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A Theory of Phonon-Like Excitations
in Non-Crystalline Solids and Liquids

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Elementary excitations associated with atomic motion in non-crystalline solids and liquids are studied with particular attention paid to the dependence of their dispersion on local order. In doing this, an attempt is made to obtain an exact formal expression for an effective dynamical matrix giving the eigenfrequencies of phonons in a non-crystalline solid in terms of "effective pair-correlation functions". A brief remark is also given on the moment method and sum rules for the dynamic structure factor to study high-frequency collective motion in liquids. It is suggested that under certain restrictions the phonon-roton-like behavior of excitations as observed in liquid helium is likely to exist in almost all types of structure or topological disorder systems (amorphous and glassy solids, liquids, etc.). To substantiate this, a model one-dimensional system is chosen to show how a phonon dispersion curve in a crystal lattice is modified, as the partial disorder characterizing a structure disorder system is introduced. Such a local disorder is shown to give rise to a frequency gap which decreases with increasing local order and eventually vanishes in the case of complete order. This result is also in qualitative agreement with the pressure- and the temperature-dependence of the roton minimum energy in liquid helium. Simple numerical calculations are made to compare the obtained results with experiments for collective motion in liquid argon and also in liquid helium. Fairly good agreement is obtained.

§ 1. Introduction

In spite of growing interest in the physical properties of disordered systems, little theoretical work has been made on elementary excitations in non-crystalline solids such as amorphous and glassy solids.[1]~[3] Recent development of neutron scattering measurements has brought attention to collective motion in classical liquids.[4],[5] It has been suggested that high-frequency collective modes in simple liquids are rather similar to phonons in polycrystalline or amorphous solids.[6],[7] Historically, elementary excitations in disordered systems have been studied most extensively for quantum liquids or liquid helium.[8],[9] On the other hand, several works, both experimental[10]~[12] and theoretical,[2],[8],[13]~[18] have implied that dispersion curves of collective motion in simple liquids bear some resemblance to those of phonon-roton-like excitations as observed in liquid helium. It is worthy of note in this connection that the general behavior of phonon dispersion curves in solid helium, which is a typical quantum crystal, is little different from those in ordinary

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or classical solids.[19],[20]   The present authors have occasionally wondered why there has been little discussion on the interrelationship of phonon-like excitations in crystal lattices, non-crystalline solids and liquids, including quantum solids and quantum liquids themselves.

One of the most important points in studying the properties of phonon-like excitations in non-crystalline solids and liquids, being categorized as topological or structure disorder systems,[21] is probably the dependence of their dispersion on the degree of local ordering.   Almost all previous theoretical results for the dispersion of collective motion in classical liquids have been obtained by means of numerical calculations.[2],[8],[13]~[18]*)   With such numerical results, however, it is not always easy to understand the general aspects of physical situations.

It is the purpose of this paper to study phonon-like elementary excitations in non-crytstalline solids and liquids.   Generally speaking, two points should be taken into account in making a theoretical study of such a problem.   One is the structural disorder inherent in the systems and the other is atomic vibrations in disordered systems in general for which the conventional harmonic approximation may not always be guaranteed.   (This is particularly so in liquids.)   In this paper we are concerned with the first point, limiting our discussion to the properties of an effective dynamical matrix associated with an averaged phonon Greens's function over spatial configurations of atoms and employing the harmonic approximation.   Particular attention is paid to see how the dispersion of such excitation modes depends on local order.   An approach to the second point was made in a previous paper by the present authors[5] by using the self-consistent phonon scheme.[19]   In contrast to our previous work,[3] an attempt is made here to understand the general properties of elementary excitations which may have several things in common in almost all types of structure disorder systems, and also their bearing on crystal phonons as a limiting case of complete ordering. For this purpose, the formulation of the problem is made which aims at obtaining analytical forms for the frequency eigenvalues of excitation modes.

The outline of this paper is as follows: In the next section a compact self-consistent method is presented to calculate the effective dynamical matrix for the evaluation of phonon eigenfrequencies in a non-crystalline solid.   In § 3 the notion of effective pair-correlation functions is introduced to obtain an exact formal expression for the effective dynamical matrix.   A brief remark is given in § 4 on high-frequency collective motion in liquids, classical or quantum, using the moment method and sum rules and also on its similarity to phonons in non-crystalline solids.   In § 5 a brief discussion is given on the general properties of phonon-like elementary excitations in classical structure disorder systems and also in liquid helium.   In § 6, an analytically tractable one-dimensional model

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*) It does not appear that similar calculations have been done for non-crystalline solids. This is probably due to the lack of reliable information on pair-correlation functions in such disordered systems.

system is employed to obtain analytical expressions for dispersion curves of
excitation modes.   Results thus obtained are compared with experiments for liquid
argon and liquid helium.   The last section is devoted to a brief summary of the
the results contained in this paper.

§ 2.   Effective dynamical matrix for a non-crystalline solid

We consider a non-crystalline solid composed of atoms of a single species.
We study phonon-like elementary excitations in the system within the framework
of the harmonic or the renormalized harmonic approximation.   Let $u_\alpha(n)$ be the
α-component of the displacement vector $u(n)$ of an atom located at the equilibrium
position n.   Then, the time-independent equation of motion obeyed by the u's can
be written in the form

$$M\omega^2 u_\alpha(n) - \sum_{m(\neq n)} \sum_\beta K_{\alpha\beta}(nm) \{u_\beta(n) - u_\beta(m)\} = 0, \qquad (2\cdot1)$$

where ω is the circular frequency, M is the atomic mass and the K's are bare
or effective force constants.[*]   We shall hereafter use a symbolic notation, whenever
appropriate, to rewrite Eq. $(2\cdot1)$ as

$$(M\omega^2 - K)u = 0 \quad \text{or} \quad (\omega^2 - D)u = 0, \qquad (2\cdot2)$$

where

$$D = K/M \qquad (2\cdot3)$$

is the dynamical matrix determining the eigenfrequencies of phonons for a fixed
spatial configuration of atoms in the system.

From Eq. $(2\cdot2)$, a phonon Green's function g is defined by

$$g(\omega) \equiv g = (\omega^2 - D)^{-1}. \qquad (2\cdot4)$$

Let A be a quantity which contains the positions of atoms in the system as a
set of parameters.   We are then interested in an average value $\langle A \rangle$ of A, rather
than A itself, over all spatial configurations of the atoms in the systems.   We
define an effective dynamical matrix $\mathcal{D}$ by the equation

$$\langle g \rangle = (\omega^2 - \mathcal{D})^{-1}. \qquad (2\cdot5)$$

To set up the self-consistency condition for the determination of this quantity,
we write down an equation of motion for g as

$$g = \langle g \rangle + \langle g \rangle (D - \mathcal{D})g. \qquad (2\cdot6)$$

Also defined here are a transition matrix T and a wave matrix Ω:[22]

$$g = \langle g \rangle + \langle g \rangle T \langle g \rangle, \qquad (2\cdot7)$$

$$g = \Omega \langle g \rangle. \qquad (2\cdot8)$$

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[*] For a discussion of effective force constants associated with the anharmonicity of atomic
vibrations and also of the renormalized harmonic approximation, see, for example, Refs. 19) and 37).

Equations obeyed by these two quantities are

$$T = D - \mathcal{D} + (D - \mathcal{D}) \langle g \rangle T, \tag{2.9}$$

$$\mathcal{Q} = 1 + \langle g \rangle (D - \mathcal{D}) \mathcal{Q}, \tag{2.10}$$

with

$$T = (D - \mathcal{D}) \mathcal{Q}. \tag{2.11}$$

Then, the condition to be satisfied by T,

$$\langle T \rangle = 0 \tag{2.12}$$

can be expressed in terms of $\mathcal{Q}$ as follows:

$$\mathcal{D} = \langle D\mathcal{Q} \rangle \quad \text{with} \ \langle \mathcal{Q} \rangle = 1. \tag{2.13}$$

Equations (2·10) and (2·13) determine the effective dynamical matrix $\mathcal{D}$ (or the self-energy of phonons) in a self-consistent manner.

The lowest order approximation to Eq. (2·13) is

$$\mathcal{D} \simeq \langle D \rangle \langle \mathcal{Q} \rangle = \langle D \rangle. \tag{2.14}$$

This is equivalent to setting $\langle (\omega^2 - D)^{-1} \rangle = (\omega^2 - \langle D \rangle)^{-1}$ or $\langle D^p \rangle = \langle D \rangle^p$ ($p = 1, 2, 3, \cdots$). We hereafter assume that the distribution of the atoms in the system is homogeneous. The quantity $\mathcal{D}$ then becomes diagonal with respect to k (in the momentum representation). An explicit form of Eq. (2·14) is obtained by comparing Eq. (2·2) with Eq. (2·1). It is given by

$$\mathcal{D}_{\alpha\beta}(k) = \left\langle (1/N) \sum_{n} \sum_{m(\neq n)} D_{\alpha\beta}(nm) \left[1 - \exp\{-ik \cdot (n - m)\} \right] \right\rangle, \tag{2.15}$$

where N is the total number of the atoms in the system. Equation (2·15) is easily calculated to be[23]

$$\mathcal{D}_{\alpha\beta}(k) = (\rho/M) \int dn\, g_2(on) K_{\alpha\beta}(on) \{1 - \exp(ik \cdot n)\}. \tag{2.16}$$

Here, $g_2(on)$ is the pair correlation function normalized to unity at large $|n|$,[24] and we have taken the origin of the coordinate (denoted by the index "zero") to be one of the equilibrium position of the atoms. Also, $\rho = N/V$ is the number density of the atoms in which V is the total volume of the system. It is of interest to note that Eq. (2·16) reduces to a conventional expression for the dynamical matrix for a crystal lattice if all the atoms in the system are taken to be definitely located at lattice points, namely

$$\rho g_2(on) = \sum_{m(\neq 0)} \delta(m - n). \tag{2.17}$$

In this sense Eq. (2·16) can be called a quasi-crystalline approximation.[25]

§ 3. Effective pair correlation functions

Equation (2·16) has been derived using the lowest order approximation in which effects of higher order correlations other than pair correlations have been neglect-

ed. In this section an attempt is made to express Eq. (2·13) in terms of effective pair correlation functions in which the effects of the higher order correlations are exactly taken into account. For this purpose, we first take the k-representation of Eq. (2·13). It is given by

$$\langle\!\langle k|D\Omega|k\rangle\!\rangle = \langle k|\mathcal{D}|k\rangle \equiv \mathcal{D}(k)$$
$$= \langle N^{-1} \sum_{nn'} \sum_{m(\neq n)} D(nm)\{\Omega(nn') - \Omega(mn')\} \exp\{-ik\cdot(n-n')\}\rangle. \quad (3\cdot1)$$

For the evaluation of the average we introduce m-body $(m \geq 1)$ probability function[*]

$$P_m(n_1 n_2 \cdots n_m)\, dn_1 dn_2 \cdots dn_m$$

with

$$\iint \cdots \int P_m(n_1 n_2 \cdots n_m)\, dn_1 dn_2 \cdots dn_m = 1, \quad (3\cdot2)$$

which denotes the probability of finding the first atom in the system in the volume element dn_1 centered about n_1 and at the same time the second atom is in dn_2 at n_2 and so forth. Also introduced here are the conditional probability distribution functions

$$P_m(n_{l+1}n_{l+2}\cdots n_m / n_1 n_2 \cdots n_l) = P_m(n_1 n_2 \cdots n_m)/P_l(n_1 n_2 \cdots n_l). \quad (l<m) \quad (3\cdot3)$$

A useful relationship between the conditional probabilities is

$$P_m(n_{l+1}n_{l+2}\cdots n_m / n_1 n_2 \cdots n_l) = P_{l+1}(n_{l+1}/n_1 n_2 \cdots n_l) P_m(n_{l+2}n_{l+3}\cdots n_m / n_1 n_2 \cdots n_{l+1}).$$
$$(3\cdot4)$$

Then, the average value of the quantity $A \equiv A(n_1 n_2 \cdots n_N)$ is written explicitly as

$$\langle A(n_1 n_2 \cdots n_N)\rangle \equiv \langle A\rangle$$
$$= \iint \cdots \int dn_1 dn_2 \cdots dn_N P_N(n_1 n_2 \cdots n_N) A(n_1 n_2 \cdots n_N). \quad (3\cdot5)$$

Similarly, a conditional average $\langle A\rangle_{n_1 n_2 \cdots n_m}$ of A with one or more atomic positions held fixed is defined by

$$\langle A\rangle_{n_1 n_2 \cdots n_m}$$
$$= \iint \cdots \int dn_{m+1} dn_{m+2} \cdots dn_N P_N(n_{m+1}n_{m+2}\cdots n_N / n_1 n_2 \cdots n_m) A(n_1 n_2 \cdots n_N).$$
$$(3\cdot5')$$

Conditional probability distributions may be converted to conditional number density distributions or correlations by multiplying by the number of atoms:

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[*] The probability function $P_m(n_1 n_2 \cdots n_m)$ here is connected with the m-body distribution functions $F_m(n_1 n_2 \cdots n_m)$ defined in Ref. 24) by the relation $P_m(n_1 n_2 \cdots n_m) = (1/V^m) F_m(n_1 n_2 \cdots n_m)$. See also Ref. 25) for a more detailed discussion on the averaging procedure.

$$N_1(n_1) = NP_1(n_1) = N/V = \rho \,(\text{homogeneous system}), \tag{3.6a}$$

$$N_2(n_2/n_1) = (N-1)P_2(n_2/n_1) \simeq NP_2(n_2/n_1), \tag{3.6b}$$

$$N_3(n_3/n_1n_2) = (N-2)P_3(n_3/n_1n_2) \simeq NP_3(n_3/n_1n_2), \quad \text{etc.} \tag{3.6c}$$

We give, in passing, a relationship between the pair correlation function $g_2(nm)$ $= V^2P_2(nm)$ and the "second-order conditional number density function" $N_2(n/m)$,[*]

$$\rho g_2(nm) = N_2(n/m). \tag{3.7}$$

Using Eqs. $(3.2) \sim (3.7)$, we can rewrite Eq. (3.1) as

$$\mathcal{D}(k) = \rho \int dn\, g_2(on) D(on) \{f(on, k) - f(no, k) \exp(ik \cdot n)\}, \tag{3.8}$$

where

$$f(nm, k) = \int dl\, N_3(l/mn) \langle \Omega(nl) \rangle_{mnl} \exp\{-ik \cdot (n-l)\}. \tag{3.9}$$

Incidentally, an explicit form of the second part of Eqs. (2.13) is given by

$$\int dl\, N_2(l/n) \langle \Omega(nl) \rangle_{nl} \exp\{-ik \cdot (n-l)\} = 1. \tag{3.10}$$

In view of this, it is convenient to re-express Eq. (3.8) in the form

$$\mathcal{D}(k) = \rho \int dn\, g_2{}^*(on) D(on) \{1 - \exp(ik \cdot n)\}, \tag{3.11}$$

where

$$g_2{}^*(on) = g_2(on) f^*(n, k). \tag{3.12}$$

Here, the quantity $f^*(n, k)$ is defined by the equation

$$f(on, k) - f(no, k) \exp(ik \cdot n) = f^*(n, k)\{1 - \exp(ik \cdot n)\}. \tag{3.13}$$

Equation (3.11) with $g_2{}^*(on)$ replaced by $g_2(on)$ has exactly the same form as Eq. (2.16). The quantity $g_2{}^*(on)$ thus defined can be thought of as an effective pair carrelation function in which effects of three-body and higher order correlation functions have been taken into account. It is seen from Eqs. (3.9) and (3.10) that approximating $N_3(l/mn)$ and $\langle \Omega(nl) \rangle_{mnl}$ by $N_2(l/n)$ and $\langle \Omega(nl) \rangle_{nl}$, respectively, is equivalent to setting $g_2{}^*(on) = g_2(on)$. Due to the presence of the factor $\Omega \equiv \Omega(\omega)$, the effective pair correlation function g^* or each element of the effective dynamical matrix $\mathcal{D}$ generally becomes complex, thus giving finite lifetime to excitation modes.[**]

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[*] Equation (3.7) is readily obtained by using the relations $V^2P_2(nm) = V^2P_1(m)P_2(n/m)$ $= (V/N)N_2(n/m)$.

[**] The imaginary part of $\mathcal{D}$ appears through the factor $\Omega(\omega \pm i\varepsilon)$ $(\varepsilon \to 0_+)$ when calculating various quantities of physical interest.

We give a brief comment on the result obtained above. Once the pair-correlation function and the pair potential (from which the force constants are derived) are known, Eq. (2·16) can be used to calculate the eigenfrequencies of phonon-like excitation modes in disordered systems *with no adjustable parameter*. This has been done previously for liquid argon, with the result in fair agreement with experiment. We can also use Eq. (3·11) for the same purpose, but with $g_2{}^*$ taken as an adjustable parameter to get better agreement with experiment. The pair-correlation function $g_2{}^*$ thus determined then is generally different from the pair correlation function g_2 obtainable from the X-ray or the the neutron diffraction. In this sense, for example, the notion of the effective pair-correlation function may be used. It may be interesting to examine the difference between $g_2{}^*$ and g_2 for various types of disordered systems.

§4. Moment method, sum rules and elementary excitations in liquids

We have shown in the previous paper[3] that Eq. (2·16) can also be applied to collective motion in simple liquids, provided we look at short-time behavior of atomic motion. Underlying fact in using such a physical reasoning is that as far as the response to a high-frequency external disturbance is concerned, atoms in liquids look something like those in solids.[26] Here, Eq. (2·16) is simply related to the instantaneous elastic properties of liquids. It is worthy of note in this connection that for simple liquids Eq. (2·16) or its variant has been derived by several workers using various methods, which do not always appear to be akin to one another.[27),2),8),13)~18] In this meaning such a result can be considered as a fairly general expression for the dispersion of elementary excitations in liquids as well as in non-crystalline solids. We do not intend here to dwell upon the interrelationship of these methods. We shall merely give a brief remark that Eq. (2·16) can also be derived from moments or sum rules for the dynamical structure factor of liquids. Several points to be touched upon herein is not intended to be original, but they are to be considered rather subsidiary to the results obtained in our previous work.[3]

We begin the discussion of this section by defining the dynamical structure factor $S(k, \omega)$ of a liquid by the equation

$$S(k, \omega) = (1/2\pi) \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \rho(-k, 0)\rho(k, t)\rangle_T, \qquad (4·1)$$

where $\rho(k, t) = \exp(iHt)\rho(k)\exp(-iHt)$,[*] in which

$$\rho(k) = \sum_n \exp(-ik \cdot n) \qquad (4·2)$$

is the Fourier transform of the density of atoms in the system, and the angular bracket with subscript T denotes a canonical average at temperature T. De

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[*] We use units with $\hbar = 1$.

Gennes computed the moments of $S(k, \omega)$ in the classical approximation.[28]~[30]   It is to be noticed that the classical limit of $S(k, \omega)$ yields a function that is symmetrical in ω, so all of its odd moments vanish.   The results obtained by him can be written in the form

$$\int_{-\infty}^{\infty} d\omega\omega^2 S(k, \omega) = k^2 k_B T/M , \tag{4.3}$$

$$\int_{-\infty}^{\infty} d\omega\omega^4 S(k, \omega) = (k^2 k_B T/M)$$

$$\times \left[(3k^2 k_B T/M) + (\rho/M) \int dn g_2(on) \nabla\nabla v(on)\{1 - \exp(ik\cdot n)\} \right], \tag{4.4}$$

where k_B is the Boltzmann constant, T the absolute temperature and $v(on)$ is the interatomic potential.   To extract a single elementary excitation, or quasi-particle, of momentum k associated with the density fluctuation, we take $S(k, \omega)$ to be of the form[31]

$$S(k, \omega) = Z(k, \omega) \{\delta(\omega - \omega^*(k)) + \delta(\omega + \omega^*(k))\} + S^{(1)}(k, \omega), \tag{4.5}$$

where $\omega^*(k)$ is the energy of this quasi-particle mode and $S^{(1)}(k, \omega)$ is the contribution from all the other modes including two and more quasi-particles. Inserting Eq. (4.5) into Eqs. (4.3) and (4.4) and neglecting terms involving $S^{(1)}(k, \omega)$, we obtain[*]

$$\omega^*(k)^2 = (3k^2 k_B T/M) + (\rho/M) \int dn g_2(on) \nabla\nabla v(on)\{1 - \exp(ik\cdot n)\}. \tag{4.6}$$

The first term of this equation represents the mean thermal energy.   Equation (4.6) without this term has a form similar to Eq. (2.16).   The force constants appearing in Eq. (2.16) are generally derived by the second derivatives of an interatomic potential.   It is shown that if both of the pair correlation function and the pair-potential are spherically symmetric, the dynamical matrix $\mathscr{D}$ becomes diagonal.[8]   Then, it is seen that one of diagonal elements yielding the squared-eigenfrequencies of longitudinal phonons is equivalent to the second term on the right-hand side of Eq. (4.6).

Following Miller, Pines and Nozières,[31] we further remark that the Bijl-Feynman formula[32],[33]

$$\epsilon(k) = k^2/2MS(k) \tag{4.7}$$

for the energy $\epsilon(k)$ of elementary excitations in liquid helium can also be obtained from the f-sum rule[31] for the dynamic structure factor defined by

$$\mathscr{S}(k\omega) = (1/\rho) \sum_{\alpha(\neq 0)} |\langle\alpha|\rho(k)|0\rangle|^2 \delta(\omega - \omega(\alpha)). \qquad (\omega(\alpha) > 0) \tag{4.8}$$

Here, $\langle\alpha|\rho(k)|0\rangle$ is the matrix element of the density fluctuation $\rho(k)$ of the

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[*] The result thus obtained using the moment method generally describes the short-time behavior of liquids or high-frequency collective modes.

liquid at $T=0°K$ taken between the ground state $|0\rangle$ and the excited state $|\alpha\rangle$, to which it is coupled, while $\omega(\alpha)$ is the corresponding excitation frequency. Two moments of $\mathscr{S}(k, \omega)$ are of interest. These are[31),34),35)]

$$\int_0^\infty d\omega \mathscr{S}(k, \omega) = S(k), \tag{4.9}$$

$$\int_0^\infty d\omega \omega \mathscr{S}(k, \omega) = k^2/2M. \tag{4.10}$$

Equation (4.10) is a statement of the f-sum rule. As in the previous case, we put

$$\mathscr{S}(k, \omega) = Z'(k, \omega)\delta(\omega - \epsilon^*(k)) + \mathscr{S}^{(1)}(k, \omega). \tag{4.11}$$

Inserting this into Eqs. (4.9) and (4.10) and neglecting terms involving the factor $\mathscr{S}^{(1)}(k, \omega)$, we obtain Eq. (4.7).

The interrelationship between the quantities $S(k, \omega)$ and $\mathscr{S}(k, \omega)$ defined above are seen by observing the fact that Eq. (4.1) for $T=0°K$, when expressed in the form of the so-called Fermi's golden rule, reduces to Eq. (4.8) (apart from unimportant factors). Thus, it is likely that Eqs. (2.16) or (4.6) and (4.7) are of the same nature in the sense that they are derivable from the sum rule for the dynamical structure factor and that dispersion curves of excitations obtainable from these equations have similar forms.[9),2),8),14)~18)]

§ 5. Qualitative properties of the dispersion of excitation modes in structure disorder systems and in liquid helium

We are concerned here with the qualitative properties of the eigenfrequencies of excitation modes given by Eq. (2.16) or (3.11). We first study the interrelationship between such phonon-like excitations and crystal phonons. Equation (2.16), when combined with Eq. (2.17), reduces to

$$\mathscr{D}(k) = (1/M)\sum_{n(\neq 0)} K(on)[1 - \exp(ik \cdot n)] \equiv D_L(k). \tag{5.1}$$

This is the conventional expression for the dynamical matrix for a crystal lattice. In terms of this quantity, we re-express $\mathscr{D}(k)$ as

$$\mathscr{D}(k) = D_L(k) + \varDelta\mathscr{D}(k), \tag{5.2}$$

where

$$\varDelta\mathscr{D}(k) = \mathscr{D}(k) - D_L(k). \tag{5.3}$$

As is well known, the eigenvalue of the dynamical matrix $D_L(k)$ is a periodic function of k. Therefore, it vanishes at reciprocal lattice points. The eigenvalues of the matrix $\varDelta\mathscr{D}(k)$, however, generally remain finite at, or in the vicinity of, a lattice point $k=k_0$ in the reciprocal lattice space. Due to this fact, there arises a frequency gap which decreases with increasing local ordering and eventually

vanishes in the limit of complete order corresponding to the crystal lattice. This result is to be expected from the lack of a kind of selection rule since the periodicity of the field is destroyed in our system. Thus, a dispersion curve for frequency eigenvalues of, say, longitudinal modes may have a form as depicted in Fig. 1. Such a result is reminiscent of phonon-roton-like modes in liquid helium.[86] It may be concluded that a dispersion curve as shown in Fig. 1 is rather common to phonon-like elementary excitations in almost all types of non-crystalline solids and classical liquids. In fact, such a behavior has been observed experimentally for liquid lead.[10] Several numerical calculations of Eq. (2·16) or its variant[2),3),13)~18)] and also the results of computer simulation of molecular dynamics in classical liquids[12)] have given similar results. According to the result obtained above, more than one minima in the dispersion curve can appear. Such a behavior may exist in the case of amorphous solid. In the case of classical liquids, however, the effect of single-particle excitations and the other effects giving rise to phonon damping become more and more important in the high-wave number region, so only the first minimum as shown in Fig. 1 may be well observable.

Finally, a brief remark is given on elementary excitations in liquid helium. We observe that Eq. (2·16) has been used previously as a phonons-in-amorphous-solids approach to collective motion in classical liquids.[2),3)] In analogy with this case, a phonon-in-amorphous-quantum-solids approach may be used for elementary excitations in quantum liquids. Here, this is to replace the force constant K in Eq. (2·16) by the second derivatives of an effective potential[19),87)] in which both of the anharmonicity of atomic vibrations and the short-range correlation effect resulting from large zero-point motion and strong repulsive part of the interatomic potential,[88),89)] respectively, have been incorporated. Thus, the main result obtained above may be considered to hold in the case of amorphous quantum solids or quantum liquid. Without detailed numerical calculation, we may conclude that the eigenvalues of the dynamical matrix thus obtained, corresponding to longitudinal phonons, as a function of k also have a form as shown in Fig. 1. We now make an attempt to examine the dependence of the frequency gap or the roton energy minimum Δ on the local order, taking the case of liquid helium as an example. Several experiments have shown that in this case the quantity Δ decreases as an external pressure increases[40)~45)] and also that it decreases with increasing temperature.[42),45)] It has also been shown experimentally that the first maximum of the radial distribution function in liquid helium becomes sharper and higher as
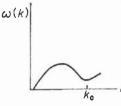

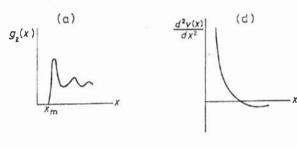Fig. 1. Schematic feature of phonon eigenfrequencies $\omega(k)$ in a structure disorder system.

temperature as well as external pressure increases.[46],[47] These results are in qualitative agreement with our result that the quantity Δ decreases as the local order increases.

§ 6. An analytically tractable one-dimensional model system

To substantiate the results obtained in the previous two sections, an analytically (rather than numerically) tractable model is required to get more physical insight into the problem. Our particular intention here is to obtain an analytically closed expression for $\omega(k)$, with attention paid to its dependence on the local order in structure disordered systems. For this purpose, we consider a one-dimensional (1-D) system. Equation (2·16) then reduces to

$$\mathcal{D}(k) = \omega(k)^2 = (2\rho/M) \int_0^\infty dx\, g_2(x)\, (d^2v(x)/dx^2)\, \{1 - \cos(kx)\}. \quad (6\cdot1)$$

We want to obtain an approximate simple analytical expression for the quantity $g_2(x)d^2v(x)/dx^2$ which makes the above integral analytically tractable, yet it contains an essential feature of the problem. We observe the fact that the product $g_2(x)v(x)$ or $g_2(x)d^2v(x)/dx^2$ is very sensitive to the value of $g_2(x)$ at small values of x. In the limit $x \to 0$, $g_2(x)$ vanishes sufficiently strongly that the product vanishes. Thus, the peak value of such a quantity is obtained for x just above x_m, when x_m is the smallest value of x for which $g_2(x) \sim 0$. This behavior is illustrated in Fig. 2. It is seen that the range of the product is roughly the range of $v(x)$, and the long-range behavior of $g_2(x)$
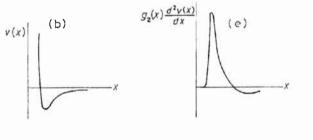
Fig. 2. Illustration of the functions $g_2(x)$, $v(x)$, $dv(x)/dx$, $d^2v(x)/dx^2$, and $g_2(x)d^2v(x)/dx^2$. These curves are of qualitative significance only.
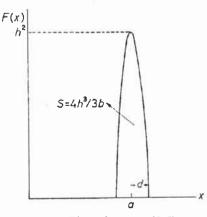
Fig. 3. Plot of curve (6·2).

does not affect it. A dominant contribution to the product $g_2(x)d^2v(x)/dx^2$ therefore comes from the region around $x=a$, where a is the average distance of nearest neighbour atoms in our model system. With these situations in mind, we put (see Fig. 3)

$$\rho g_2(x)(d^2v(x)/dx^2) \equiv F(x) = \begin{cases} h^2 - b^2(x-a)^2 & \text{for} \quad a-(h/b)<x<a+(h/b), \\ 0 & \text{otherwise}. \end{cases}$$

$$(6\cdot 2)$$

The area S occupied by $F(x)$ is

$$S = 4h^3/3b, \qquad (6\cdot 3)$$

which is taken to be constant. Insertion of Eq. (6·2) into Eq. (6·1) gives

$$\omega^2(k) = \frac{2K_L}{M}\left[1 - \frac{3}{2}\left\{\frac{\sin(kd)}{kd} + \frac{\cos(kd)}{(kd)^2} - \frac{\sin(kd)}{(kd)^3}\right\}\right]\cos(ka), \qquad (6\cdot 4)$$

where

$$d = h/b \qquad (6\cdot 5)$$

is the half-width of the curve of $F(x)$. We will take the quantity d as an adjustable parameter to specify the local order of the system.

We are solely interested in the case in which d is much smaller than a, namely $d \ll a$. As in the case for Eq. (5·2), we rewrite Eq. (6·4) as

$$\omega(k) = [\omega_L(k)^2 + \varDelta\omega(k)^2]^{1/2}. \qquad (6\cdot 6)$$

Here,

$$\omega_L(k)^2 = (2K_L/M)\{1 - \cos(ka)\} \qquad (6\cdot 7)$$

is the squared-eigenfrequency of phonons when the system constitutes a crystal lattice with lattice constant a. The quantity

$$\varDelta\omega(k)^2 = \frac{2K_L}{M}\left[1 - \frac{3}{2}\left\{\frac{\sin(kd)}{kd} + \frac{\cos(kd)}{(kd)^2} - \frac{\sin(kd)}{(kd)^3}\right\}\right]\cos(ka) \qquad (6\cdot 8)$$

thus defined is called here a frequency gap. It is expanded in powers of kd as follows:

$$\varDelta\omega(k)^2 = \frac{2K_L}{M}\frac{3}{2}\sum_{p=1}^{\infty}(-1)^{p-1}\frac{1}{(2p+1)!}\frac{2p+2}{2p+3}(kd)^{2p}\cos(ka). \qquad (6\cdot 9)$$

Thus, the quantity $\varDelta\omega(k)^2$ is shown to be directly conneted with the width d. Here, an increase of the local order corresponds to a decrease of d and therefore of $\varDelta\omega(k)^2$.

We now investigate the general behavior of phonon dispersion curves given by Eq. (6·4) or (6·6) as a function of k. In the long wavelength region the contribution of $\varDelta\omega(k)^2$ to $\omega(k)^2$ can be neglected as compared with $\omega_L(k)$, and

therefore $\omega(k)$ is little different from $\omega_L(k)$. Such a result is of course to be expected from the Debye theory. In this region, where the continuum model holds, phonon dispersion curves are generally insensitive to the microscopic structure of the system. Of particular interest here is the behavior of $\omega(k)$ near $k=2\pi/a$. It is seen that the phonon eigenfrequencies remain finite in the vicinity of $k=2\pi/a$ due to the presence of the factor $\Delta\omega(k)^2$. It is then shown that the function $\omega(k)$ has a minimum in this region with a gap which decreases as the local order increases. As in the case in § 5, let k_0 be the value of k at which such a minimum takes place. We then obtain Taylor's series for $\omega(k)$:

$$\omega(k) \simeq \omega(k_0) + (1/4\omega(k_0))[d^2\omega(k)^2/dk^2]_{k=k_0}(k-k_0)^2 + \cdots$$
$$= \Delta + \{(k-k_0)^2/2\mu\}, \tag{6·10}$$

where

$$\Delta = \omega(k_0) \tag{6·11}$$

is the frequency gap and

$$\mu = 2\omega(k_0)/[d^2\omega(k)^2/dk^2]_{k=k_0} \tag{6·12}$$

is an effective mass of the elementary excitations. Equation (6·12) is the same as the Landau formula for elementary excitations in liquid helium.[86]

We now obtain explicit expressions for k_0, Δ and μ defined above. For this purpose, we approximate Eq. (6·9) by

$$\Delta\omega(k)^2 = (2K_L/M)\{(1/5)(kd)^2 - (3/280)(kd)^4 + \cdots\}\cos(ka)$$
$$\simeq (2K_L/M)(1/5)(kd)^2\cos(ka). \tag{6·13}$$

Inserting this into Eq. (6·4), we obtain an approximate value of k_0 and Δ, correct to the first order in (d/a):

$$k_0 a \simeq 2\pi - (4\pi/5)\gamma^2/[1 - \{(4\pi^2/5) + (2/5)\}\gamma^2]$$
$$\simeq 2\pi - (4\pi/5)\gamma^2/[1 - (4\pi^2/5)\gamma^2] \tag{6·14}$$

and

$$\Delta = (2/5)^{1/2}\omega_{Lm}\gamma, \tag{6·15}$$

where

$$\gamma = d/a \quad \text{and} \quad \omega_{Lm}^2 = 4K_L/M \tag{6·16}$$

is the maximum eigenfrequency of phonons in the case of the crystal lattice. A similar procedure yields an approximate result $(d^2\omega(k)^2/dk^2)_{k=k_0} \simeq 1 - (4\pi^2/5)\gamma^2$. From Eq. (6·12) we thus obtain

$$\mu = 16\pi\gamma/[5^{1/2}\omega_{Lm}a^2\{1 - (4\pi^2/5)\gamma^2\}]. \tag{6·17}$$

Eliminating the factor ω_{Lm} from Eqs. (6·15) and (6·17), we also obtain a relationship between μ and Δ:

$$\mu = (8\pi\gamma^2/5)/[\Delta a^2\{1 - (4\pi^2/5)\gamma^2\}]. \tag{6·18}$$
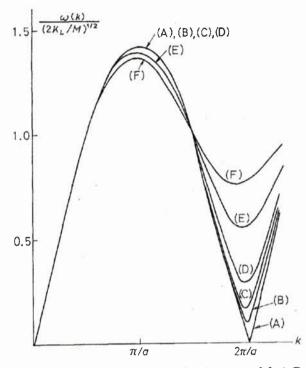
Fig. 4. Phonon eigenfrequencies in a model 1-D structure disorder system (Eq. (6·4)) for various values of $\gamma = d/a$; (A): $\gamma = 0.00$ (crytical lattice), (B): $\gamma = 0.02$, (C): $\gamma = 0.05$, (D): $\gamma = 0.10$, (E): $\gamma = 0.20$ and (F): $\gamma = 0.30$.

It is seen that the value of μ decreases as γ decreases or the local order increases.

We are now in a position to make a numerical analysis of the results obtained above. The results of numerical calculations of phonon dispersion curves as given by Eq. (6·4) are plotted in Fig. 4 for $\gamma = 0.00$ (crystal lattice), 0.02, 0.05, 0.10, 0.20 and 0.30. The cases of $\gamma = 0.30$ and 0.14 roughly correspond to liquid helium[48],[49] and liquid argon,[50] respectively. Figure 4 shows how phonon dispersion curves are modified as the local order changes. It is seen that an ω-versus-k curve for $\gamma = 0.3$ roughly corresponds to the results obtained by Henshaw and Woods for liquid helium II using neutron diffraction measurements.[42] Next, we apply Eq. (6·15) to the case of liquid argon by identifying ω_{Lm} with the maximum value $\omega_{max} \sim 10^{13} sec^{-1}$ of phonon eigenfrequencies observed experimentally. Taking $\gamma = 0.14$ in Eq. (6·15), we then obtain

$$\varDelta \sim 3 \times 10^{12} sec^{-1}, \qquad (6·19)$$

which is also in fair agreement with the experimental result of Sköld and Larsson[11] and that of Rahman.[12] Finally, an attempt is made to apply Eq. (6·18) again to the case of liquid helium. Putting $a = 3.6 \times 10^{-8} cm$, $\gamma = 0.30$ and $\varDelta = 8°K$ we obtain

$$\mu/M(\text{He}) \simeq 0.3, \qquad (6·20)$$

where $M(\text{He})$ is the atomic mass of helium. In view of the crudeness of our model and approximation, the above result may be considered to be fairly satisfactory.[42],[51]

§7. Concluding remarks

The main result obtained in this paper is that the phonon-roton-like behaviour of excitations (See Fig. 1) in classical liquids stems from the local disorder inherent in structure disorder systems and therefore that it is likely to exist,

within certain restrictions, in almost all non-crystalline solids and simple liquids, including liquid helium itself. In advancing such an argument the importance of the interrelationship between such excitation modes and phonon modes in crystal lattices, classical or quantum is pointed out. We have arrived at the above result by expressing the eigenfrequencies of phonon-like excitation modes in terms of effective pair correlation functions as well as of the second derivatives of pair potentials. Throughout this paper, we have neglected the damping or finite lifetime of such excitation modes. We have shown in §3 that for non-crystalline solids this arises, within the framework of the harmonic approximation, from the imaginally part of effective pair correlation functions. There is good reason to believe that the damping effect is quite different for different types of structure disorder systems. This may be particularly so if we consider two contrasting cases, such as quantum liquids and classical liquids, non-crystalline solids and liquids, and so on.

In this paper we have entirely omitted the discussion on the frequency spectrum of excitation modes and its effects on the thermodynamical properties of structure disorder systems, particularly of non-crystalline solids. The next step we should make for this purpose is to obtain the wave-number distribution function $f(k)$, which is the number of modes per unit range of k and may be called the density of states in the k-space. These problems will be studied in a separate paper.

We have also made an attempt to calculte the dispersion curve of elementary excitations in liquid helium. This has been done by merely inserting the value of the half-width of the first peak of the pair correlation function, obtainable from experimental data, to Eqs. (6·4), (6·15) and (6·18). Although fairly good agreement with experiment has been obtained, further analysis of this problem along the line with the method developed in this paper is required to see whether the above-mentioned agreement with experiment is accidental or not. As mentioned in §5, one of possible approaches is to generalize the concept of phonons in quantum crystals to the case of non-crystalline quantum solids and quantum liquids. The point here would be to investigate the connection between the behavior of phonon-like excitation modes in the vicinity of $k = k_0$ and the concept of roton in liquid helium.[56],[52]

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