molecular parameters, according to the model of Cohen and Turnbull,[33] who suggest that the fluidity of a liquid is given by the possibility of correlations in free volumes similarly to the Rice normal-mode analysis of diffusion in crystals.[34] In fact the pseudo-activation energy of the process should vary with the molecular parameters of the tracers only insofar as its diameter increases much over the diameter of the solvent molecule. Where the Cohen-Turnbull theory is very rough indeed is in the mechanism by which the diffusing molecule moves once the step has been made possible by the free-volume fluctuations. In this respect also the refinement by Naghizadeh[35] does not give any better improvement and leaves $D\propto 1/\sqrt{m_2}$.

Probably the free movement in the enlarged cage should be replaced by a quasi-Brownian motion, but this is not a simple change in the Cohen-Turnbull theory, since it will involve the condition under which a free-volume fluctuation is useful for the diffusive steps to start. Incidentally, we must point out that the discrepancies found[20] between self-diffusion data and the Cohen-Turnbull theory are mainly connected with the pre-exponential factor which is given by just those features of the model we do not rely on.

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[33] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959).

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Elementary Excitations in Classical Liquids*

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Collective dynamical variables in classical liquids, having the character of longitudinal and transverse phonons, are proposed. A variational argument is used to determine their frequency spectrum; the sound velocities of long-wavelength modes are determined by elastic moduli of the liquid. Their lifetimes are estimated, and turn out to be of the order of 10^{-13} sec for normal liquids, but much longer for highly viscous liquids (glasses).

I. INTRODUCTION

THE question to be discussed here is: Do there exist collective variables, in classical liquids, analogous to longitudinal and transverse phonons in solids? The answer to this question is a qualified "yes". A physically reasonable basis can be found for the construction of longitudinal and transverse phonons in classical liquids, and it is possible even to calculate their frequency spectrum. The physical existence of these phonons is more doubtful. Except for liquids at very low temperatures, e.g., in the glassy state, their lifetimes are expected to be very short.

In this paper, I discuss the mathematical and physical basis for the construction of phonons in liquids, and I give some estimates of their dispersion and lifetimes.

II. DEFINITIONS

The concept of an elementary excitation is very familiar in connection with the theory of solids and also the theory of superfluids. In solids, for example, the dynamical behavior of a lattice is usually discussed by means of normal modes of vibration; these are the longitudinal and transverse phonons. Internal electronic states are described by excitons. Excitations in superconductors are described by Cooper pairs. Excitations in liquid helium are described by longitudinal phonons and by rotons. And so on.

All these elementary excitations are used in what is essentially a quantum-mechanical way. That is, creation and annihilation operators, in the language of second quantization, are used to characterize states of excitation of a system from its quantum-mechanical ground state.

The same language could be used, in principle, to describe classical systems also (e.g., liquid xenon); but a quantum-mechanical description is extremely cumbersome because of the high degree of excitation involved. For classical liquids it seems far simpler to use a characteristically classical description in the first place.

But then what classical quantities correspond to elementary excitations in quantum mechanics? The following definition appears reasonable.

First, we recall that a characteristic property of any elementary excitation (in quantum mechanics and in the classical limit) is that it varies approximately periodically with time. Let A be some property of the system,

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either a Heisenberg operator representing some observable, or else a classical function of coordinates and momenta. Then we shall refer to A as an *elementary excitation* if A varies periodically, or

$$dA/dt \cong i\omega A. \tag{1}$$

This definition can be used in classical mechanics just as in quantum mechanics; the only difference is in the prescription for calculating the time derivative.

III. ANALOG OF SECOND QUANTIZATION

The idea of an elementary excitation in a classical system is particularly useful if one can find a classical analog to the language and techniques of second quantization. An analog may be constructed as follows.

(It should be noted that the following scheme has not yet been put to the test of utility in actual calculations. Also, certain hypotheses of a mathematical kind have to be made, and these have not yet been verified by rigorous arguments. For these reasons, the following remarks must be regarded as plausible conjectures.)

Equations of motion in classical mechanics can always be written in operator form by using the Liouville operator L,

$$dA/dt = iLA. \tag{2}$$

The operator iL is the poisson bracket of the variable on which it operates, and the Hamiltonian function H. The imaginary unit i is introduced so that L is itself Hermitian with respect to a certain class of functions. (The mathematical theory underlying operator methods in classical mechanics has been developed by Koopman[1] and von Neumann.[2])

Suppose that A is an elementary excitation. Then it is approximately periodic. In operator notation, A obeys the equation

$$dA/dt = iLA \cong i\omega A \tag{3}$$

or

$$LA \cong \omega A. \tag{4}$$

Elementary excitations, according to our definition, are approximate eigenfunctions of the Liouville operator, and their frequencies are approximate eigenvalues.

For a further discussion of eigenfunctions and eigenvalues of L, see a recent article by the author.[3]

Let us now suppose that some reasonably simple set of approximate eigenfunctions has been found. These will be denoted by $\{\phi_\alpha\}$ where $\alpha = 1, 2, 3, \cdots$. If they are linearly independent, if there are enough of them, and if they have the right form, then they can be used as a basis for expansion. That is, a set of orthonormal functions may be constructed from them by the Schmidt process.

For this construction a metric is needed. The inner product of two functions ϕ_1 and ϕ_2 will be defined by

$$(\phi_1,\phi_2) = \langle \phi_1^* \phi_2 \rangle, \tag{5}$$

where $\langle \ \rangle$ denotes an equilibrium average (e.g., over a canonical ensemble at temperature T). As usual the asterisk denotes complex conjugate. By taking suitable linear combinations we can arrange that the set $\{\phi_\alpha\}$ is itself orthonormal.

From these we construct a new set of functions, in effect by taking "powers" of the ϕ_α,

$$\begin{aligned} \phi^{(1)}(\alpha) &= \phi_\alpha, \\ \phi^{(2)}(\alpha,\beta) &= \phi_\alpha \phi_\beta, \\ \phi^{(3)}(\alpha,\beta,\gamma) &= \phi_\alpha \phi_\beta \phi_\gamma, \end{aligned} \tag{6}$$

and so on. The functions $\phi^{(2)}(\alpha,\beta)$, which may be regarded as "double excitations," can be orthogonalized to the "single excitations" $\phi^{(1)}(\alpha)$ by the Schmidt process. Then the functions $\phi^{(3)}(\alpha,\beta,\gamma)$ describing "triple excitations" can be orthogonalized to the preceding ones, etc. This leads to a complete set of orthonormal functions which we denote by $\{\Psi_\nu\}$.

(The completeness of the resulting set must depend on a good initial choice of approximate eigenfunctions ϕ_α; and all we can do at present is conjecture that it is indeed possible to carry out the procedure as outlined.)

Now we can use the orthonormal set $\{\Psi_\nu\}$ to expand any arbitrary dynamical variable A, as follows:

$$A = \sum_\nu a_\nu \Psi_\nu, \tag{7}$$

where the coefficients are

$$a_\nu = \langle \Psi_\nu^* A \rangle. \tag{8}$$

In exactly the same way we can write the general equation of motion (2) in matrix form,

$$\frac{da_\nu}{dt} = i \sum_\mu L_{\nu\mu} a_\mu, \tag{9}$$

where all dynamical properties of the system are contained in the matrix $L_{\nu\mu}$,

$$L_{\nu\mu} = \langle \Psi_\nu^* L \Psi_\mu \rangle. \tag{10}$$

This is perhaps as close as one can come to the language and technique of second quantization in a classical theory. Classical observables are expanded into contributions from various "multiple excitations," and dynamical interactions are represented by matrix elements of the classical Liouville operator between different multiple excitations.

In the case of a harmonic oscillator, the classical language just described and the familiar quantum-mechanical language of second quantization are in close correspondence. The basic classical functions ϕ_α can be chosen as normal mode variables for a single oscillator.

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[1] B. O. Koopman, Proc. Natl. Acad. Sci. U. S. **17**, 315 (1931).
[2] J. von Neumann, Ann. Math. **33**, 587 (1932); **33**, 789 (1932).
[3] R. Zwanzig, Phys. Rev. **144**, 170 (1966).

These correspond in quantum mechanics to creation and annihilation operators for single excitations. The derived classical functions $\phi^{(2)}$, $\phi^{(3)}$, etc., correspond to products of creation and annihilation operators and therefore describe multiple excitations. The metric $\langle\ \rangle$ used here corresponds to a quantum-mechanical average over the ground state (vacuum). The classical Liouville operator corresponds to the quantum-mechanical commutator of an observable with the Hamiltonian.

One difference, which may turn out to be useful in quantum-mechanical applications as well as classical ones, is that we propose to consider excitations from the state of thermal equilibrium, rather than just from the ground state.

It is our hope that by suitable choice of the basic approximate eigenfunctions ϕ_α the off-diagonal elements of the matrix $L_{\nu\mu}$ will be "small." If this works out, then dynamical processes can be described mostly by diagonal elements of L, and the effects of off-diagonal elements can be accounted for by low-order perturbation theory. (For a slightly anharmonic oscillator this appears to be feasible, so it is natural to hope that the same procedure will work in less familiar circumstances.)

IV. ELIMINATION OF THE REFERENCE LATTICE

The problem of constructing phonon-like elementary excitations for liquids in analogy with those in solids is greatly complicated by lack of a reference lattice. Normal modes of solids are linear combinations of displacements of molecules from equilibrium lattice positions. But in a liquid no such equilibrium lattice exists. Because of this, a different approach has to be taken.

However, many characteristic properties of solids are shared by liquids, especially in the extreme case of a supercooled liquid or glass. For this reason it would be of great value to be able to describe solids and liquids in a uniform way by means of elementary excitations. This suggests that the first step should be the elimination of the reference lattice from the standard theory of solids. If this can be done, then perhaps the same method will work for liquids.

The procedure to be followed in this article is best explained by an extremely simplified example. It must be understood that this example is for illustration only, and is *not* intended to apply in a precise way to liquids.

Consider a single harmonic oscillator, with momentum p and position q, and let q_0 be the equilibrium position of the oscillator, or the reference lattice. The Hamiltonian is

$$H=(1/2m)p^2+\tfrac{1}{2}m\omega^2(q-q_0)^2, \qquad (11)$$

and the equations of motion are

$$\begin{aligned}\dot{q}&=p/m,\\ \dot{p}&=-m\omega^2(q-q_0).\end{aligned} \qquad (12)$$

Note that the equilibrium position appears in the Hamiltonian and in the equations of motion.

Now we change variables as follows. Instead of q we use the new variable F, the force on the oscillator,

$$F=-m\omega^2(q-q_0). \qquad (13)$$

On eliminating q, the equations of motion become

$$\begin{aligned}\dot{p}&=F,\\ \dot{F}&=-\omega^2 p.\end{aligned} \qquad (14)$$

These equations of motion, expressed in the variables p and F (or dp/dt), contain exactly the same information as when they are expressed in the variables q and p (or dq/dt); they consist of two simultaneous linear equations in two variables, and a complete solution requires specification of two initial values. But observe that the equilibrium position q_0 no longer appears in the equations. When the new variables are used, we do not need to know the location of the origin; we need instead the force, which is invariant to displacements of origin.

(This transformation can be made in a canonical way by scaling the variables appropriately, e.g.,

$$\begin{aligned}P&=-F/\omega,\\ Q&=p/m\omega.\end{aligned} \qquad (15)$$

It is easy to verify that the new P, Q are canonically conjugate.)

Oscillator normal modes, in the usual variables, are

$$\alpha=p\pm i\omega m(q-q_0) \qquad (16)$$

and they obey the equation

$$d\alpha/dt=\pm i\omega\alpha. \qquad (17)$$

In the new variables p and F the oscillator normal modes are

$$\phi=p\pm(1/i\omega)F \qquad (18)$$

and they obey the equation

$$d\phi/dt=\pm i\omega\phi. \qquad (19)$$

Clearly there is no reason to prefer one set of variables to the other.

The preceding remarks can be extended easily to all normal modes of coupled oscillators, and so to phonons in solids.

The procedure that will be used in this article to construct phonons in liquids is based on the same change of variables, from positions and momenta to momenta and forces. This change in variable is a way of eliminating the reference lattice from the theory of solids.

V. WARNINGS

The dynamical description of a system of interacting particles by means of momenta and forces, while evidently feasible and correct for harmonic oscillators, presents certain pitfalls in other cases. The two main problems are to express the Hamiltonian in terms of the new variables (i.e., to eliminate positions in favor of forces), and to find appropriate frequencies for the normal modes.

Probably the positions can be eliminated in the way described only when the system is sufficiently dense. Consider a system with the potential energy $U(\mathbf{R}_1,\mathbf{R}_2,\cdots,\mathbf{R}_N)$, which is a function of positions $\mathbf{R}_1,\mathbf{R}_2,\cdots,\mathbf{R}_N$. The corresponding forces are

$$\begin{aligned}\mathbf{F}_j&=-\nabla_{\mathbf{R}_j}U\\&=\mathbf{F}_j(\mathbf{R}_1,\mathbf{R}_2,\cdots\mathbf{R}_N).\end{aligned}\tag{20}$$

The hope is to solve these coupled equations for positions as functions of forces. This is easy when the system is a sufficiently dense lattice. But in a gas at low density, for example, the force on a molecule vanishes for most configurations, so that the desired inversion is not possible. A similar difficulty arises when the force on a molecule is the same for configurations that are not trivially different. Then the multiple-valued nature of the inverse causes serious trouble.

If, however, the inversion can be accomplished successfully, so that

$$\mathbf{R}_j=\mathbf{R}_j(\mathbf{F}_1,\mathbf{F}_2,\cdots,\mathbf{F}_N),\tag{21}$$

then we can eliminate positions to give the potential energy as a function of the forces,

$$U=U(\mathbf{F}_1,\mathbf{F}_2,\cdots,\mathbf{F}_N).\tag{22}$$

In the absence of any contradictory information, it will be assumed that the inversion is possible, so that the state of a liquid can be defined by momenta $\mathbf{p}_j$ and forces $\mathbf{F}_j$.

The other problem alluded to is that of finding appropriate frequencies. If one is able to start from an equilibrium lattice, defined by the configuration for which the forces vanish,

$$\mathbf{F}_j=0,\quad (j=1,2,\cdots,N),\tag{23}$$

then there is no intrinsic difficulty in expanding the potential energy in powers of F,

$$U=U_0+\tfrac{1}{2}\sum_{i\neq j}\sum \mathbf{A}_{ij}:\mathbf{F}_i\mathbf{F}_j+\cdots.\tag{24}$$

The result of the expansion can be found easily, for example, from the conventional treatment of lattice dynamics in terms of displacements.

But if one wants to avoid the use of a reference lattice, as in connection with liquids, some other procedure is required. The next part of this article discusses a possible method.

VI. VARIATIONAL CALCULATION OF EIGENFREQUENCIES

The frequencies associated with phonons in liquids, or other elementary excitations, can be found by using the definition of an elementary excitation as an approximate eigenfunction of the Liouville operator. Thus the frequencies are approximate eigenvalues.

There are basically only three ways of finding eigenfunctions and eigenvalues of a given operator. The first way, to solve the eigenvalue problem exactly with analytic techniques, is hardly feasible for liquids (although it works for harmonic lattices). The second way is to use perturbation theory. For a perturbational approach, some practical zeroth-order approximation is needed, and the only one which seems accessible at present is to treat molecules as free particles. But then the interactions, which are strong in liquids, would have to be accounted for by high-order perturbation theory. At present the third approach, which is to use a variational technique, seems preferable.

Some background material on variational calculations of approximate eigenfunctions of the Liouville operator, and a relevant application, have been described already in a recent article.[3]

Any variational calculation starts with the assumption that a trial function has some particular mathematical form. What kind of approximate trial function is most appropriate for liquids? Let us argue from analogy with solids.

We know already that for a harmonic lattice, the exact eigenfunctions have the form

$$\phi=p_{\mathbf{k}}+(1/i\omega_{\mathbf{k}})\dot{p}_{\mathbf{k}}.\tag{25}$$

The subscript $\mathbf{k}$ denotes a Fourier component in the reciprocal lattice, and $p_{\mathbf{k}}$ is the $\mathbf{k}$th component of the *linearized* momentum density,

$$p_{\mathbf{k}}=\sum_j p_j e^{i\mathbf{k}\cdot\mathbf{R}_j^0}.\tag{26}$$

The equilibrium position of the jth molecule is $\mathbf{R}_j^0$, and its momentum density is

$$J_{\mathbf{k}}=\sum_j p_j e^{i\mathbf{k}\cdot\mathbf{R}_j}.\tag{27}$$

Instead of the equilibrium position $\mathbf{R}_j^0$, which is not defined for a liquid, we use the actual position $\mathbf{R}_j$. Because of this, it will turn out that our trial function cannot reduce to the exact eigenfunctions for a harmonic lattice, unless we first linearize in deviations from equilibrium. This point is discussed in greater detail elsewhere.[4]

Analogy suggests that we use as a trial function for a liquid the quantity

$$\phi=J_{\mathbf{k}}+(1/i\omega_{\mathbf{k}})\dot{J}_{\mathbf{k}}.\tag{28}$$

The unknown coefficient $1/i\omega_{\mathbf{k}}$ will be treated as a variational parameter, and we shall see that $\omega_{\mathbf{k}}$ is in fact the approximate eigenvalue.

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[4] R. Nossal and R. Zwanzig (to be published).

So for the moment let us consider a particular class of trial functions having the general structure

$$\phi = A + a\dot{A}, \tag{29}$$

where a is a variational parameter. We require the function A to be either even or odd in momentum; and we require that its equilibrium average vanish,

$$\langle A\rangle = 0. \tag{30}$$

[It is evident that if $\langle A\rangle \neq 0$ then one cannot satisfy the eigenvalue equation $LA = \omega A$ even on the average unless ω itself vanishes.]

The variational principle has been discussed before[3]; here we only repeat the main equations. The quantity $[\omega]$ is defined by

$$[\omega] = \langle \phi^* L\phi\rangle / \langle \phi^*\phi\rangle, \tag{31}$$

where present notation is exactly the same as used before. The condition that $[\omega]$ be stationary with respect to arbitrary variations in the trial function ϕ,

$$\delta[\omega]/\delta\phi = 0 \tag{32}$$

leads directly to eigenfunctions and eigenvalues.

When the trial function (29) is put into (31) we obtain

$$i[\omega] = \frac{(a^* - a)\langle |\dot{A}|^2\rangle}{\langle |A|^2\rangle + aa^*\langle |\dot{A}|^2\rangle}. \tag{33}$$

In deriving (33) it is necessary to note that

$$\langle A^* LA\rangle = 0 \tag{34}$$

because of symmetry in momentum. (If we had allowed the function A to have both even and odd parts, this would not be true.) The extra time derivatives in (33) come from

$$i\langle A^* L\dot{A}\rangle = -\langle \dot{A}^*\dot{A}\rangle \tag{35}$$

which is a consequence of the Hermitian character of L.

On variation of the parameter a^*, the requirement that $[\omega]$ be stationary leads directly to

$$a = 1/i\omega. \tag{36}$$

When this is put back into (33), the eigenvalues are given by

$$\omega^2 = \frac{\langle |\dot{A}|^2\rangle}{\langle |A|^2\rangle}. \tag{37}$$

To each eigenvalue there is associated an eigenfunction

$$\phi = A \pm (1/i\omega)\dot{A}. \tag{38}$$

This has exactly the form of the trial function proposed in (28); and the frequencies are now determined.

VII. FREQUENCY SPECTRUM OF PHONONS IN LIQUID

The preceding results can be used to calculate the frequency spectrum of elementary excitations in a liquid.

Because of isotropy, it is convenient to use the familiar decomposition of Fourier components into longitudinal and transverse parts, by means of three orthogonal unit vectors $\epsilon_{\mathbf{k}\lambda}$, $(\lambda = 1,2,3)$. The longitudinal one is

$$\epsilon_{k3} = \mathbf{k}/|k|. \tag{39}$$

Components of the momentum density are

$$J_{\mathbf{k}\lambda} = \mathbf{J}_{\mathbf{k}}\cdot\epsilon_{\mathbf{k}\lambda}. \tag{40}$$

The eigenfunctions are

$$\phi_{\mathbf{k}\lambda} = J_{\mathbf{k}\lambda} + (i\omega_{\mathbf{k}\lambda})^{-1}\dot{J}_{\mathbf{k}\lambda} \tag{41}$$

and the corresponding eigenvalues are determined by

$$\omega_{\mathbf{k}\lambda}{}^2 = \langle |\dot{J}_{\mathbf{k}\lambda}|^2\rangle / \langle |J_{\mathbf{k}\lambda}|^2\rangle. \tag{42}$$

The $\mathbf{k}$ dependence of the eigenfrequencies, i.e., phonon dispersion, can be found by working out the averages in the preceding expression. This is particularly easy when the total intermolecular potential energy U can be expressed as a sum of pair potentials $u(R_{ij})$,

$$U = \tfrac{1}{2}\sum_i \sum_j u(R_{ij}). \tag{43}$$

In this case the frequency spectrum is determined by the radial distribution function $g(r)$ of the fluid as follows:

$$\omega_{\mathbf{k}\lambda}{}^2 = (m\beta)^{-1}(1 + 2\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}\cdot\boldsymbol{\varepsilon}_{\mathbf{k}3})k^2 - m^{-1}\rho\int d^3r\, g(r)(\cos\mathbf{k}\cdot\mathbf{r} - 1)(\boldsymbol{\varepsilon}_{\mathbf{k}\lambda}\cdot\boldsymbol{\nabla})^2 u(r). \tag{44}$$

(Here ρ is the number density N/V, and m is the mass of an individual molecule.)

The averages contained in (44) have already been evaluated in the limit of long wavelength.[5] In this limit we introduce longitudinal and transverse sound velocities C_λ, so that

$$\lim_{k\to 0} \omega_{k\lambda}{}^2/k^2 = C_\lambda{}^2. \tag{45}$$

These sound velocities are related to the high-frequency shear modulus G_∞ and the high-frequency bulk modulus K_∞,

$$\begin{aligned} C_1{}^2 = C_2{}^2 &= G_\infty/m\rho, \\ C_3{}^2 &= (\tfrac{4}{3}G_\infty + K_\infty)/m\rho. \end{aligned} \tag{46}$$

Numerical tables of the two elastic moduli, for corresponding states fluids, are provided in Ref. 5.

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[5] R. Zwanzig and R. Mountain, J. Chem. Phys. 43, 4464 (1965).

When (42) is used to calculate the frequency spectrum of phonons in a harmonic lattice, the correct long-wavelength longitudinal and transverse sound velocities are obtained. For shorter wavelengths, the present procedure leads to results slightly different from the correct phonon dispersion; this is a consequence of our use of the total momentum density in the trial function, rather than the linearized momentum density.

VIII. LIFETIMES

The lifetimes of elementary excitations in liquids may be estimated from experimental information about elastic moduli and viscosities. They are, as we shall see, essentially just the relaxation times associated with shear and bulk relaxation processes.

In the physical picture taken earlier in this article, the momentum density plays the role of an oscillator coordinate; the force density plays the role of an oscillator momentum. This suggests, as a rough guess, that the momentum density might obey the equation of motion of a damped oscillator,

$$\frac{d^2}{dt^2}J_{\mathbf{k}\lambda}=-\omega_{\mathbf{k}\lambda}^2J_{\mathbf{k}\lambda}-\frac{1}{\tau_{\mathbf{k}\lambda}}\frac{d}{dt}J_{\mathbf{k}\lambda}. \tag{47}$$

The quantity $\tau_{\mathbf{k}\lambda}$ is a lifetime. The frequency $\omega_{\mathbf{k}\lambda}$ is the same as before.

Now we use this equation of motion to calculate viscosity coefficients from time correlation function formulas.[5] The shear viscosity η is given by

$$\eta=V^{-1}\beta\lim_{\mathbf{k}\to 0}\int_0^\infty dt\,\langle S_{\mathbf{k}}^{xy}(0)S_{\mathbf{k}}^{xy}(t)\rangle, \tag{48}$$

where $\mathbf{S}_{\mathbf{k}}^{xy}$ is the (x,y) component of the stress tensor $\mathbf{S}_{\mathbf{k}}$, defined by the momentum conservation law

$$d\mathbf{J}_{\mathbf{k}}/dt=i\mathbf{k}\cdot\mathbf{S}_{\mathbf{k}}. \tag{49}$$

Note that (48) refers to the limit of long wavelength only. Let us take the vector $\mathbf{k}$ in the y direction, and look at the component of $\mathbf{J}_{\mathbf{k}}$ in the x direction, or $\mathbf{J}_{\mathbf{k}1}$. Then (49) becomes

$$d\mathbf{J}_{\mathbf{k}1}/dt=ik\mathbf{S}_{\mathbf{k}}^{xy}. \tag{50}$$

The equation of motion (47) is solved for $\dot{J}_{\mathbf{k}1}$ as a function of time; by (50) this gives the time dependence of $\mathbf{S}^{xy}$. The solution contains two initial values, $J_{\mathbf{k}1}(0)$ and $\dot{J}_{\mathbf{k}1}(0)$. The solution is put into (48), and the average over an initial equilibrium ensemble is performed.

The two coefficients in (48) are

$$\langle\mathbf{S}_{-\mathbf{k}}^{xy}(0)J_{\mathbf{k}1}(0)\rangle=0 \tag{51}$$

which vanishes by symmetry, and

$$\langle\mathbf{S}_{-\mathbf{k}}^{xy}(0)\mathbf{S}_{\mathbf{k}}^{xy}(0)\rangle=V\beta^{-1}G_\infty \tag{52}$$

which introduces the high-frequency shear modulus G_∞. On performing the time integral, we obtain finally

$$\eta=m\rho C_1^2\tau_1=G_\infty\tau_1, \tag{53}$$

where τ_1 is the long-wavelength limit of the transverse lifetime.

In exactly the same way we can calculate the longitudinal viscosity,

$$\eta_l=\tfrac{4}{3}\eta+\eta_v, \tag{54}$$

where η_V is the coefficient of bulk viscosity. The result is

$$\begin{aligned}\eta_l&=m\rho C_3^2\tau_3\\&=(\tfrac{4}{3}G_\infty+K_\infty)\tau_3,\end{aligned} \tag{55}$$

where τ_3 is the long-wavelength limit of the longitudinal lifetime.

Then if we have at hand numerical values for the viscosity coefficients and the elastic moduli, we can estimate the lifetimes of long-wavlength elementary excitations, from (53) and (55). Estimates have already been made,[6] though in a different connection, by Mountain and the author. It was found that for liquid argon, and similar materials, typical lifetimes are of the order of 10^{-13} sec. This seems sufficiently small, in comparison with periods of oscillation of the elementary excitations, that the concept of an elementary excitation may not be useful for liquid argon.

For a glassy material, however, viscosity coefficients are abnormally large compared with ordinary liquids and the corresponding lifetimes are large. For such materials, the concept of an elementary excitation of the sort discussed here has a definite physical meaning.

But even if the lifetimes are very short, perhaps as a result of strong anharmonic interactions between elementary excitations, the elementary excitations will themselves still be useful as a beginning step in more detailed theories.

ACKNOWLEDGMENT

The idea of using trial functions of the form (28) developed out of conversations with Dr. Ralph Nossal. I wish to express my deep gratitude here.

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[6] R. Mountain and R. Zwanzig, J. Chem. Phys. 44, 2777 (1966).