

A Theory of Phonons in Amorphous Solids and Its Implications to Collective Motion in Simple Liquids

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A theoretical study is made of phonons in amorphous solids using a self-consistent phonon scheme. In treating the structural disorder inherent in the problem, a theory is formulated from the viewpoint of multiple scattering theory and designed to give phonon eigenfrequencies which are expressed in terms of many-body correlation functions of atoms as well as of interatomic potentials in the solids. For this purpose, a conditional averaging procedure is applied to equations for phonon Green's functions, obtainable using the renormalized harmonic approximation. A set of hierarchy equations is thereby obtained, for which various decoupling approximations are employed. As an application of the results obtained here, numerical calculations of the eigenfrequencies of longitudinal and transverse phonons in liquid argon are made using the "quasi-crystalline approximation" and the Lennard-Jones model potential. Fairly good agreement with experiment is obtained. A systematic and approximate self-consistent method for treating the hierarchy equations, which may be of some use in studying the general properties of the energy spectra of elementary excitations in disordered systems, is also obtained.

§ 1. Introduction

The traditional theory of lattice dynamics has been developed, as in the case of other fields of solid state physics, for perfect crystal lattices characterized by their periodic structure.^{1),2)} Much progress has also been made recently in lattice dynamics of disordered crystal lattices, impure crystals,³⁾ and mixed crystals or alloys.⁴⁾ In spite of their wide-spread existence in nature, however, the vibrational properties of amorphous solids, glassy solids, etc., belonging to a different class of disordered solids, have received little attention among theoretical solid state physicists.

If we are concerned only with phonons of long wavelength, then we may think of these disordered solids as a continuum and deduce the frequency spectra by a combination of the Debye model and the mechanics of an elastic body. When we study phonons of shorter wavelength, however, such an approach is no longer appropriate, and a microscopic theory taking into account the microscopic structure of the solids is required. Gubanov has formulated a variational method for calculating the frequency spectra of amorphous solids.⁵⁾ The result obtained by him is rather formal and no explicit result has been presented.

Historically, it has been known for a long time that the thermal conductivity of glassy solids has a different feature from that of pure or impure crystals.⁶⁾ Several experiments have also revealed that there exists excess low-temperature specific heat in glassy solids^{7)~8)} or glassy polymers⁹⁾ which cannot be accounted for by the conventional Debye theory. Bell, Bird and Dean have made numerical calculations of the vibrational spectra of model glassy solids.¹⁰⁾ In recent years, neutron scattering data from short-wavelength phonons in amorphous solids,¹¹⁾ as well as liquids,^{12),13)} have become increasingly available. It has been shown that there is a remarkable similarity between the scattered neutron spectra of amorphous or polycrystalline solids near their melting temperatures and those of liquids.^{14),15)} In the field of physics of liquids, there has recently been a growing interest in collective motion or high-frequency phonons in simple liquids.¹²⁾

It is the purpose of this paper to develop a theory of phonons in amorphous solids, with application to high-frequency phonons in simple liquids of the results obtained. This paper is the first of a series of papers to be devoted to developing theory of elementary excitations in disordered systems, impure or mixed crystals, amorphous solids or liquids, from the viewpoint of multiple scattering theory. In this series, a configurational averaging procedure, utilized in a previous paper by one of the authors (S.T.), for studying the multiple scattering of waves or particles in random media,¹⁶⁾ is applied with modification and generalization. Particular effort is made to obtain results for the energy spectra and the other physical properties of elementary excitations in disordered systems, which are expressed in terms of many-body correlation functions of scatterers in the systems, in an approximate self-consistent manner. Such a method, when viewed from many-body theory, is obviously a generalization of the conventional random phase approximation. The method utilized in this paper has, in its spirit, some similarity to that of Hubbard and Beeby in their theory of collective motion in simple liquids.¹⁷⁾ However, it is much more systematic, and also self-consistent, in treating the effect of spatial randomness on phonons in disordered systems. In the second and the third papers of this series, the energy spectra of an electron in mixed crystals or alloys and those in liquid metals will be studied.

In the next section, a brief discussion is given of a general self-consistent phonon scheme^{18),19)} to take into account the anharmonicity of atomic vibrations to all orders of magnitude. In § 3 a conditional averaging procedure is applied to equations for phonon Green's functions. A set of hierarchy equations is thereby obtained, which are designed to be written in terms of many-body correlation functions of atoms in amorphous solids. In § 4 the lowest order decoupling approximation, called the quasi-crystalline approximation, is employed for terminating the hierarchy. Formal expressions for phonon eigenfrequencies are obtained, which are written in terms of "effective pair potential" and pair correlation functions. An attempt is made in the appendix to proceed to the second

order approximation which yields the phonon damping. Section 5 is devoted to obtaining a self-consistent method for treating the hierarchy equations from the viewpoint of multiple scattering theory. An approximate self-consistent expression for phonon eigenfrequencies is obtained. In § 6, as an application of the results obtained in § 4, numerical calculations are made to obtain the eigenfrequencies of high frequency phonons in liquid argon. The last section is devoted to a brief summary of the results obtained in this paper.

§ 2. A self-consistent phonon theory

We consider the vibrational motion of N atoms in a solid. In view of the possible importance of the anharmonicity of atomic vibrations in disordered systems, particularly in liquids, no harmonic approximation is employed from the outset. As a preliminary for later discussions, a brief account is given of a general scheme to set up an equation of motion which yields the renormalized eigenfrequencies of phonons in solids, using a self-consistent method.^{20),*)} To treat structureless solids in general, the solid under consideration is taken to be arbitrary in structure and in composition. Let \mathbf{r}_n and \mathbf{P}_n be the position vector and the momentum of an atom, which are numbered by index n , in the solid respectively. Throughout this paper, the index n and the Cartesian component α are subsumed in a composite index x , whenever appropriate. The α component $A_{n\alpha}$ of a vector \mathbf{A}_n , referring to the n atom, is abbreviated as $A(x)$ ($x = (n, \alpha)$). The Hamiltonian which describes the motion of atoms in the solid is generally taken to be of the form

$$H = (1/2) \sum_x [P(x)^2/M(x)] + V_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (2.1)$$

where $M(x) \equiv M_n$ is the mass of the n -atom, and $V_N \equiv V_N(\{\mathbf{r}\}) \equiv V_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is the N -body potential which describes interactions of all the atoms in the solid. We decompose $\mathbf{r}(x)$ into two terms:

$$\mathbf{r}(x) = \langle \mathbf{r}(x) \rangle + \mathbf{u}(x) \equiv \mathbf{R}(x) + \mathbf{u}(x), \quad (2.2)$$

where $\mathbf{R}(x)$ is a mean or an equilibrium position of $\mathbf{r}(x)$, $\mathbf{u}(x)$ is the displacement of the n atom from its equilibrium position, and the angular bracket denotes a thermal average. Here, it is understood that the solid under consideration is in thermal equilibrium with a heat bath. The underlying assumption in using Eq. (2.2) is that the free energy of the system has a minimum at a set of atomic equilibrium positions $\{\mathbf{R}\}$, which can be used for crystals and amorphous solids at low temperatures. However, for amorphous or glassy solids near their melting temperatures, the equilibrium positions $\{\mathbf{R}\}$ may not be defined in a strict

*) Reference 20) will hereafter be referred to as (I).

sense, so Eq.(2.2) may be used with certain restrictions. The physical background of the use of a solid-state-approach to phonons in liquids will be discussed in the beginning of § 6.

We study atom-displacement waves or phonons in the solid. We therefore expand the potential function in powers of the u 's:

$$V_N(\{r\}) = V_N(\{\mathbf{R}\}) + \sum_{n=1}^{\infty} (1/n!) \sum_{x_1, x_2, \dots, x_n} K_n(x_1, x_2, \dots, x_n) u(x_1) u(x_2) \dots u(x_n), \quad (2.3)$$

where

$$K_n(x_1, x_2, \dots, x_n) = [\nabla(x_1) \nabla(x_2) \dots \nabla(x_n) V_N]_0 \quad (2.4)$$

is the n -th order force constant. Here, the symbol $[]_0$ means that the bracketed expression is evaluated with all atomic coordinates at the equilibrium positions. We introduce the mass-reduced coordinates and momenta:

$$u(x) = M(x)^{-1/2} q(x) \quad \text{and} \quad P(x) = M(x)^{1/2} p(x). \quad (2.5)$$

The commutation relations obeyed by the q 's and the p 's are:^{*}

$$[q(x), q(x')] = [p(x), p(x')] = 0 \quad \text{and} \quad [q(x), p(x')] = \delta(xx'). \quad (2.6)$$

The Hamiltonian of the system is then rewritten as

$$H = (1/2) \sum_x p(x)^2 + \sum_{n=1}^{\infty} (1/n!) \sum_{x_1, x_2, \dots, x_n} D_n(x_1, x_2, \dots, x_n) q(x_1) q(x_2) \dots q(x_n) + \text{constant terms}, \quad (2.7)$$

where

$$D_n(x_1, x_2, \dots, x_n) = K_n(x_1, x_2, \dots, x_n) [M(x_1) M(x_2) \dots M(x_n)]^{-1/2}. \quad (2.8)$$

To study elementary excitations associated with the atomic motion in the solid, we introduce a retarded or an advanced double-time Green's function,¹¹⁾ composed of a pair of operators A and B and its Fourier transform

$$\langle\langle A(t); B(t') \rangle\rangle = \mp i\theta(\pm(t-t')) \langle [A(t), B(t')] \rangle, \quad (2.9)$$

$$\langle\langle A; B \rangle\rangle_{\omega} = (1/2\pi) \int_{-\infty}^{\infty} \langle\langle A(t); B(t') \rangle\rangle \exp[i\omega(t-t')] d(t-t'), \quad (2.9')$$

where $A(t) = \exp(iHt) A \exp(-iHt)$ is the Heisenberg operator for A , and $\theta(t)$ is Heaviside's step function. We are concerned here with Green's function $G(xx', t-t') \equiv \langle\langle q(x, t); q(x', t') \rangle\rangle$ and its Fourier transform $\langle\langle q(x); q(x') \rangle\rangle_{\omega} \equiv G(xx', \omega) \equiv G(x, x')$. From Eqs.(2.6) and (2.7) an equation of motion satisfied by $G(xx', t-t')$ is given by

^{*}) We use units with $\hbar=1$ throughout this paper.

$$idG(xx', t-t')/dt = i\langle\langle p(x, t); q(x', t') \rangle\rangle. \quad (2.10)$$

Differentiating the above equation again with respect to t and taking into account the fact that $D_n(x_1x_2\cdots x_n)$ is a symmetric function of x_1, x_2, \cdots, x_n , we obtain

$$-d^2G(xx', t-t')/dt^2 = \delta(t-t')\delta(xx') + \sum_{n=1}^{\infty} (1/n!) \sum_{x_1, x_2, \dots, x_n} D_{n+1}(xx_1x_2\cdots x_n) \langle\langle q(x_1, t) \cdots q(x_n, t); q(x', t') \rangle\rangle. \quad (2.11)$$

An equation obeyed by $G(xx', \omega)$ is therefore given by

$$\omega^2G(xx', \omega) = (1/2\pi)\delta(xx') + \sum_{n=1}^{\infty} (1/n!) \sum_{x_1, x_2, \dots, x_n} D_{n+1}(xx_1\cdots x_n) \times \langle\langle q(x_1) \cdots q(x_n); q(x') \rangle\rangle. \quad (2.12)$$

We employ a self-consistent procedure to treat Eq.(2.12). It amounts to using the following decoupling approximations:

$$\begin{aligned} \langle\langle q(x_1)q(x_2)\cdots q(x_n); q(x') \rangle\rangle &= \sum_{i=1}^n \langle \prod_{j(\neq i)} q(x_j) \rangle \langle\langle q(x_i); q(x') \rangle\rangle \\ &+ \sum_{i < j} \langle \prod_{k(\neq i, j)} q(x_k) \rangle \langle\langle q(x_i)q(x_j); q(x') \rangle\rangle \\ &+ \sum_{i < j < k} \langle \prod_{l(\neq i, j, k)} q(x_l) \rangle \langle\langle q(x_i)q(x_j)q(x_k); q(x') \rangle\rangle + \dots \end{aligned} \quad (2.13)$$

Inserting this into Eq.(2.12), we get

$$\omega^2G(xx', \omega) = (1/2\pi)\delta(xx') + \sum_{n=1}^{\infty} (1/n!) \sum_{x_1, x_2, \dots, x_n} \mathcal{D}_{n+1}(xx_1\cdots x_n) \times \langle\langle q(x_1)q(x_2)\cdots q(x_n); q(x') \rangle\rangle, \quad (2.14)$$

where

$$\mathcal{D}_n(x_1x_2\cdots x_n) = [M(x_1)M(x_2)\cdots M(x_n)]^{-1/2} \mathcal{V}(x_1)\mathcal{V}(x_2)\cdots \mathcal{V}(x_n) \langle V_N(\{\mathbf{r}\}) \rangle. \quad (2.15)$$

Here $\langle V_N(\{\mathbf{r}\}) \rangle = \langle \exp(\sum_{n=1}^N \mathbf{u}_n \cdot \mathbf{V}_n) \rangle V_N(\{\mathbf{R}\})$ is the "effective potential" associated with the "bare potential" $V_N(\{\mathbf{R}\})$, and $\mathcal{D}_n(x_1, x_2, \dots, x_N)$ is the mass-reduced "effective force constants". In obtaining the above result, we have made use of the following relation

$$\begin{aligned} &\sum_{n=1}^{\infty} (1/n!) \sum_{x_1, x_2, \dots, x_n} D_{n+1}(xx_1x_2\cdots x_n) \sum_{i_1 < i_2 < \dots < i_m} \langle \prod_{j(\neq i_1, i_2, \dots, i_m)} q(x_j) \rangle \\ &\times \langle\langle q(x_{i_1})q(x_{i_2})\cdots q(x_{i_m}); q(x') \rangle\rangle \\ &= (1/m!) \sum_{y_1, y_2, \dots, y_m} \mathcal{D}_{m+1}(xy_1y_2\cdots y_m) \langle\langle q(y_1)q(y_2)\cdots q(y_m); q(x') \rangle\rangle. \end{aligned} \quad (2.16)$$

Equation (2.14) gives renormalized eigenfrequencies of phonons. Truncating the

series at $n=1$ and $n=m (>1)$ yields renormalized harmonic phonons and renormalized anharmonic phonons with $(m+1)$ phonon scattering processes taken into account, respectively. It is seen that the phonon eigenfrequencies are determined by the effective force constants, rather than by the bare force constants.

An expression for the effective potential $\langle V_N(\{\mathbf{r}\}) \rangle$ can be obtained most easily by introducing the Fourier transform of V_N :

$$V_N(\{\mathbf{R}\}) = (2\pi)^{-3N} \int \cdots \int d\{\mathbf{k}\} V_N(\{\mathbf{k}\}) \exp(i \sum_{n=1}^N \mathbf{k}_n \cdot \mathbf{R}_n) \quad (2.17)$$

or

$$\langle V_N(\{\mathbf{r}\}) \rangle = (2\pi)^{-3N} \int \cdots \int d\{\mathbf{k}\} V_N(\{\mathbf{k}\}) \langle \exp(i \sum_{n=1}^N \mathbf{k}_n \cdot \mathbf{r}_n) \rangle. \quad (2.18)$$

$$(d\{\mathbf{k}\} = d\mathbf{k}_1 d\mathbf{k}_2 \cdots d\mathbf{k}_N)$$

Using Eq.(2.17), we obtain

$$\begin{aligned} \langle V_N(\{\mathbf{r}\}) \rangle &= \int \cdots \int d\{\mathbf{R}'\} V_N(\{\mathbf{R} + \mathbf{R}'\}) P_N(\{\mathbf{R}'\}) \\ &= \int \cdots \int d\{\mathbf{R}'\} V_N(\{\mathbf{R}'\}) P_N(\{\mathbf{R} - \mathbf{R}'\}), \end{aligned} \quad (2.19)$$

$$(d\{\mathbf{R}\} = d\mathbf{R}_1 d\mathbf{R}_2 \cdots d\mathbf{R}_N)$$

where

$$P_N(\{\mathbf{R}\}) = (2\pi)^{-3N} \int \cdots \int d\{\mathbf{k}\} \langle \exp(i \sum_{n=1}^N \mathbf{k}_n \cdot \mathbf{u}_n) \rangle \exp(-i \sum_{n=1}^N \mathbf{k}_n \cdot \mathbf{R}_n) \quad (2.20)$$

is the probability function for the displacement of all the atoms in the solids, in which $\langle \exp(i \sum_{n=1}^N \mathbf{k}_n \cdot \mathbf{u}_n) \rangle$ is the characteristic function or the moment generating function of $P_N(\{\mathbf{R}\})$. In almost all cases, the potential function V_N can be constructed by pair-wise and spherically symmetric potentials, namely

$$V_N(\{\mathbf{r}\}) = (1/2) \sum_{m \neq n} V_1(|\mathbf{r}_m - \mathbf{r}_n|). \quad (2.21)$$

As is the case for the N -body potential, an effective two-body potential is then expressed in the form

$$\langle V_1(\mathbf{r}_n - \mathbf{r}_0) \rangle = \int d\mathbf{R}' V_1(\mathbf{R}_n + \mathbf{R}') P_1(\mathbf{R}') = \int d\mathbf{R}' V_1(\mathbf{R}') P_1(\mathbf{R}_n - \mathbf{R}'), \quad (2.22)$$

where

$$P_1(\mathbf{R}_n) = (2\pi)^{-3} \int d\mathbf{k} \langle \exp(i\mathbf{k} \cdot \mathbf{u}_{n0}) \rangle \exp(-i\mathbf{k} \cdot \mathbf{R}_n), \quad (2.23)$$

in which

$$\mathbf{u}_{n0} = \mathbf{u}_n - \mathbf{u}_0. \quad (2.24)$$

Here, \mathbf{r}_0 is the instantaneous position of an atom whose mean position $\langle \mathbf{r}_0 \rangle \equiv \mathbf{R}_0$ is taken to be the origin of the coordinate.

The conventional procedure here is to approximate $P_1(\mathbf{R})$ {or $P_N(\{\mathbf{R}\})$ } by a Gaussian distribution function.²²⁾ With the use of this approximation, Eq.(2·22) reduces to (see Eq.(3·21) in (I))

$$\begin{aligned} \langle V_1(\mathbf{r}_n - \mathbf{r}_0) \rangle &\equiv \mathcal{C}V_1(\mathbf{R}, A) = (2\pi)^{-3/2} (\det A_1(n0))^{-1/2} \int d\mathbf{R}' V_1(\mathbf{R}_n + \mathbf{R}') \\ &\quad \times \exp\left\{-\frac{1}{2} \sum_{\alpha\beta} A_1^{-1}(n0)_{\alpha\beta} \mathbf{R}'_{\alpha} \mathbf{R}'_{\beta}\right\} \\ &= (2\pi)^{-3/2} (\det A_1(n0))^{-1/2} \int d\mathbf{R}' V_1(\mathbf{R}') \\ &\quad \times \exp\left\{-\frac{1}{2} \sum_{\alpha\beta} A_1^{-1}(n0)_{\alpha\beta} (\mathbf{R}_n - \mathbf{R}')_{\alpha} (\mathbf{R}_n - \mathbf{R}')_{\beta}\right\}, \end{aligned} \tag{2·25}$$

where

$$A_1(n0) = (A_1(n0)_{\alpha\beta}) = \langle\langle (\mathbf{u}_n - \mathbf{u}_0)_{\alpha} (\mathbf{u}_n - \mathbf{u}_0)_{\beta} \rangle\rangle \tag{2·26}$$

is a 3×3 correlation matrix composed of the pair correlation function of the relative displacement $\mathbf{u}_n - \mathbf{u}_0$. To reduce Eq.(2·25) to a tractable form, we make use of a further approximation to neglect the correlation of the different components of the displacement vectors of atoms:^{*)}

$$A_1(n0)_{\alpha\beta} = \lambda(n0) \delta(\alpha\beta) = (1/3) \langle (\mathbf{u}_n - \mathbf{u}_0)^2 \rangle \delta(\alpha\beta). \tag{2·27}$$

The last expression of Eq.(2·25) then reduces to (see Eq.(6·3) in (I))

$$\begin{aligned} \langle V_1(\mathbf{r}_n - \mathbf{r}_0) \rangle &\equiv \mathcal{C}V_1(\mathbf{R}_n, \lambda) = [2\pi\lambda(n0)]^{-1/2} \int d\mathbf{R}' V_1(\mathbf{R}') \\ &\quad \times \exp\left[-\frac{(\mathbf{R}' - \mathbf{R}_n)^2}{2\lambda(n0)}\right] \\ &= (1/\pi^{1/2} R_n) \int_{R_n/[2\lambda(n0)]^{1/2}}^{\infty} \{[2\lambda(n0)]^{1/2} x + R_n\} V_1([2\lambda(n0)]^{1/2} x + R_n) \\ &\quad \times \exp(-x^2) dx - \int_{-R_n/[2\lambda(n0)]^{1/2}}^{\infty} \{[2\lambda(n0)]^{1/2} x - R_n\} \\ &\quad \times V_1([2\lambda(n0)]^{1/2} x - R_n) \exp(-x^2) dx. \end{aligned} \tag{2·28}$$

Using this result, we can evaluate analytically or numerically the effective pair potential in a straightforward manner, once the bare pair potential is given.

§ 3. An averaging procedure using a renormalized harmonic approximation

Let us suppose that the solid under consideration is a non-crystalline solid

^{*)} This relation holds for cubic crystals,

or an amorphous solid. We assume that probability functions for the distribution of all the atoms in the solid are given. Then, Eq.(2·14) constitutes a difference equation whose coefficients are stochastic variables. There have been mainly two kinds of methods to treat such a stochastic equation. One is to solve the difference equation for a fixed set of atomic positions and then average over all possible atomic configurations. The other is to make use of a procedure for first averaging the equation and then solving it. These two methods have sometimes been called honest and dishonest methods, respectively.²⁸⁾ We follow the latter method in this paper. In doing this, we employ the renormalized harmonic approximation, thus truncating the series on the right-hand side of Eq.(2·14) at $m=1$, namely

$$\omega^2 G(xx', \omega) = (1/2\pi) \delta(xx') + \sum_{x_1} \mathcal{D}_2(xx_1) G(x_1x', \omega). \quad (3.1)$$

We limit our discussion henceforth to the case in which all the atoms in the solid are identical. Let M be the mass of the atom in the solid. Equation (3·1) is then rewritten as^{*)}

$$M\omega^2 G_{\alpha\alpha'}^u(nn') - \sum_{\beta} \sum_{m(\neq n)} \mathcal{K}_{\alpha\beta}(nm) \{G_{\beta\alpha'}^u(nn') - G_{\beta\alpha'}^u(mn')\} \\ = (1/2\pi) \delta(nn') \delta(\alpha\alpha'), \quad (3.2)$$

where $G_{\alpha\alpha'}^u(nn') = \langle\langle u_{\alpha}(n); u_{\alpha'}(n') \rangle\rangle_u^{**)}$ and

$$\mathcal{K}_n(x_1x_2\cdots x_n) = \nabla(x_1)\nabla(x_2)\cdots\nabla(x_n) \langle V_N(\{r\}) \rangle, \quad (3.3)$$

where $\mathcal{K}_n(xx') \equiv \mathcal{K}(xx')$, is the n -th order effective force constant. Here, it is convenient to introduce the "mixed" Fourier transform of $G_{\alpha\alpha'}(nn')$:

$$G_{\alpha\alpha'}(nn') = (2\pi)^{-3} \int dk G_{\alpha\alpha'}(n, k) \exp[ik \cdot (n - n')]. \quad (3.4)$$

Insertion of Eq.(3·4) into Eq.(3·2) gives

$$M\omega^2 G_{\alpha\alpha'}(n, k) - \sum_{\beta} \sum_{m(\neq n)} \mathcal{K}_{\alpha\beta}(nm) \{G_{\beta\alpha'}(n, k) - \exp\{-ik \cdot (n - m)\} G_{\beta\alpha'}(m, k)\} \\ = (1/2\pi) \delta(\alpha\alpha'). \quad (3.5)$$

To make mathematical procedures more compact, we define three 3×3 matrices:

$$F(n, k) = (G_{\alpha\alpha'}(n, k)), \quad L(nn') = (\mathcal{K}_{\alpha\alpha'}(nn')), \quad I_1 = (\delta(\alpha\alpha')/2\pi) \equiv I/2\pi. \quad (3.6)$$

Equation (3·5) is then rewritten as

^{*)} We hereafter rewrite R_n , the equilibrium position of the n atom, as n for brevity, whenever appropriate.

^{**)} We henceforth omit the superscript u attached on the G 's for brevity.

$$M\omega^2 F(\mathbf{n}, \mathbf{k}) - \sum_{m(\neq \mathbf{n})} L(\mathbf{nm}) \{F(\mathbf{n}, \mathbf{k}) - \exp\{-i\mathbf{k} \cdot (\mathbf{n} - \mathbf{m})\} F(\mathbf{m}, \mathbf{k})\} = I_1. \quad (3.7)$$

We now apply a configurational averaging procedure¹⁶⁾ to Eq.(3.7). Let

$$P_N(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_N)$$

with

$$\int \dots \int P_N(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_N) d\mathbf{n}_1 d\mathbf{n}_2 \dots d\mathbf{n}_N = 1 \quad (3.8)$$

be the probability of finding the first atom in the solid in the region with its center in the volume element $d\mathbf{n}_1$ at \mathbf{n}_1 , while at the same time the second atom is in $d\mathbf{n}_2$, at \mathbf{n}_2 , and so forth. Also introduced here is the conditional probability functions:

$$P_{N-m}(\mathbf{n}_{m+1}, \mathbf{n}_{m+2}, \dots, \mathbf{n}_N | \mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_m) = P_N(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_N) / P_m(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_m), \quad (3.9)$$

which denotes the probability of finding the $(m+1)$ atom in $d\mathbf{n}_{m+1}$ at \mathbf{n}_{m+1} , etc., when m atoms are definitely located at the positions $\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_m$. A useful relationship between the conditional probabilities is

$$P_{N-m}(\mathbf{n}_{m+1}, \mathbf{n}_{m+2}, \dots, \mathbf{n}_N | \mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_m) = P_1(\mathbf{n}_{m+1} | \mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_m) P_{N-m-1}(\mathbf{n}_{m+2}, \dots, \mathbf{n}_N | \mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_{m+1}). \quad (3.10)$$

$(m < N)$

It is also convenient to introduce the number density and the conditional or correlation number density functions by the equations

$$\begin{aligned} N_1(\mathbf{n}_1) &\equiv N_1 = NP_1(\mathbf{n}_1), \\ N_2(\mathbf{n}_2 | \mathbf{n}_1) &\equiv N_2 = (N-1)P_1(\mathbf{n}_2 | \mathbf{n}_1), \\ N_3(\mathbf{n}_3 | \mathbf{n}_1, \mathbf{n}_2) &\equiv N_3 = (N-2)P_1(\mathbf{n}_3 | \mathbf{n}_1, \mathbf{n}_2), \quad \text{etc.} \end{aligned} \quad (3.11)$$

In terms of these probability and conditional probability functions, the average and the conditional averages with one or more atomic positions held fixed, of a function $f(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_N)$ are defined as*)

$$\langle f \rangle = \int \dots \int d\mathbf{n}_1 d\mathbf{n}_2 \dots d\mathbf{n}_N P_N(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_N) f(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_N), \quad (3.12)$$

$$\begin{aligned} \langle f \rangle_{\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_m} &\equiv \langle f \rangle^m = \int \dots \int d\mathbf{n}_{m+1} d\mathbf{n}_{m+2} \dots d\mathbf{n}_N \\ &\times P_{N-m}(\mathbf{n}_{m+1}, \mathbf{n}_{m+2}, \dots, \mathbf{n}_N | \mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_m) f(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_N). \end{aligned} \quad (3.13)$$

With the aid of the above prescription, we apply the first-order conditional average to Eq.(3.7), obtaining

*) Use is hereafter made of a symbolic notation $\langle f \rangle^m$ for the m -th order conditional average of f . In this connection, $\langle f \rangle^m$ is not to be confused with $\langle f \rangle_n$ which denotes the first order conditional average of f with one atomic position held fixed, where \mathbf{n} , written in *Roman letter*, stands for the position of an atom in the solid.

$$M\omega^2 \langle F(\mathbf{n}) \rangle_{\mathbf{n}} - \int d\mathbf{m}_1 N_2(\mathbf{m}_1|\mathbf{n}) L(n\mathbf{m}_1) \\ \times \{ \langle F(\mathbf{n}) \rangle_{\mathbf{m},\mathbf{n}} - \exp\{-ik \cdot (\mathbf{n} - \mathbf{m}_1)\} \langle F(\mathbf{m}_1) \rangle_{\mathbf{m}\mathbf{m}_1} \} = I_1, \quad (3.14)$$

where we have omitted the index \mathbf{k} appearing in the argument of the F 's for the sake of brevity. Equation (3.14) expresses the first order conditional average of F in terms of the second order conditional average, thus constituting a set of hierarchy equations. These equations are written in the form

$$M\omega^2 \langle F(\mathbf{n}) \rangle_{\mathbf{m},\mathbf{n}} - \int d\mathbf{m}_2 N_3(\mathbf{m}_2|\mathbf{m}_1\mathbf{n}) L(n\mathbf{m}_2) \\ \times \{ \langle F(\mathbf{n}) \rangle_{\mathbf{m},\mathbf{m}_1\mathbf{n}} - \exp\{-ik \cdot (\mathbf{n} - \mathbf{m}_2)\} \langle F(\mathbf{m}_2) \rangle_{\mathbf{m},\mathbf{m}_1\mathbf{m}_2} \} = I_1, \quad (3.15)$$

$$M\omega^2 \langle F(\mathbf{n}) \rangle_{\mathbf{m},\mathbf{m}_1\mathbf{n}} - \int d\mathbf{m}_3 N_4(\mathbf{m}_3|\mathbf{m}_1\mathbf{m}_2\mathbf{n}) L(n\mathbf{m}_3) \\ \times \{ \langle F(\mathbf{n}) \rangle_{\mathbf{m},\mathbf{m}_1\mathbf{m}_2\mathbf{n}} - \exp\{-ik \cdot (\mathbf{n} - \mathbf{m}_3)\} \langle F(\mathbf{m}_3) \rangle_{\mathbf{m},\mathbf{m}_1\mathbf{m}_2\mathbf{m}_3} \} = I_1. \quad (3.16)$$

Each successive equation contains more and more information about the precise details of atom-displacement waves multiply scattered by the structural disorder of the solid. In the following two sections and also in the Appendix, we employ several approximation procedures to obtain approximate solutions of the hierarchy equations.

§ 4. Quasi-crystalline approximation

In this section we use the lowest order approximation, putting

$$\langle F(\mathbf{n}) \rangle_{\mathbf{m},\mathbf{n}} = \langle F(\mathbf{n}) \rangle_{\mathbf{n}}. \quad (4.1)$$

With the use of such a closure procedure, Eq.(3.14) reduces to

$$M\omega^2 \langle F(\mathbf{n}) \rangle_{\mathbf{n}} - \int d\mathbf{m}_1 N_2(\mathbf{m}_1|\mathbf{n}) L(n\mathbf{m}_1) \\ \times \{ \langle F(\mathbf{n}) \rangle_{\mathbf{n}} - \exp\{-ik \cdot (\mathbf{n} - \mathbf{m}_1)\} \langle F(\mathbf{m}_1) \rangle_{\mathbf{m}_1} \} = I/2\pi. \quad (4.2)$$

We limit our discussion henceforth to the case in which the distribution of all the atoms in the system is homogeneous, namely

$$P_1(\mathbf{n}) = 1/V \quad \text{or} \quad N_1(\mathbf{n}) = N/V = \rho, \quad (4.3)$$

where V is the volume of the solid. Then, $\langle F(\mathbf{n}) \rangle_{\mathbf{n}}$ becomes independent of \mathbf{n} , and the eigenvalues of Eq.(4.2) give the phonon eigenfrequencies in the system. In this case it is convenient to rewrite Eq.(4.2) as

$$M\omega^2 \langle F(\mathbf{n}) \rangle_{\mathbf{n}} - \rho \int d\mathbf{m} g(n\mathbf{m}) L(n\mathbf{m}) [\langle F(\mathbf{n}) \rangle_{\mathbf{n}} \\ - \exp\{-ik \cdot (\mathbf{n} - \mathbf{m})\} \langle F(\mathbf{m}) \rangle_{\mathbf{m}}] = I/2\pi, \quad (4.4)$$

where

$$g(\mathbf{nm}) = (1/\rho) N_2(\mathbf{m}|\mathbf{n}) \equiv g(|\mathbf{n} - \mathbf{m}|) \quad (4.5)$$

is the pair correlation function normalized to unity at large $|\mathbf{n} - \mathbf{m}|$.

Equation (4.1) has sometimes been called a "quasi-crystalline approximation".²⁴⁾ Let

$$\det|\omega^2\delta(\alpha\beta) - \mathcal{D}_{\alpha\beta}(\mathbf{k})| = 0 \quad (4.6)$$

be the secular equation giving the phonon eigenfrequencies, where $\mathcal{D}_{\alpha\beta}(\mathbf{k})$ is the dynamical matrix. From Eq.(4.4), we then obtain

$$\mathcal{D}_{\alpha\beta}(\mathbf{k}) = (\rho/M) \int d\mathbf{m} g(|\mathbf{n} - \mathbf{m}|) \mathcal{K}_{\alpha\beta}(\mathbf{nm}) [1 - \exp\{i\mathbf{k} \cdot (\mathbf{m} - \mathbf{n})\}]. \quad (4.7)$$

It is to be noted that within this approximation there exists no phonon damping arising from the structural disorder. The second order approximation which yields the phonon damping is discussed in the Appendix. Equation (4.4), when specialized to the case of a crystal lattice in which all the atoms are definitely located at the lattice points, namely*)

$$N_2(\mathbf{m}|\mathbf{n}) = \sum_{\mathbf{l}(\neq\mathbf{n})} \delta(\mathbf{l} - \mathbf{m}), \quad (4.8)$$

gives the following expression for the dynamical matrix:

$$\mathcal{D}_{\alpha\beta}(\mathbf{k}) = (1/M) \sum_{\mathbf{m}(\neq\mathbf{n})} \mathcal{K}_{\alpha\beta}(\mathbf{nm}) [1 - \exp\{-i\mathbf{k} \cdot (\mathbf{n} - \mathbf{m})\}]. \quad (4.9)$$

Equation (4.6) with $\mathcal{D}_{\alpha\beta}(\mathbf{k})$ given by Eq.(4.9) is an eigenvalue equation for phonons traditionally used in lattice dynamics of a crystal lattice, provided the effective force constants \mathcal{K} are replaced by bare force constants K .

If the effective force constants are derived from a spherically symmetric two-body potential, Eq.(4.9) is written in the form

$$\begin{aligned} \mathcal{D}_{\alpha\beta}(\mathbf{k}) = (\rho/M) \int d\mathbf{m} g(|\mathbf{m} - \mathbf{n}|) \nabla_\alpha \nabla_\beta \langle V_1(|\mathbf{r}_\mathbf{m} - \mathbf{r}_\mathbf{n}|) \rangle \\ \times [1 - \exp\{i\mathbf{k} \cdot (\mathbf{m} - \mathbf{n})\}]. \end{aligned} \quad (4.10)$$

Here, replacing the effective potential $\langle V_1(|\mathbf{r}_\mathbf{m} - \mathbf{r}_\mathbf{n}|) \rangle$ by the bare potential $V(|\mathbf{R}_\mathbf{m} - \mathbf{R}_\mathbf{n}|)$ is equivalent to the conventional harmonic approximation. Within this approximation, an alternative expression for the dynamical matrix written in terms of the Fourier transform $V_1(\mathbf{k})$ of $V_1(\mathbf{R})$ is given by

$$\begin{aligned} \mathcal{D}_{\alpha\beta}(\mathbf{k}) = (\rho/M) (2\pi)^{-3} \int d\mathbf{q} V_1(\mathbf{q}) q_\alpha q_\beta \\ \times \{S(\mathbf{k} - \mathbf{q}) - S(\mathbf{q}) + (2\pi)^3 \delta(\mathbf{k} - \mathbf{q})\}, \end{aligned} \quad (4.11)$$

*) Here, no averaging procedure is required.

where

$$V_1(\mathbf{R}) = (2\pi)^{-3} \int d\mathbf{k} V_1(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{R}) \quad (4.12)$$

and

$$S(\mathbf{k}) - 1 = \int d\mathbf{n} \{g(\mathbf{n}) - 1\} \exp(-i\mathbf{k} \cdot \mathbf{n}) \quad (4.13)$$

is the structure factor of the amorphous solid.

As an application of Eq.(4.10) for the calculation of the phonon frequencies, we make use of the renormalized harmonic approximation, replacing $\langle V_1(|\mathbf{r}_m - \mathbf{r}_0|) \rangle$ by $\mathcal{C}V_1(R_m, \lambda)$ (see Eq.(2.28)). For the evaluation of the integral on the right-hand side of Eq.(4.10), we choose the Cartesian coordinate with the z -axis in the direction of the wave vector \mathbf{k} . Performing the volume integral in spherical coordinate, we obtain*)

$$\begin{aligned} \mathcal{D}_{xx}(\mathbf{k}) = \mathcal{D}_{yy}(\mathbf{k}) = \omega_T(\mathbf{k})^2 = (\rho/M) 4\pi \int_0^\infty dR \cdot g(R) & \left[R \mathcal{C}V_1'(R) \left(1 - \frac{\sin(kR)}{kR} \right) \right. \\ & \left. + \{R^2 \mathcal{C}V_1''(R) - R \mathcal{C}V_1'(R)\} \left\{ \frac{1}{3} + \frac{\cos(kR)}{(kR)^2} - \frac{\sin(kR)}{(kR)^3} \right\} \right], \end{aligned} \quad (4.14)$$

$$\begin{aligned} \mathcal{D}_{zz}(\mathbf{k}) = \omega_L(\mathbf{k})^2 = (\rho/M) 4\pi \int_0^\infty dR g(R) & \left[R \mathcal{C}V_1'(R) \left(1 - \frac{\sin(kR)}{kR} \right) \right. \\ & \left. + \{R^2 \mathcal{C}V_1''(R) - R \mathcal{C}V_1'(R)\} \left\{ \frac{1}{3} - \frac{\sin(kR)}{kR} - 2 \frac{\cos(kR)}{(kR)^2} + 2 \frac{\sin(kR)}{(kR)^3} \right\} \right], \end{aligned} \quad (4.15)$$

$$\mathcal{D}_{xy}(\mathbf{k}) = \mathcal{D}_{yx}(\mathbf{k}) = \mathcal{D}_{yz}(\mathbf{k}) = \mathcal{D}_{zy}(\mathbf{k}) = \mathcal{D}_{zx}(\mathbf{k}) = \mathcal{D}_{xz}(\mathbf{k}) = 0, \quad (4.16)$$

where the conventional abbreviations $\mathcal{C}V_1'(R) = \partial \mathcal{C}V_1(R) / \partial R$ and $\mathcal{C}V_1''(R) = \partial^2 \mathcal{C}V_1(R) / \partial R^2$ have been used. Here, vanishing of the nondiagonal terms stems from the use of the spherically symmetric pair-potential model, and $\mathcal{D}_{xx}(\mathbf{k}) = \mathcal{D}_{yy}(\mathbf{k}) = \omega_T(\mathbf{k})^2$ and $\mathcal{D}_{zz}(\mathbf{k}) = \omega_L(\mathbf{k})^2$ themselves are equal to the squared-frequencies of the transverse (two-fold degenerate) phonon modes and those of the longitudinal phonon modes, respectively.

Certain asymptotic properties of the phonon eigenfrequencies in the long wave-length limit can be obtained from Eqs.(4.14) and (4.15). It can be shown that for small values of \mathbf{k} $\omega_T(\mathbf{k})$ and $\omega_L(\mathbf{k})$ are proportional to $|\mathbf{k}| \equiv k$, thus having the character of elastic waves, namely

$$\omega_T(\mathbf{k}) = C_T k, \quad (4.17)$$

$$\omega_L(\mathbf{k}) = C_L k, \quad (4.18)$$

*) We omit λ in the argument of $\mathcal{C}V_1(R, \lambda)$ for the sake of simplicity.

where

$$C_T = [(\rho/M)(4\pi/30) \int_0^\infty dR R^3 g(R) \{R^2 \mathcal{V}_1''(R) + 4\mathcal{V}_1'(R)\}]^{1/2} \quad (4.19)$$

and

$$C_L = [(\rho/M)(4\pi/30) \int_0^\infty dR R^3 g(R) \{3R^2 \mathcal{V}_1''(R) + 4\mathcal{V}_1'(R)\}]^{1/2} \quad (4.20)$$

can be identified with the velocities of the transverse and the longitudinal elastic waves, respectively. An approximate relationship between C_T and C_L can be obtained by observing the fact that the contribution from the terms involving the first derivative of the effective potential $\mathcal{V}_1(R)$ is small. Thus, we get

$$C_L \cong 3^{1/2} C_T. \quad (4.21)$$

An application of the results obtained in this section will be made in § 6.

§ 5. Formal properties of hierarchy equations

We are concerned in this section with the formal properties of solutions of the hierarchy equations, which may be of some use in studying the energy spectra of disordered systems in general. We begin our discussion by introducing a symbolic notation to rewrite Eq.(3.7) and Eqs.(3.14), (3.15), (3.16), etc. as

$$(M\omega^2 I - L)F = I_1 \quad (5.1)$$

and

$$M\omega^2 \langle F \rangle^p - N_{p+1} L \langle F \rangle^{p+1} = I_1, \quad p=1, 2, 3, \dots, \quad (5.2)$$

respectively, where L is an operator. It is understood that Eq.(5.2) is derived from Eq.(5.1) by applying the p -th order conditional average to it. Combining Eqs.(5.1) with (5.2) gives a formal relationship:

$$\langle LF \rangle^p = N_{p+1} L \langle F \rangle^{p+1} \quad (5.3)$$

or

$$\langle L \rangle^p = N_{p+1} L. \quad (5.4)$$

Let us define a factor $S(p+1, p)$ which characterizes the hierarchy equations by relating $\langle F \rangle^p$ to $\langle F \rangle^{p+1}$ in the form

$$\langle F \rangle^{p+1} = S(p+1, p) \langle F \rangle^p. \quad (5.5)$$

Then, truncating the hierarchy equations at $p=p'$ is equivalent to setting

$$S(p'+1, p') = 1. \quad (5.6)$$

In terms of this factor, an equation obeyed by $\langle F \rangle^p$ is written as

$$\langle F \rangle^p = \langle F \rangle^{p-1} + (1/M\omega^2) \{ \langle L \rangle^p S(p+1, p) - \langle L \rangle^{p-1} \} \langle F \rangle^p, \quad (5.7)$$

which is an obvious generalization of Eq.(A.3). Equation (5.7), when combined with Eq.(5.5), gives the following recurrence formula for the S 's:

$$S(p, p-1) = [I - (1/M\omega^2) \{\langle L \rangle^p S(p+1, p) - \langle L \rangle^{p-1}\}]^{-1} \quad (5.8)$$

which has the form of a continued fraction.

We next introduce an "effective force constant operator"^{*)} by the equation

$$(M\omega^2 I - \mathcal{L}^p) \langle F \rangle^p = I_1, \quad (5.9)$$

which has a property similar to the self-energy in many-body problems. This definition, in conjunction with Eqs.(5.1) and (5.5), yields the following expressions for \mathcal{L}^p :

$$\mathcal{L}^p = \langle L \rangle^p S(p+1, p). \quad (5.10)$$

Such a result written in the form of a continued fraction, although formally elegant, is of less practical use for the evaluation of phonon eigenfrequencies. It is seen that the zero-th and the first order approximations for \mathcal{L}^p can be expressed symbolically as

$$\mathcal{L}^p = \langle L \rangle^p \equiv \mathcal{L}_0^p \quad (5.11)$$

and

$$\mathcal{L}^p = \langle L \rangle^p [I - (1/M\omega^2) \{\langle L \rangle^{p+1} - \langle L \rangle^p\}]^{-1} \equiv \mathcal{L}_1^p, \quad (5.12)$$

respectively. We now make a correspondence of the above results with those obtained in the other parts of this paper. It can be shown that $\mathcal{L}^1 = \langle L \rangle^1$ is a symbolic notation of the result obtained in §4. Its explicit form is written as

$$\langle L \rangle^1 = N_2 L = \rho \int dm g(|m-n|) \nabla \nabla \langle V_1(|r_m - r_n|) \rangle [1 - \exp\{ik \cdot (m-n)\}]. \quad (5.13)$$

It can also be shown that Eq.(5.12) with $p=1$ is equivalent to a solution of Eqs.(A.11) and (A.12).

We now give a self-consistent procedure^{2b)} for the evaluation of \mathcal{L}^p . An equation for F is generally expressed as

$$F = \langle F \rangle^p + \langle F \rangle^p (L - \mathcal{L}^p) F = \langle F \rangle^p + F (L - \mathcal{L}^p) \langle F \rangle^p. \quad (5.14)$$

Applying the p -th order conditional average, we get the equation determining the self-consistent \mathcal{L}^p :

$$\langle (L - \mathcal{L}^p) F \rangle^p = 0 \quad \text{or} \quad \langle F (L - \mathcal{L}^p) \rangle^p = 0. \quad (5.15)$$

Here, it is convenient to introduce the related t -matrix T^p by the equation

*) In this paper the phrase "effective force constants" has been used in two senses. The one is dynamical in origin, and is defined as derivatives of dynamically smeared effective potentials due to the anharmonicity of atomic vibrations (see Eq. (2.19)). The other is statistical in character, and originates from the spatial randomness of the distribution of atoms in the solids.

$$F = \langle F \rangle^p + \langle F \rangle^p T^p \langle F \rangle^p. \quad (5.16)$$

Averaging of Eq.(5.16) gives

$$\langle T^p \rangle^p = 0 \quad (5.17)$$

for the self-consistent \mathcal{L}^p . Inserting Eq.(5.16) to Eq.(5.15), we then obtain an implicit equation for \mathcal{L}^p

$$\mathcal{L}^p = \langle L \rangle^p + \langle L \langle F \rangle^p T^p \rangle^p. \quad (5.18)$$

An equation obeyed by T^p is

$$T^p = L - \mathcal{L}^p + (L - \mathcal{L}^p) \langle F \rangle^p T^p \quad (5.19)$$

or

$$T^p = L - \mathcal{L}^p + T^p \langle F \rangle^p (L - \mathcal{L}^p). \quad (5.19')$$

An equation satisfied by $\langle L \langle F \rangle^p T^p \rangle^p$ is directly obtained from Eq. (5.19) or Eq. (5.19'). Using Eq.(5.19), we get

$$\begin{aligned} \langle L \langle F \rangle^p T^p \rangle^p &= \langle L \langle F \rangle^p L \rangle^p - \langle L \rangle^p \langle F \rangle^p \mathcal{L}^p + \langle L \langle F \rangle^p L \langle F \rangle^p T^p \rangle^p \\ &\quad - \langle L \langle F \rangle^p \mathcal{L}^p \langle F \rangle^p T^p \rangle^p. \end{aligned} \quad (5.20)$$

The third and the fourth terms on the right-hand side of the above equation can also be calculated in a straightforward manner, using the same procedure as before. A set of equations obtainable using such a procedure in a successive manner constitutes hierarchy equations.

Here, we make use of an approximation to terminate such hierarchy equations at Eq.(5.20), thus putting

$$\langle L \langle F \rangle^p L \langle F \rangle^p T^p \rangle^p \simeq \langle L \rangle^p \langle F \rangle^p \langle L \langle F \rangle^p T^p \rangle^p. \quad (5.21)$$

In the spirit of the same approximation, the last term on the right-hand side of Eq.(5.20) can be neglected in view of Eq.(5.17). Combining Eqs.(5.20) and (5.21) with Eq. (5.18) gives

$$\mathcal{L}^p = \langle L \rangle^p + \langle L \langle F \rangle^p L \rangle^p - \langle L \rangle^p \langle F \rangle^p \langle L \rangle^p, \quad (5.22)$$

which is a self-consistent expression for \mathcal{L}^p , correct to the first order with respect to the $\langle F \rangle^p$'s. It is easily seen that Eq.(5.12) can be derived from Eq. (5.22) by replacing $\langle F \rangle^p$ and $\langle L \rangle^p$ by $1/M\omega^2$ and \mathcal{L}^p , respectively. The effective force constants thus obtained yield the shift and the damping of phonon eigenfrequencies which are obtained by using the lowest order approximation $M\omega^2 - \langle L \rangle^p = 0$ for $\langle F \rangle^p$.

§ 6. A numerical example and phonons in liquid argon

Once pair correlation function and pair potential are given, the phonon eigenfrequencies can be calculated, within the framework of the quasi-crystalline ap-

proximation, in a quite straightforward manner using Eqs. (4.14) and (4.15). As a typical example for which such a simple model is applicable, an attempt is made here to study phonons in liquid argon. Before calculating phonon dispersion curves using such a procedure, a brief remark is given on a possible approach to collective motion or phonons in simple liquids, which is a generalization of the present theory developed originally for phonons in disordered anharmonic solids.*)

When studying atomic motions in classical liquids, we can distinguish two possible regimes, depending on whether we look at short- or long-time behavior of atomic motion. Let τ be some time scale characterizing atom-atom collisions in the liquids, which may be of the order of $10^{-11} \sim 10^{-12}$ sec, while typical vibrational frequencies of an atom are of the order of 10^{13} sec $^{-1}$. Then, the two limits $t \ll \tau$ and $t \gg \tau$ are known as the collisionless and statistical or hydrodynamical regimes, respectively.²⁶⁾ Historically, most of the work on liquids has been concentrated on the hydrodynamic regime. Our observation is that in the limit $t \ll \tau$ atoms in liquids look something like those in solids.²⁷⁾ Recently, there have been several experimental indications that a remarkable similarity exists between the scattered neutron spectra of liquids and those of polycrystalline or amorphous solids near their melting temperatures.^{14),15)} It should be noted that results for phonons in liquids, obtainable using the method developed here, can be considered to be valid for frequencies greater than the inverse characteristic relaxation time for local thermal equilibrium, and/or for wave vectors greater than the mean free path or mean collision distance, i.e., in the zero-sound region.

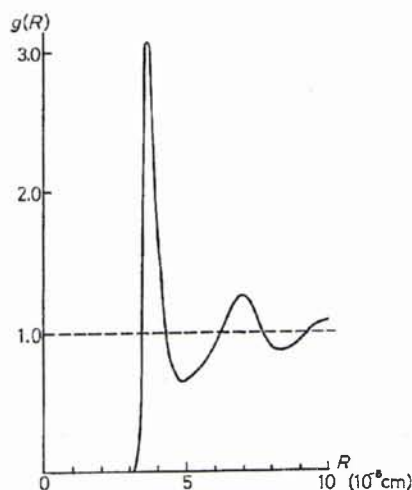


Fig. 1. Pair distribution function $g(R)$ for liquid argon at 84.4°K calculated by Khan.

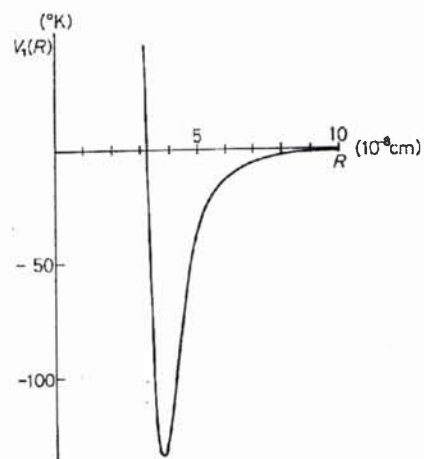


Fig. 2. Lennard-Jones 12-6 potential for liquid argon used to calculate the pair distribution function. The energy is in degrees Kelvin.

*) This line of approach has also been made previously by Hubbard and Beeby (reference 17)).

Keeping the above situation in mind, of a number of results obtained theoretically or experimentally for pair correlation functions and pair potentials, we have adopted the result of the calculations of Khan for the pair correlation function as an example, which is also in good agreement with experimental data.²⁸⁾ The numerical result of the pair correlation function for liquid Ar at 84.4°K with $\rho = 2.113 \times 10^{-23} / \text{\AA}^3$ is reproduced in Fig. 1. The corresponding Lennard-Jones potential is

$$V_1(R) = 4\epsilon \{ (\sigma/R)^{12} - (\sigma/R)^6 \} \quad (6.1)$$

with

$$\epsilon/k_B = 119.7^\circ\text{K} \quad \text{and} \quad \sigma = 3.405 \text{\AA}, \quad (6.2)$$

in which k_B is the Boltzmann constant. Equation (6.1) is depicted in Fig. 2. Using these data, we have evaluated the integrals (4.14) and (4.15) numerically using Simpson's rule, replacing $\mathcal{C}V_1(R)$ by the bare potential $V_1(R)$. As mentioned before, this amounts to using the conventional harmonic approximation for describing atomic vibrations in the liquid. Similar results have been obtained previously by Zwanzig,²⁹⁾ by Hubbard and Beeby,¹⁷⁾ by Schneider, Stoll and Szabo,³⁰⁾ which are equivalent to Eq. (4.10) with the effective potential replaced by bare potential. It is worth

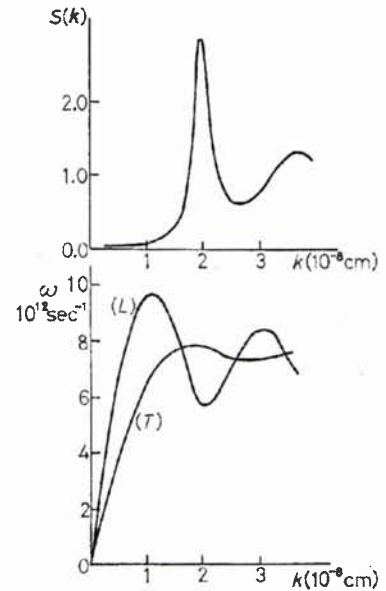


Fig. 3. Calculated dispersion curves of longitudinal (L) and transverse (T) phonons in liquid argon. The structure factor $S(k)$ is also drawn to show its relation with the dispersion of the longitudinal phonons.

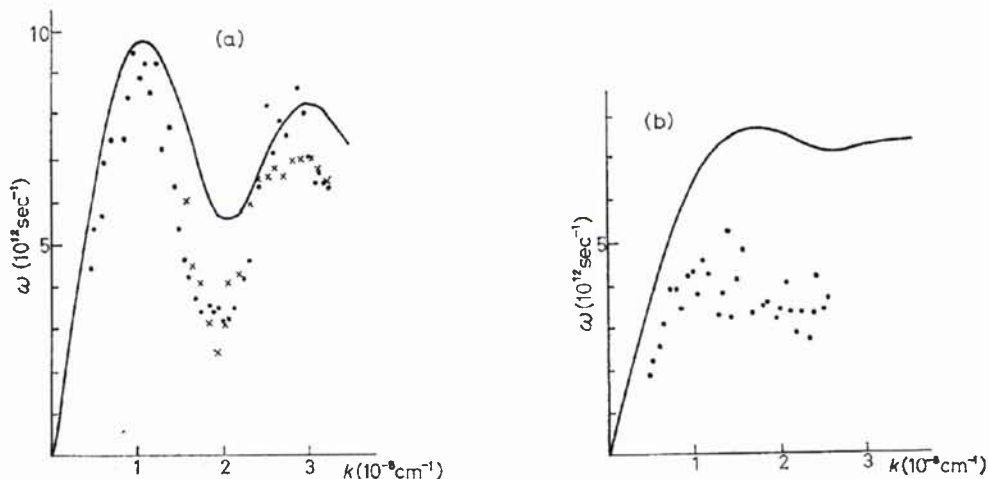


Fig. 4. Comparison of the calculated dispersion curves of the longitudinal (Fig. 4(a)) and the transverse (Fig. 4(b)) phonons with experiments. The solid circles gives the results of the machine calculations of Rahman and the crosses give the experimental results of Shöld and Larsson.

mentioning that the harmonic approximation itself is only a zero-th order approximation since the atomic vibration in liquids can be considered to be highly anharmonic. We should instead employ a self-consistent procedure, a brief account of which has been given in § 2. In this paper its implementation, which generally leads to involved calculations, is omitted. Phonon dispersion curves thus obtained are shown in Fig. 3, together with the schematic feature of the structure factor $S(\mathbf{k})$. It may be noted that the first minimum in $\omega(\mathbf{k})$ for longitudinal phonon modes and the first maximum in the structure factor $S(\mathbf{k})$ occur nearly at the same value of $k \simeq 2\text{\AA}^{-1}$. In Fig. 4 the calculated dispersion curves for the longitudinal and the transverse modes are compared with the results of machine calculations of Rahman³¹⁾ and those of the experimental results of Sköld and Larsson.³²⁾ In view of the fact that there is no adjustable parameter in our calculations, agreement between the theory and the experiments is rather good, particularly for the longitudinal modes. In the case of transverse modes, the results obtained here give frequencies generally larger than those obtained by Rahman. This fact may suggest that the transverse phonons undergo larger modulation than do longitudinal phonons due to the anharmonicity of atomic vibrations, which may be intimately connected with the instability of transverse phonons in liquids. For a crystal lattice, the equivalent conclusion has been reached by the author using a self-consistent phonon theory,³⁰⁾ which is also in qualitative agreement with the result obtained by Dickey and Paskin using computer simulations.³³⁾ Besides the use of the self-consistent phonon scheme, the main difference of the results obtained in this section from those of Zwanzig, of Hubbard and Beeby, and of Schneider, Stoll and Szabo is the elucidation of the existence of "high frequency" transverse phonons in simple liquids. We must also mention here that there have recently been several theoretical studies of phonons in simple liquids by Rahman,³⁴⁾ by Singwi, Sköld and Tosi,³⁵⁾ by Chung and Yip,³⁶⁾ by Chihara,³⁷⁾ using different methods from that employed here.

Finally, Eqs.(4·19) and (4·20) are applied to evaluate the velocities of the transverse and the longitudinal phonons. The result obtained is

$$C_T = 7.9 \times 10^4 \text{ cm/sec} \quad \text{and} \quad C_L = 1.3 \times 10^5 \text{ cm/sec}, \quad (6\cdot3)$$

whereas the experimental value for C_L is

$$C_L = 8.7 \times 10^4 \text{ cm/sec}. \quad (6\cdot4)$$

It is seen that Eqs.(6·3) and (6·4) satisfy the relation (4·21). The slight discrepancy between theory and experiment may be due to the use of the harmonic approximation and the inadequacy of the use of a solid-state-approach to phonons in liquids in the low frequency region. Together with the implementation of the self-consistent procedure for the evaluation of phonon eigenfrequencies, these points will be discussed elsewhere.

§ 7. Concluding remarks

The purpose of this paper is to develop a theory of phonons in amorphous solids and liquids. In view of the possible importance of the anharmonicity of atomic vibrations in disordered solids as well as in liquids, the formulation of the problem has been intentionally based on the self-consistent phonon scheme. In treating such structureless disordered systems, our particular intention was to obtain expressions for phonon eigenfrequencies which, aside from the interatomic potential, are written in terms of many-body correlation functions of atoms. This objective has been achieved, using a conditional averaging procedure and techniques employed in multiple scattering theory. Such a theory could be considered as a generalization of the conventional phonon theory in crystal lattices. In this connection it is of interest to note that the method utilized here may be equally applicable to electrons in amorphous solids, and liquid metals using the tight-binding approximation, excitons in disordered systems, etc.

In the calculation of phonon eigenfrequencies, as an application of the results obtained here, a simple model for the pair potential and the pair correlation function has been used, both of which have been taken to be spherically symmetric. No discussion has been given to phonons in glassy solids, for which such a simple model cannot be used at it stands. As a typical example for which such a simplified model can be applicable, numerical calculations of the phonon frequencies in liquid argon have been made using the quasi-crystalline approximation. Although fairly good agreement with experiments has been obtained, there remain several points to be taken into account in the calculation of the phonon eigenfrequencies. These are, for example, an implementation of the self-consistent procedure in the numerical calculation and the evaluation of the life-time of phonons in liquid argon. Also, it is of interest to do such calculations for a series of other simple liquids. These will be studied in a forthcoming paper.

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Appendix

Second order approximation

To take into account phonon damping, we employ the second order approximation:

$$\langle F(\mathbf{n}) \rangle_{m_1, m_2, n} = \langle F(\mathbf{n}) \rangle_{m_2, n} \quad \text{and} \quad \langle F(\mathbf{m}_2) \rangle_{m_1, m_2} \simeq \langle F(\mathbf{m}_2) \rangle_{m_2} \quad (\text{A} \cdot 1)$$

on the right-hand side of Eq.(3.15). Inserting these into Eq.(3.15), we obtain

$$M\omega^2 \langle F(\mathbf{n}) \rangle_{m_1, n} - \int d\mathbf{m}_2 N_3(\mathbf{m}_2 | \mathbf{m}_1, \mathbf{n}) L(\mathbf{n}\mathbf{m}_2) \{ \langle F(\mathbf{n}) \rangle_{m_1, n} - \exp[i\mathbf{k}(\mathbf{m}_2 - \mathbf{n})] \langle F(\mathbf{m}_2) \rangle_{m_1, n} \} = I_1. \quad (\text{A}\cdot 2)$$

In view of Eq.(3.14), Eq.(A.2) is rewritten as

$$\langle F(\mathbf{n}) \rangle_{m_1, n} = \langle F(\mathbf{n}) \rangle_n + (M\omega^2)^{-1} \int d\mathbf{m}_2 \{ N_3(\mathbf{m}_2 | \mathbf{m}_1, \mathbf{n}) - N_2(\mathbf{m}_2 | \mathbf{n}) \} \times L(\mathbf{n}\mathbf{m}_2) [\langle F(\mathbf{n}) \rangle_{m_1, n} - \exp[i\mathbf{k} \cdot (\mathbf{m}_2 - \mathbf{n})] \langle F(\mathbf{m}_2) \rangle_{m_1, n}]. \quad (\text{A}\cdot 3)$$

It is seen that a solution of this equation for $\langle F(\mathbf{n}) \rangle_{m_1, n}$ characterized by the factor $N_3 - N_2$, when inserted into Eq.(3.14), gives a phonon damping.

To express the conditional number density functions defined by Eq.(3.11) in a more familiar form, we introduce the s -body correlation function ($s=1, 2, 3, \dots$)

$$V^s P(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_s) = g_s(\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_s), \quad (\text{A}\cdot 4)$$

which is normalized to unity at a large mutual separation of the atoms in the solid. In terms of this the factor $N_3(\mathbf{m}_2 | \mathbf{m}_1, \mathbf{n}) - N_2(\mathbf{m}_2 | \mathbf{n})$ is rewritten as

$$N_3(\mathbf{m}_2 | \mathbf{m}_1, \mathbf{n}) - N_2(\mathbf{m}_2 | \mathbf{n}) = \rho \{ g_3(\mathbf{n}\mathbf{m}_1, \mathbf{m}_2) / g_2(\mathbf{n}\mathbf{m}_1) - g_2(\mathbf{n}\mathbf{m}_2) \}. \quad (\text{A}\cdot 5)$$

To treat the three-body correlation function, an attempt is made here to employ the Kirkwood superposition approximation which has been used extensively in the theory of physics of liquids.¹³⁾ We then obtain

$$N_3(\mathbf{m}_2 | \mathbf{m}_1, \mathbf{n}) - N_2(\mathbf{m}_2 | \mathbf{n}) = \rho g(\mathbf{n}\mathbf{m}_2) h(\mathbf{m}_1, \mathbf{m}_2), \quad (\text{A}\cdot 6)$$

where

$$h(\mathbf{m}_1, \mathbf{m}_2) = g(\mathbf{m}_1, \mathbf{m}_2) - 1 \quad (\text{A}\cdot 7)$$

is the total correlation function. By virtue of Eq.(A.6), Eq.(A.3) reduces to

$$\langle F(\mathbf{n}) \rangle_{m_1, n} = \langle F(\mathbf{n}) \rangle_n + (\rho/M\omega^2) \int d\mathbf{m}_2 g(\mathbf{n}\mathbf{m}_2) h(\mathbf{m}_1, \mathbf{m}_2) L(\mathbf{n}\mathbf{m}_2) \times [\langle F(\mathbf{n}) \rangle_{m_1, n} - \exp[i\mathbf{k} \cdot (\mathbf{m}_2 - \mathbf{n})] \langle F(\mathbf{m}_2) \rangle_{m_1, n}]. \quad (\text{A}\cdot 8)$$

Equation (3.14) with $N_2(\mathbf{m}_1 | \mathbf{n})$ replaced by $\rho g(\mathbf{n}\mathbf{m}_1)$ and Eq.(A.8) must be treated simultaneously.

To proceed further, we introduce the momentum representation for $\langle F(\mathbf{n}) \rangle_{m_1, n}$:

$$\langle F(\mathbf{n}) \rangle_{m_1, n} = (2\pi)^{-3} \int d\mathbf{q} F'(\mathbf{q}) \exp\{i(\mathbf{m}_1 - \mathbf{n})\mathbf{q}\} \quad (\text{A}\cdot 9)$$

as well as

$$\langle F(\mathbf{n}) \rangle_n = F \text{ (independent of } \mathbf{n}\text{)}. \quad (\text{A}\cdot 10)$$

Then, we can reduce Eqs(3.14) and (A.8) to

$$\omega^2 F - (2\pi)^{-3} \int \{c(\mathbf{k}-\mathbf{q}) - c(\mathbf{q})\} F'(\mathbf{q}) d\mathbf{q} = I_1 \quad (\text{A}\cdot 11)$$

and

$$F'(\mathbf{q}) = (2\pi)^{-3} \delta(\mathbf{q}) F + (h(\mathbf{q})/\omega^2) (2\pi)^{-3} \int \{c(\mathbf{k}-\mathbf{q}-\mathbf{q}') - c(\mathbf{q}'-\mathbf{q})\} F'(\mathbf{q}') d\mathbf{q}' \quad (\text{A}\cdot 12)$$

respectively, where

$$h(\mathbf{q}) = g(\mathbf{q}) - 1 \quad (\text{A}\cdot 13)$$

and

$$c(\mathbf{k}) = (\rho/M) (2\pi)^{-3} \int d\mathbf{q} \mathcal{V}_1(\mathbf{q}) g(\mathbf{k}-\mathbf{q}). \quad (\text{A}\cdot 14)$$

Here $\mathcal{V}_1(\mathbf{q})$ is the Fourier transform of $\mathcal{V}_1(R)$ the definition of which is similar to Eq.(4.12). Thus, within the second order approximation the problem is reduced to solving the simultaneous equations (A.11) and (A.12). It is seen that a solution of the integral equation (A.12), when inserted into Eq.(A.11), gives the shift and the damping of phonon frequencies which are obtained by using the quasi-crystalline approximation. A study of such a higher order effect is omitted in this paper.

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