ATTENUATION OF ZERO SOUND IN CLASSICAL LIQUIDS

By V. B. Prezzhev

Joint Institute for Nuclear Research, Dubna*

An expression for the dynamical structure factor $S(k, \omega)$ for the simple classical liquid is obtained. It is shown that the diffusion process leads to the considerable attenuation of the cooperative excitations. This attenuation causes the disappearance of the zero sound-type exitations in the long-wavelength limit.

1. Introduction

The dynamic properties of a classical liquid may be described relatively simply in two extreme cases. The first is when the considered perturbations are slowly variable in time and space, and the other, opposite case, is when the times characterizing the investigated processes are of the order of the period of atomic thermal vibrations. In the first case ordinary hydrodynamics is applicable, whereas in the second use is made of many different quasi-crystal models based on the similarities between liquids and crystals [1–4]. The applicability of hydrodynamics is limited by the condition that there be local equilibrium in regions which are small compared with the wavelength. This is why classical hydrodynamics must be replaced by relaxational hydrodynamics already in the ultrasonic region, the latter taking account of the frequency dependence of the kinetic coefficients [5–6]. In the very high frequency range ($\omega \simeq 10^{11}$ to 10^{13} Hz) the hydrodynamic description cannot be applied. It should be said here that attempts have been made recently to extend hydrodynamics to the range of high frequencies and wavelengths comparable with atomic distances [7]. These attempts, however, are intended to provide a model of correlation functions rather than to give a microscopic description of a liquid. The applicability of the quasicrystal models is also limited, but from the low frequency side.

With respect to perturbations of a frequency of the order of 10^{13} Hz and more a liquid behaves like a solid. The diffusional displacement within a time of 10^{-13} sec is small and may be neglected. This circumstance constitutes the basis of most quasicrystal models. At frequencies $\omega \lesssim 10^{12}$ Hz, when the period of the investigated density oscillations is of the same order as the characteristic time of diffusional displacement, the quasicrystal

---

* Address: Joint Institute for Nuclear Research, Head Post Office, P. O. Box 79, Moscow, USSR.

model approximation is very coarse. Thus, there is a rather broad interval of frequencies and wavelengths, known as the transitory region, where neither the hydrodynamic, nor the quasicrystal approaches are valid.

Note should be made of the qualitative difference between perturbations of the liquid in the hydrodynamic region and those in the region where quasicrystal models are applicable. Hydrodynamics treats cooperative excitations, which together represent a macroscopic change in density. Here, the microscopic properties of the system only determine the kinetic coefficients, and it is not possible to examine an atom by itself. On the other hand, within the framework of a quasicrystal model cooperative excitations having a wavelength of the order of interatomic spacings are examined. Cooperative excitations in this region can be said to be the resultant of the vibrations of the individual atoms. These vibrations are synchronized in such a way that they depict a density wave. Such perturbations are analogous to phonons in crystals, the only difference being that in crystals there is space symmetry, whereas in a liquid there is none. Perturbations of the phonon type in liquids are commonly known as quasiphonons, but sometimes the term "zero sound" is used. The latter term is adopted from the quantum theory of liquids. We shall be dealing here with cooperative excitations of the second kind, so the notion of quasiphonons is somewhat more appropriate in our case. The introduction of phonons in the crystalline lattice theory is a convenient way of describing atomic displacements. In a liquid, however, quasiphonons give only an approximate picture of the complex character of atomic displacements. This is why the definition of quasiphonons in terms of atomic displacements in quite intricate. The natural way of defining quasiphonons is linked with the interpretation of experimental data from inelastic scattering of slow neutrons in liquids. Such experiments show that in the distribution of coherently scattered neutrons there are singularities similar to phonon peaks in the case of crystals. Thus, it is convenient to define quasiphonons as singularities of the scattering function $S(\boldsymbol{k}, \omega)$ [8].

Quasiphonons, like phonons, are characterized by the dispersion relation $\omega(\boldsymbol{k})$ and lifetime τ. The function $\omega(\boldsymbol{k})$ has been found experimentally [9] and theoretically [1–4], and for a number of liquids its behaviour is known, qualitatively at least. The value of lifetime τ and especially its dependence on frequency is known much less accurately. At high frequencies quasiphonons can be computed quite well from definite excitations, what agrees excellently with neutron scattering experiments. When the frequency approaches the transitory region the lifetime of the quasiphonons should become shortened due to the increased role of diffusion. In the transitory region the zero sound waves should be strongly attenuated and, finally, in the hydrodynamic region ordinary sound waves propagate in the liquid instead of zero sound. Despite the fact that this picture seems to be quite natural, it has not yet been corroborated theoretically. And so, the study [2] partially takes account of quasiphonon attenuation due to diffusion. It was found that with decreasing frequency the lifetime τ grows continuously right up to the applicability limits of the model used. Taking account of quasiphonon decay due to anharmonicity also does not appear to provide the required dependence of τ on ω, for from the theory of anharmonic crystals we know that at low frequencies $\tau = \dfrac{1}{\omega^2}$.

In this paper we present a mechanism of quasiphonon attenuation which leads to their disappearance in the transitory region. The model is described in detail in Sec. 3. We shall only note here that its range of applicability is not wider than that of other quasicrystal models, say, that of Hubbard [2]. However, in contradistinction to the results in Ref. [2], in our approach the lifetime of quasiphonons at small ω becomes shortened with decreasing ω. In Sec. 2 the general formulae for the scattering function $S(\boldsymbol{k}, \omega)$ are given. The derivation of $S(\boldsymbol{k}, \omega)$ is given in Secs 3, 4 and 5, while Sec. 6 presents the results obtained.

2. Dynamic structure factor $S(\boldsymbol{k}, \omega)$

The two-differential neutron scattering cross-section for a liquid is determined from the momenta of incident and scattered neutrons, $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$, the cross-section for the inter-action of neutrons with target nuclei, σ, and a factor which depends only on the properties of the liquid, namely, the dynamic structure factor. The cross-section for coherent neutron scattering with a momentum change of k and energy change of $\hbar\omega$ can be written in the form

$$\left\{\frac{d^2\sigma}{d\omega d\Omega}\right\}_{\text{coh}} = \frac{1}{4\pi} \frac{k_1}{k_2} \sigma_{\text{coh}} S(\boldsymbol{k}, \omega) \tag{1}$$

where $S(\boldsymbol{k}, \omega)$ is the dynamic structure factor, otherwise known as scattering function, introduced by Van Hove [8]. As had been mentioned in the Introduction, the properties of cooperative excitations are determined by singularities of the function $S(\boldsymbol{k}, \omega)$; hence, our first task is to derive this function. Coherent neutron scattering is conditioned by scattering on density fluctuations. Therefore, there is a straight relationship between the dynamic structure factors and the time-dependent correlation density function,

$$S(\boldsymbol{k}, \omega) = \frac{1}{2\pi N} \int dt e^{i\omega t} \langle n(\boldsymbol{k}, t) n(-\boldsymbol{k}, 0) \rangle. \tag{2}$$

Here,

$$n(\boldsymbol{k}, t) = \sum_i e^{i\boldsymbol{k}r_i(t)} \tag{3}$$

is the Fourier component of the density of the particles, $\boldsymbol{r}_i(t)$ is the radius vector of particle i at instant t, and N is the number of particles in the system.

When solving dynamic problems it is more convenient to calculate not the correlation function $\langle n(\boldsymbol{k}, t) n(-\boldsymbol{k}, t) \rangle$, but the function of the response of the system to external perturbation. If a weak external field,

$$V_{\text{ext}} = U e^{i\boldsymbol{k}r - i\omega t} \tag{4}$$

acts on the system, then the change in particle density due to this field can be found by means of formulae of the linear response theory,

$$\langle \delta n(\boldsymbol{k}, t) \rangle = \chi(\boldsymbol{k}, \omega) U e^{-i\omega t} \tag{5}$$

where $\chi(\boldsymbol{k}, \omega)$ is the complex susceptibility. The imaginary part of the function $\chi(\boldsymbol{k}, \omega)$ is called simply susceptibility, and is defined by the mean value of the density operators in the following manner:

$$\operatorname{Im} \chi(\boldsymbol{k}, \omega) = \chi''(\boldsymbol{k}, \omega) = \frac{i}{2N} \int dt e^{i\omega t} \langle [n(\boldsymbol{k}, t), n(-\boldsymbol{k}, 0)] \rangle. \qquad (6)$$

The symbol $\langle [\ldots] \rangle$ denotes the mean value of the commutator taken over the unperturbed ensemble. The relationship between the correlation function $\langle n,(\boldsymbol{k}, t)\, n(-\boldsymbol{k}, 0) \rangle$ and the commutator correlation function $\langle [n(\boldsymbol{k}, t)\, n(-\boldsymbol{k}, 0)] \rangle$ is established by the fluctuation--dissipation theorem. With the help of this theorem and formulae (2) and (6) it is possible to link up the dynamic structure factor with susceptibility $\chi''(\boldsymbol{k}, \omega)$. In the classical approximation this relationship has the form

$$S(\boldsymbol{k}, \omega) = \frac{\chi''(\boldsymbol{k}, \omega)}{n\beta\pi\omega} \qquad (7)$$

where n is the mean density of particles, $\beta = \dfrac{1}{k_B T}$, T being temperature and k_B the Boltzman constant.

Using formuale (5) and (7) we get

$$S(\boldsymbol{k}, \omega) = \frac{1}{n\beta\pi\omega} \operatorname{Im} \left\{ \frac{\langle \delta n(\boldsymbol{k}, t) \rangle}{U e^{-i\omega t}} \right\} = \frac{i}{n\beta\pi\omega^2} \operatorname{Im} \left\{ \frac{\langle \delta \dot{n}(\boldsymbol{k}, t) \rangle}{U e^{-i\omega t}} \right\}. \qquad (8)$$

This last expression for the dynamic structure factor will prove to be convenient in the following. Calculation of $S(\boldsymbol{k}, \omega)$ is brought down to calculation of the mean value of the quantity $\langle \delta \dot{n}(\boldsymbol{k}, t) \rangle$. Subsequent calculations call for considerations based on models.

3. Relaxational model of quasiphonon attenuation

The model which we shall use here is based above all on the possibility of separating the displacement of the atoms of the liquid into vibrational and diffusional displacements and the assumption that the correlation between them is small. In accordance with the basic assumptions of the model we shall write the radius vector $\boldsymbol{r}_i(t)$ in the form $\boldsymbol{R}_i(t) + \boldsymbol{u}_i(t)$, where $\boldsymbol{R}_i(t)$ is the particle's equilibrium position vector, which is slowly variable in time, and $\boldsymbol{u}_i(t)$ is the displacement of the particle relative to this equilibrium position. Here, contrary to the standard quasicrystal model, the equilibrium position of atoms are assumed to be time dependent. This kind of approximation was used in Ref. [2] when dealing with a non--stationary disordered system. Other assumptions concern the diffusion mechanism. We shall assume that a weak external field may bring about a change in density due to vibrational motions, but does not affect the diffusional movements of the particles. Physically speaking, this is associated with the jump mechanism of diffusion, *i.e.* the equilibrium position of an atom remains stationary until a vacancy appears in its nearest neighbourhood.

We shall try to find the relationship the diffusional and vibrational displacements in the following manner. Let us consider the distribution of particles relative to a certain

chosen particle. If the chosen particle is at test, then the equilibrium distribution of the particles surrounding it is described by an even correlation function $g(r)$. When the chosen particle is diplaced by a vector u, then the distribution of the surrounding particles changes by the value $\nabla g(r)u$. We shall assume that diffusional displacement is what causes the relaxation of this perturbation. The above listed assumptions require some more elaboration. It will be convenient to do this later on. Now, we proceed to the calculation of the quantity $\langle \delta \dot{n}(k, t)\rangle$.

In accordance with definition (3) we have

$$\delta n(k, t) = \sum_i (e^{-ik(R_i+u_i)} - e^{-ikR_i}) \simeq -ik \sum_i u_i e^{-ikR_i}. \tag{9}$$

In this equation we assume that the displacement of the particles, u_i, due to the external field of Eq. (4) is small. Differentiation of Eq. (9) with rescpect to time and averaging over all configurations $\{R_i(t)\}$ yields

$$\langle \delta \dot{n}(k, t)\rangle = -i \sum_i \langle (k\dot{u}_i)e^{-ikR_i}\rangle - \sum_i \langle (ku_i)(k\dot{R}_i)e^{-ikR_i}\rangle. \tag{10}$$

Let us compare the correlation functions in the right-hand part of Eq. (10). By assumption we have $\dot{u}_i \gg \dot{R}_i$. Besides this, we assumed the smallness of the correlation between the vibrational displacements $u_i(t)$ and the diffusional displacements of the same particle, $\dot{R}_i(t)\Delta t$. Hence, we get the inequality

$$\langle \dot{u}_i e^{-ikR_i}\rangle \gg \langle u_i(k\dot{R}_i)e^{-ikR_i}\rangle$$

and may drop the second term in Eq. (10). We introduce the new variable

$$\xi_i(t) = \dot{u}_i(t) \frac{e^{i\omega t - ikR_i}}{U} \tag{11}$$

and write Eq. (10) in the form

$$\langle \delta \dot{n}(k, t)\rangle = -ik \sum_i \langle \xi_i(t)\rangle U e^{-i\omega t}. \tag{12}$$

Thus, by virtue of Eqs (7), (5) and (12), the expression for the dynamic structure factor becomes

$$S(k, \omega) = \frac{k}{\pi\beta n\omega^2} \operatorname{Im} \sum_i \langle \xi_i(t)\rangle. \tag{13}$$

Let us notice that the mean value $\langle \xi_i \rangle$ does not depend on the index of the particle because of the homogeneity of the system. Therefore, it is sufficient to consider the behaviour of a single chosen particle, the coordinates of which will be labelled by the subscript "0".

We write the equation of motion of our chosen particle in the form

$$\ddot{u}_0(t) = -n \int dr \nabla V(r_0-r)\varrho(r, t) - iUke^{ikR_0 - i\omega t}. \tag{14}$$

The last term in Eq. (14) appears because the external field is present. The function $\varrho(r, t)$ denotes the averaged distribution of the particles surrounding the chosen one at the instant t.

The exchange of the summation over particle coordinates in the equation of motion by integration with the distribution function is an approximation analogous to the self-consistent field approximation.

We note here some remarks regarding the behaviour of the function $\varrho(\mathbf{r}, t)$. The equilibrium distribution $\varrho_0(\mathbf{r}, t)$ in the absence of external field is described by a simple even correlation function $g(r)$,

$$\varrho_0(\mathbf{r}, t) = g(\mathbf{r}_0(t) - \mathbf{r}). \tag{15}$$

The development of the distribution function with time is caused by the displacement of the chosen particle, the action of the external field, and relaxation due to the motion of the surrounding particles. The rate of the vibrational motion is much greater than that of diffusional motion. It is plausible, therefore, to assume that the vibrational "subsystem" reaches equilibrium with the external field much faster than the diffusional one. We denote the relaxation times in the vibrational and diffusional "subsystems" by τ_K and τ_D, respectively. Let the distribution function of the particles surrounding our chosen one be $\varrho(\mathbf{r}, 0) = F[(\mathbf{r}(0) - \mathbf{r}), 0]$ at the instant when the external field, Eq. (4), is switched on. Then after a time t, satisfying the condition $\tau_D \gg t \gg \tau_K$, the distribution function looks as

$$\varrho(\mathbf{r}, t) = F[\{\mathbf{R}_0(t) + \mathbf{u}_0(t) - \mathbf{r} - \mathbf{u}_0(t) \cos \mathbf{k}(\mathbf{R}_0(t) - \mathbf{r})\}, t]. \tag{16}$$

Hence, there takes place a slow relaxation process with the characteristic time τ_D leading to the function

$$g[\mathbf{R}_0(t) + \mathbf{u}_0(t) - \mathbf{r} - \mathbf{u}_0(t) \cos \mathbf{k}(\mathbf{R}_0(t) - \mathbf{r})]. \tag{17}$$

The function $\mathbf{u}_0(t)$ in expressions (16) and (17) should be defined self-consistently with the use of Eq. (14).

We shall now check the correctness of the assertions made above in the case of a quasi-crystal model. In such model the equilibrium position of the oscillating atoms, R_i, is assumed to motionless and distributed according to the function $g(r)$. This kind of assumption corresponds to the neglection of the explicit time dependence of the function on the right-hand side of Eq. (16) and the postulation of expression (17) as the distribution function $\varrho(\mathbf{r}, t)$. Indeed, expanding function (17) into a series with respect to the displacements and taking only the first two terms of the expansion,

$$\varrho(\mathbf{r}, t) = g(\mathbf{R}_0 - \mathbf{r}) + \nabla g(\mathbf{R}_0 - r) \mathbf{u}_0(t)(1 - \cos \mathbf{k}(\mathbf{R}_0 - \mathbf{r})) + \ldots$$

yields with the use of Eq. (14) the expression for the frequency of longitudinal vibrations in the quasicrystal model,

$$\omega^2(\mathbf{k}) = n \int \left(\frac{\mathbf{k}\nabla}{k}\right)^2 V(r) g(r)(1 - \cos \mathbf{k}r) d\mathbf{r}. \tag{18}$$

We shall now try to improve the quasicrystal approximation by taking account of the explicit time dependence of the function $F(\mathbf{r}, t)$ due to diffusional motion. In other words, we shall consider the relaxation of the distribution function towards the form (17). For this purpose,

we must have a formula for the function $\varrho(\boldsymbol{r}, t)$. It is a very complicated task to derive the kinetic equation for a liquid; therefore, we shall use the approximate method of Singwi and Sjölander [10]. A brief outline of this method, without entering into details, is given in the following section.

4. The Singwi and Sjölander method

Let $f(\boldsymbol{x}, \boldsymbol{p}, t)$ be an independent particle distribution function of the atoms surrounding our chosen particle, whereas $f_0(\boldsymbol{x}, \boldsymbol{p}, t)$ its equilibrium value. The time dependence of this function is due to the motion of the chosen atom, as in Eqs (15) and (16) of the preceding section. We assume that we can separate the coordinate and momentum dependences of the equilibrium distribution function and write

$$f_0(\boldsymbol{x}, \boldsymbol{p}, t) = f_0(p)f_0[\boldsymbol{x}_0(t)-\boldsymbol{x}] \tag{19}$$

where $f_0(p)$ is the Maxwellian distribution with respect to momenta.

The simplest kinetic equation for the function $f(x, p, t)$ is

$$\frac{\partial f(\boldsymbol{x}, \boldsymbol{p}, t)}{\partial t} + \vec{v}\nabla f(\boldsymbol{x}, \boldsymbol{p}, t) = \frac{f_0(\boldsymbol{x}, \boldsymbol{p}, t)-f(\boldsymbol{x}, \boldsymbol{p}, t)}{\tau} \tag{20}$$

and corresponds to a gas of non-interacting particles which are placed in the field of the chosen atom. The solution to Eq. (20) is found by means of the Laplace transformation and has the form

$$f(\boldsymbol{x}, \boldsymbol{p}, t) = f_0(\boldsymbol{x}, \boldsymbol{p}, t) + \int_{-\infty}^{t} dt' \int dx' \left\{ \int \frac{d\boldsymbol{q}}{(2\pi)^3} \, e^{i\boldsymbol{q}(\boldsymbol{x}-\boldsymbol{x}')-iv\boldsymbol{q}(t-t')} \right\} \times$$

$$\times e^{-\frac{t-t'}{\tau}} f_0(\tau)\nabla f_0[x_0(t')-x']\dot{\boldsymbol{u}}_0(t). \tag{21}$$

The density of particles surrounding the chosen one at instant t is found by integrating expression (21) over momenta, viz.,

$$\varrho(\boldsymbol{x}, t) = f_0[\boldsymbol{x}_0(t)-\boldsymbol{x}] + \int_{-\infty}^{t} dt' \int dx' e^{\frac{t-t'}{\tau}} g_s^0(\boldsymbol{x}-\boldsymbol{x}', t-t') \times$$

$$\times \nabla f_0[\boldsymbol{x}_0(t')-\boldsymbol{x}']\dot{\boldsymbol{u}}_0(t) \tag{22}$$

where

$$g_s^0(\boldsymbol{x}, t) = [\pi a(t)]^{-3/2} \exp\left(-\frac{x^2}{a(t)}\right) \tag{23}$$

$$a(t) = \frac{2k_B T}{m} t^2. \tag{24}$$

The function $g_s^0(\boldsymbol{x}, t)$ is the Gaussian approximation of the correlation function $g_s(\boldsymbol{x}, t)$ which describes the probability of a particle becoming displaced from the coordinate origin to a position x within time t. The width of the Gaussian curve, $a(t)$, or the root mean square

displacement within time t the form (24) reveals the gaseous character of the particle motion. In the case of a liquid this function should fulfill the condition

$$a(t) = C + 6Dt \quad \text{when} \quad t \to \infty,$$

where D is diffusion coefficient. The method of Singwi and Sjölander consists in the use of the functional form (22) of the expression from $\varrho(x, t)$ for describing the density of the particles surrounding the chosen one in a liquid, but the "gaseous" correlation function $g_s^0(x, t)$ is replaced by a more complex form, $g(x, t, x', t'|x_0)$. The latter correlation function gives the probability that a particle which is at point x' at instant t' will move to point x within time $t - t'$, assuming the condition that the chosen particle is found at point x_0 at the instant t. We shall not write out any concrete expression for this function, but use the results of Ref. [10] in our numerical calculations.

We shall now employ the described method to our problem. In accordance with formula (17), we write the equilibrium distribution (19) in the form

$$f_0(x, p, t) = f_0(p)g[R_0(t) + u_0(t) - r - u_0(t) \cos k(R_0(t) - r)]. \tag{25}$$

The distribution function written in the form (25) means that its dependence on time is already taken into account. That is, there remains to account for the time dependence of $\varrho(r, t)$ due to diffusional motion. We assume that for this purpose it is possible to make use of the function form (22) and only an appropriate correlation function $g(x, t, x', t'|R_0(t))$ has to be found. Singling out the effects caused by diffusion is facilitated by the fact that the function $g(x, t, x', t'|R_0(t))$ is in the end expressed by the correlation function $g_s(r, t)$ [10]. The latter function is expressed in Gaussian approximation by the root mean square displacement $a(t) = \langle r^2(t) \rangle$. Therefore, if we assume the root mean square displacement of the equilibrium position in the form

$$a(t) = \begin{cases} 6D^*(t - \tau_0) & t > \tau_0 \\ 0 & t \leqslant \tau_0 \end{cases} \tag{26}$$

characteristic of diffusional displacement, the function $g(x, t, x', t'|R_0(t))$ will ensure the development, of a distribution function in time due to diffusion. τ_0 in Eq. (26) denotes the time of "delay" or "settled life" of the atom in the given equilibrium position. Let us note here that the introduced diffusion coefficient of the equilibrium position D^* is not, generally speaking, equal to the experimentally measured self-diffusion coefficient. In the following it is considered as a parameter.

Earlier, we assumed that an external field does not affect the mechanism of diffusion. Indeed, this is why we use the solution of the kinetic equation (20) without external field, disregarding the fact that the external field (4) does act on the system.

Substitution of the expression (25) into formula (22) yields the following sequence with respect to displacements:

$$\varrho(r, t) = g(r, t) + \int\limits_{-\infty}^{t} dt' \int dx e^{-\frac{t-t'}{\tau}} g_s^0(x - x', t - t') \times$$

$$\times \nabla g[R_0(t') - x'][1 - \cos k(R_0(t) - r)]\dot{u}_0(t). \tag{27}$$

Here, as when deriving Eq. (9), we assume that $\dot{u}_0 \gg \dot{R}_0$. In accord with Ref. [10] we substitute the function g_s^0 by $g(\boldsymbol{x}, t, \boldsymbol{x}', t'|x_0)$. Defining the effective potential [10] as

$$\nabla \tilde{\tilde{V}}[\boldsymbol{R}_0(t)-\boldsymbol{x}', \, t-t'] \equiv \int \nabla V[\boldsymbol{R}_0(t)-x]g_s(\boldsymbol{x}, t, \boldsymbol{x}', t'|\boldsymbol{R}_0(t))d\boldsymbol{x} \tag{28}$$

and the effective even distribution function as

$$\nabla \tilde{\tilde{g}}[\boldsymbol{R}_0(t)-\boldsymbol{x}] \equiv \nabla g[\boldsymbol{R}_0(t)-\boldsymbol{x}](1-\cos \boldsymbol{k}(\boldsymbol{R}_0(t)-\boldsymbol{x})) \tag{29}$$

we get from Eqs (14), (25), (28) and (29) the final equation of motion of the chosen particle in the form

$$m \frac{d^2}{dt^2}\boldsymbol{u}_0(t) = -n \int\limits_{-\infty}^{t} dt' e^{-\frac{t-t'}{\tau}} \int dx' \nabla \tilde{\tilde{V}}[\boldsymbol{R}_0(t)-\boldsymbol{x}', \, t-t'] \times$$

$$\times \nabla \tilde{\tilde{g}}[\boldsymbol{x}'-\boldsymbol{R}_0(t')]\dot{\boldsymbol{u}}_0(t)-iU\boldsymbol{k}e^{i(\boldsymbol{k}\boldsymbol{R}_0(t)-\omega t)}. \tag{30}$$

5. Solution of the equation of motion

We calculate the mean value $\langle \xi_0 \rangle$ by means of Eq. (30). After integrating both parts over time, Eq. (30), with account taken of Eq. (11), takes the form

$$m\xi_0(t) = \int\limits_{-\infty}^{t} dt' \int\limits_{-\infty}^{t'} dt'' \exp\left(-\frac{t'-t''}{\tau}\right) \int dx' \nabla \tilde{\tilde{V}}[\boldsymbol{R}_0(t')-\boldsymbol{x}', \, t'-t''] \times$$

$$\times \nabla \tilde{g}[\boldsymbol{x}'-\boldsymbol{R}_0(t'')]e^{i\boldsymbol{k}[\boldsymbol{R}_0(t'')-\boldsymbol{R}_0(t)]}e^{i\omega(t-t'')}\xi_0(t'') - \int\limits_{-\infty}^{t} dt'i\boldsymbol{k}e^{i\boldsymbol{k}[\boldsymbol{R}_0(t')-\boldsymbol{R}_0(t)]}e^{i\omega(t-t')}. \tag{31}$$

The integral equation obtained thus may be solved by iteration. Taking the average of the iteration series for ξ_0 for all possible configurations $\{R_i(t)\}$ yields

$$\langle \xi_0(t) \rangle = -\frac{1}{m} \left\langle \int\limits_{-\infty}^{t} dt'i\boldsymbol{k}e^{i\boldsymbol{k}[\boldsymbol{R}_0(t')-\boldsymbol{R}_0(t)]} e^{i\omega(t-t')} \right\rangle +$$

$$+\frac{\sigma}{m^2} \left\langle \int\limits_{-\infty}^{t} dt' \int\limits_{-\infty}^{t'} dt'' \exp\left(-\frac{t'-t''}{\tau}\right) \int dx' \nabla \tilde{\tilde{V}}[\boldsymbol{R}_0(t')-\boldsymbol{x}', \, t'-t'']\nabla \tilde{g}[\boldsymbol{x}'-\boldsymbol{R}_0(t'')] \times \right.$$

$$\left. \times e^{i\boldsymbol{k}[\boldsymbol{R}_0(t'')-\boldsymbol{R}_0(t)]}e^{i\omega(t-t'')} \int\limits_{-\infty}^{t''} dt'_1 \, i\boldsymbol{k}e^{i\boldsymbol{k}[\boldsymbol{R}_0(t'_1)-\boldsymbol{R}_0(t'')]} \, e^{i\omega(t'-t'_1)} \right\rangle + \dots \tag{32}$$

The mean values in this expression are time independent. The first term on the right-hand side is by definition the Fourier presentation of the correlation function $g_s(\boldsymbol{r}, t)$ (or, to be more exact, the function $\theta(t)g_s(\boldsymbol{r}, t)$, where $\theta(t) = 1$ when $t \geqslant 0$ and $\theta(t) = 0$ when $t < 0$):

$$\frac{i\boldsymbol{k}}{m} g_s^*(\boldsymbol{k}, \omega) \equiv \frac{1}{m} \left\langle \int\limits_{-\infty}^{t} dt'i\boldsymbol{k}e^{i\boldsymbol{k}[\boldsymbol{R}_0(t')-\boldsymbol{R}_0(t)]} e^{i\omega(t-t')} \right\rangle. \tag{33}$$

The function $g_s(\boldsymbol{r}, t)$ is the probability of the equilibrium center becoming displaced by the vector $\boldsymbol{r}$ within time t.

We transform the second term on the right-hand side of Eq. (32), going over to the Fourier presentation of the functions $\widetilde{V}(\boldsymbol{R}_0(t)-\boldsymbol{x})$ and $\widetilde{g}(\boldsymbol{R}_0(t)-\boldsymbol{x})$:

$$
\frac{n}{m^2} \int\limits_{-\infty}^{t} dt' \int\limits_{-\infty}^{t'} dt'' \int\limits_{-\infty}^{t''} dt_1' \exp\left(-\frac{t'-t''}{\tau}\right) \int dx' \iint \frac{d\boldsymbol{q}_1}{(2\pi)^3} \times
$$

$$
\times \frac{d\boldsymbol{q}_2}{(2\pi)^3} \, \boldsymbol{q}_1\boldsymbol{q}_2 \widetilde{V}[\boldsymbol{q}_1, t'-t''] \widetilde{g}(\boldsymbol{q}_2) e^{i\omega(t'-t_1')} i\boldsymbol{k} \langle e^{i\boldsymbol{q}_1[\boldsymbol{R}_0(t')-\boldsymbol{x}']} e^{i\boldsymbol{q}_2[\boldsymbol{x}'-\boldsymbol{R}_0(t'')]} \times
$$

$$
\times e^{i\boldsymbol{k}[\boldsymbol{R}_0(t'')-\boldsymbol{R}_0(t)]} e^{i\boldsymbol{k}[\boldsymbol{R}_0(t_1')-\boldsymbol{R}_0(t'')]} \rangle. \tag{34}
$$

To obtain a closed expression for $\langle\xi\rangle$ we must resolve the complex correlation function in Eq. (34). After integrating over x' and q this function becomes

$$
\langle e^{i\boldsymbol{q}_1[\boldsymbol{R}_0(t')-\boldsymbol{R}_0(t'')]} e^{i\boldsymbol{k}[\boldsymbol{R}_0(t'')-\boldsymbol{R}_0(t)]} e^{i\boldsymbol{k}[\boldsymbol{R}_0(t_1')-\boldsymbol{R}_0(t'')]} \rangle. \tag{35}
$$

The accepted assumption consists in putting the mean value of the product of exponents (35) in the form of the product of the mean values of the exponential factors, viz.,

$$
\langle e^{i\boldsymbol{q}_1[\boldsymbol{R}_0(t')-\boldsymbol{R}_0(t'')]} \rangle \langle e^{i\boldsymbol{k}[\boldsymbol{R}_0(t'')-\boldsymbol{R}_0(t)]} \rangle \langle e^{i\boldsymbol{k}[\boldsymbol{R}_0(t_1')-\boldsymbol{R}_0(t'')]} \rangle
$$

$$
\equiv g_s^*(\boldsymbol{q}_1, t'-t'') g_s^*(\boldsymbol{k}, t''-t) g_s^*(\boldsymbol{k}, t_1'-t''). \tag{36}
$$

Before we define the limits of applicability of this approximation, let us note that the coordinate factors in Eqs (35) and (36) are displacements of the equilibrium position of the particle within times $(t'-t'')$, $(t''-t)$ and $(t_1'-t'')$. The approximation of Eq. (36) is equivalent to neglection of the correlation between these displacements of the particle. We now introduce the variables $\tau_1 = (t'-t'')$, $\tau_2 = (t-t'')$ and $\tau_3 = (t_1'-t'')$ and consider the range of values of these variables G in which at least one of the following inequalities is satisfied: $|\tau_1-\tau_2| \leqslant \tau_0$, $|\tau_1-\tau_3| \leqslant \tau_0$, and $|\tau_2-\tau_3| \leqslant \tau_0$. Here, τ_0 is the delay time. We denote the displacement of the equilibrium position within time τ by $\varrho(\tau)$. Outside the region G the displacements of the equilibrium position are weakly correlated because of the chaotic character of the diffusional displacements. Therefore, we may write in approximation

$$
\langle \varrho(\tau_i)\varrho(\tau_j) \rangle \cong 0 \quad (i,j = 1, 2, 3; \ i \neq j) \tag{37}
$$

and the mean value of the product of exponents becomes divided into the product of mean values. In the region G the equations (37) are not fulfilled. Therefore, in order to have the approximation satisfied it is necessary for the characteristic dimensions of the region $G-\tau_0$ to be much smaller than the region of integration. The dimensions of the latter are determined by the presence of the attenuating exponential factor of the type $g^*(\boldsymbol{k}, t) \sim \exp\left[-\frac{k^2}{4} a^*(t)\right]$, where $a^*(t)$ is the root mean square displacement of the equilibrium center within time t. Direct calculation shows that at the considered values of wave number k the dimensions of the region of integration are much larger than the delay time.

The other correlation functions appearing in the subsequent terms of the series (32) are resolved in the same way as the function (35) by seccessively singling out the auto-correlation functions $g_s^*(k, t)$. As a result, from Eq. (32) we get

$$\langle \xi_0 \rangle = - \frac{i}{m} \, \boldsymbol{k} g_s^*(\boldsymbol{k}, \omega) + \frac{i}{m^2} \, \boldsymbol{k} g_s^*(\boldsymbol{k}, \omega) \Phi(\boldsymbol{k}, \omega) - \frac{i}{m^3} \, \boldsymbol{k} g_s^*(k, \omega) \Phi^2(\boldsymbol{k}, \omega) + \dots \tag{38}$$

The following notation is introduced here

$$g_s^*(\boldsymbol{k}, \omega) = \int\limits_0^\infty dt e^{i\omega t} g_s^*(\boldsymbol{k}, t);$$

$$\Phi(\boldsymbol{k}, \omega) = n \int\limits_{-\infty}^t dt' \int\limits_{-\infty}^{t'} dt'' \exp\left(-\frac{t'-t''}{\tau}\right) \int \frac{d\boldsymbol{q}}{(2\pi)^3} \left(\frac{\boldsymbol{kq}}{k}\right)^2 \tilde{\tilde{V}}[\boldsymbol{q}, t'-t''] \times$$

$$\times \tilde{\tilde{g}}(\boldsymbol{q}) g_s^*(\boldsymbol{q}, t'-t'') e^{i\omega(t-t'')} g_s^*(\boldsymbol{k}, t''-t). \tag{39}$$

The series (38), being a geometrical progression, can be written in the form

$$\langle \xi_0 \rangle = - \frac{i\boldsymbol{k}}{m} g_s^*(\boldsymbol{k}, \omega) \frac{1}{1 + \Phi(\boldsymbol{k}, \omega)}. \tag{40}$$

The expression for the dynamic structure factor which takes account of the relations (13) and (40) becomes

$$S(\boldsymbol{k}, \omega) = \frac{k^2}{n\pi\beta\omega^2} \operatorname{Re}\left\{\frac{g_s^*(\boldsymbol{k}, \omega)}{1 + \Phi(\boldsymbol{k}, \omega)}\right\}. \tag{41}$$

Further on, calculations are associated with finding the form of the function $\Phi(\boldsymbol{k}, \omega)$. We shall show that the function $\Phi(\boldsymbol{k}, \omega)$ can be expressed by the memory function $\Gamma(t)$ and the harmonic frequency of a quasiphonon calculated in the quasicrystal approximation. The memory function is determined from the integro-differential equation for the velocity autocorrelation function $K(t) \equiv \langle v(t)v(0)\rangle$, i.e.,

$$\frac{d}{dt} K(t) = - \int\limits_0^t \Gamma(t-t') K(t') dt'. \tag{42}$$

In Ref. [10] the following expression for $\Gamma(t)$ was obtained:

$$\Gamma(t) = \exp\left(-\frac{t}{\tau}\right) \frac{n}{3m} \int g(x) \nabla^2 \tilde{\tilde{V}}(\boldsymbol{x}-\boldsymbol{x}', t) g_s(\boldsymbol{x}', t) d\boldsymbol{x} d\boldsymbol{x}'. \tag{43}$$

Let us change in formula (39) the order of integration over t' and t'', and perform the reverse Fourier transformation of the functions $\tilde{V}[\boldsymbol{q}, t]$, $\tilde{\tilde{g}}[\boldsymbol{q}]$ and $g_s^*(k, t)$. We obtain

$$\Phi(\boldsymbol{k}, \omega) = \int\limits_0^\infty dt \int\limits_0^t dt' \left[\frac{n}{m} \int \tilde{\tilde{g}}(\boldsymbol{x}) \left(\frac{\boldsymbol{k}\boldsymbol{\nabla}}{k}\right)^2 \tilde{V}(\boldsymbol{x}-\boldsymbol{x}', t_0) g_s^*(\boldsymbol{x}', t') d\boldsymbol{x} d\boldsymbol{x}'\right] \times$$

$$\times \exp\left(-\frac{t'}{\tau}\right) g_s^*(\boldsymbol{k}, t) e^{i\omega t}. \tag{44}$$

We now take advantage of the circumstance that the integrand in Eq. (44) as a function of x has a sharp maximum at values of the argument approaching the radius of the solid sphere r_0 in the interatomic potential. Exchanging the function $\nabla g(r)(1-\cos \mathbf{kr})$ by $\nabla g(r)(1-\cos \mathbf{kr_0})$, and doing the integration over the angles, we find

$$\Phi(\mathbf{k}, \omega) = f(\mathbf{k}) \int_0^\infty dt \left\{ \int_0^t \Gamma(t')dt' \right\} g_s^*(\mathbf{k}, t) e^{i\omega t} \qquad (45)$$

where

$$f(\mathbf{k}) = 1 - 3 \frac{\sin \mathbf{kr_0}}{\mathbf{kr_0}} - 6 \frac{\cos \mathbf{kr_0}}{(\mathbf{kr_0})^2} + 6 \frac{\sin \mathbf{kr_0}}{(\mathbf{kr_0})^2} \qquad (46)$$

is the result of the angular integration of the function $(1-\cos kr_0)$.

Analogously, we transform the expression for the dispersion relation $\omega(k)$ obtained in the quasicrystal approximation:

$$\omega^2(k) = \frac{n}{m} \int \frac{(\nabla k)^2}{k^2} V(r) g(r) (1-\cos \mathbf{kr}) \, dr = f(k) \frac{n}{3m} \int \nabla^2 V(r) g(r) dr. \qquad (47)$$

It was shown in Ref. [2] that the latter approximation does not lead to any substantial errors within a broad range of values of wave vector k. We define the reduced memory function $\gamma(t)$,

$$\gamma(t) = \frac{\Gamma(t)}{\Gamma(0)} \; ; \; \Gamma(0) = \frac{n}{3m} \int \nabla \nabla V(r) g(r) dr. \qquad (48)$$

Taking account of the equations (41), (45), (47) and (48), yields, finally, the expression for the dynamic structure factor in the form

$$S(\mathbf{k}, \omega) = \frac{k^2}{m\pi\beta\omega^2} \text{Re} \left\{ \frac{g_s^*(\mathbf{k}, \omega)}{1 + \omega^2(\mathbf{k}) Q(\mathbf{k}, \omega)} \right\} \qquad (49)$$

where

$$Q(\mathbf{k}, \omega) = \int_0^\infty dt \left\{ \int_0^t \gamma(t') dt' \right\} g_s^*(\mathbf{k}, t) e^{i\omega t}. \qquad (50)$$

The denominator in formula (49), which determines the position and width of the quasiphonon peaks of the scattering function, is in conformity as regards form with the denominator in the expression for $S(\mathbf{k}, \omega)$ obtained in Ref. [2]. However, contrary to the case in formula (49), the function $Q(k, \omega)$ is defined as

$$Q(\mathbf{k}, \omega) = \int_0^\infty dt\, t g_s(\mathbf{k}, t) e^{i\omega t} \qquad (51)$$

what corresponds to substituting the memory function $\gamma(t)$ by unity. This exchange in Eq. (42) for the function $k(t)$ leads to a solution of the form $\cos(\omega, t)$, i.e. to the autocorrelation function of a harmonic oscillator without attenuation. We may say that whereas in Ref. [2] the atoms of the liquid are considered as diffunding non-attenuated oscillators, in this work account is also taken of the attenuation of these oscillators.

Formula (49) allows us to calculate the dynamic structure factor and evaluate the lifetime of cooperative excitations. Numerical calculations were made for argon at a temperature of 85.9°K. The function $g_s^*(k, t)$ was taken in the Gaussian approximation,

$$g_s^*(\boldsymbol{k}, t) = e^{-\frac{k^2}{4} a(t)}. \tag{52}$$

The function of the root mean square displacement of the equilibrium position $a(t)$ was chosen in the form (26). The function $\omega(\boldsymbol{k})$ obtained in Ref. [4] was used as the dispersion relation.

The results of calculations of $S(\boldsymbol{k}, \omega)$ for values of the parameter $D^* = \frac{1}{2}D$ are shown in Fig. 1. When the parameter D^* is decreased, the quasiphonon peaks become clear-cut,
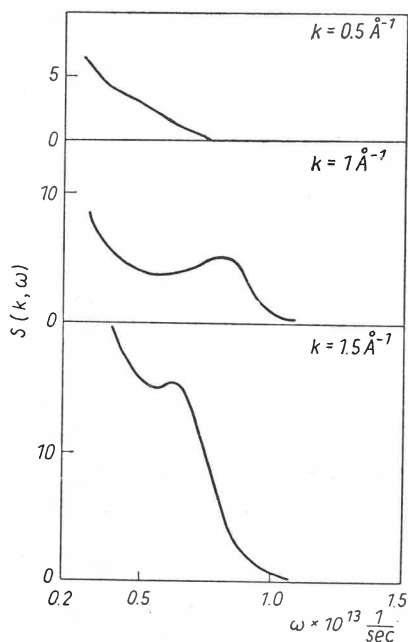

Fig. 1.

going over at the limit $D^* \to 0$ into δ-like singularities of the ordinary quasicrystals model. And in reverse — when D^* is increased, the peaks become diffused at all values of wave number k.

5. Discussion

The derived dynamic structure factor $S(\boldsymbol{k}, \omega)$ features the following peculiarities. At values of number k of the order of 1 Å^{-1} the function $S(\boldsymbol{k}, \omega)$ has a clear-cut maximum which is proof that cooperative excitations of the phonon or zero sound type appear in the system. When k grows, these excitations become attenuated. This conclusion is in agreement with the results of the studies by Hubbard and Beeby [2]. When k decreases, the zero sound is

414

also attenuated, while the width of the phonon peak, defined in Ref. [2], becomes smaller when $k \to 0$. The attenuation of the zero sound, what represents the cooperation of the independent particle excitations, was assigned to the disturbance of the vibration coherency of the atoms of the liquid at low frequencies because of diffusional motion. In the low frequency range there may be hydrodynamic excitations, with which we are not dealing with in this paper.

In their work, Hybbard and Beeby [2] state that the theory they developed underrates quasiphonon attenuation caused by the chaotic motion of the atoms of the liquid. In the approach presented here, this attenuation is apparently overrated, for a fitted parameter D^* has to be introduced. The diffusion coefficient of the equilibrium position should, according to physical intuition, be close to the diffusion coefficient D, since within long times the difference between the motion of the equilibrium position of a particle and it itself is insignificant. The necessity of introducing the parameter $D^* < D$ is connected with the fact that quasiphonon attenuation arises not so much because of the behaviour of the time correlation over long times as over times comparable with the period of atomic vibrations relative to the equilibrium position. Namely, in this time interval the microscopic behaviour of the particle must be described very accurately, whereas here the suggested approach is found to be only a rough approximation. Is it plausible to give a model of the function $a(t)$, for example, by assuming the following relations:

$$a(t) = \begin{cases} 6D^*(t-\tau_0) & \tau^* > t > \tau_0 \\ 6D(t-\tau_0) & t > \tau^* \\ 0 & t < \tau_0. \end{cases} \tag{53}$$

Here, yet another parameter, τ^*, is introduced, but the correct behaviour of the correlation function $g_s^*(\mathbf{k}, t)$ at $t \to \infty$ is ensured. The qualitative behaviour of the function $S(\mathbf{k}, \omega)$ remains like that presented earlier. It is necessary to note also that $S(\mathbf{k}, \omega)$, being a function of ω, is proportional to $1/\omega^2$ at small ω. Thus, the known sum rule,

$$\int_{-\infty}^{\infty} S(\mathbf{k}, \omega)d\omega = S(\mathbf{k}) \tag{54}$$

where $S(\mathbf{k})$ is the structure factor, is not satisfied. This is associated with the approximation (12), which is not true when $\omega \leqslant 3 \times 10^{13} \text{sec}^{-1}$, when the period of atomic vibrations relative to the equilibrium position is of the order of the delay time. For the sum rule (54) to be fulfilled, a theory is needed which would take in the entire frequency range of cooperative excitations in a liquid. The difficulties which are encountered in attempts to develop such a theory are primarily associated with the complex character of the cooperative motions in the transitory region.

In conclusion, the author takes the pleasure of thanking N. M. Plakida for helpful discussions.

REFERENCES

[1] P. Schofield, *Symposium on Neutron Inelastic Scattering*, SM-104/135, Copenhagen 1968.
[2] J. Hubbard, J. L. Beeby, *J. Phys.*, (*Solid State Phys.*), ser. 2, **2**, 556 (1969).
[3] G. Kemeny, *Ann. Phys.*, **53**, 1 (1969).

[4] V. B. Prezzhev, *Preprint Joint Institute for Nuclear Research*, R 4-4502, Dubna 1969.
[5] M. A. Leontovich, L. I. Mandelshtam, *Zh. Eksper. Teor. Fiz.*, **7**, 438 (1937).
[6] Ya. I. Frenkel *Kineticheskaya teoriya zhidkostei*, Sobranie izb. trudov, **3**, 1959.
[7] Chang-Hyun Chung, Sidney Yip, *Phys. Rev.*, **182**, 323 (1969).
[8] L. Van Hove, *Phys. Rev.*, **95**, 249 (1954).
[9] *Thermal Neutron Scattering*, edited by P. A. Egelstaff, Academic Press Juc., New York 1965.
[10] K. S. Singwi, A. Sjölander, *Phys. Rev.*, **167**, 152 (1968).