupling in the integrodifferential equations for the initial TFC lead, as seen from the figure, to solutions in which the region of applicability of the long-time (high-frequency) approximations extends far into the region of high frequencies (short times) $\omega \sim 10^{13}$ s^{-1}. This attests to the effectiveness of a decoupling based on the different time scales of the molecular relaxations.

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