

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office © Copyright, 1964, by the American Chemical Society

VOLUME 86, NUMBER 17

SEPTEMBER 4, 1964

## PETER J. W. DEBYE 80TH ANNIVERSARY ISSUE

[CONTRIBUTION FROM WESTINGHOUSE RESEARCH LABORATORIES, PITTSBURGH 35, PENNSYLVANIA]

### The Lattice Thermal Conductivity of an Isotopically Disordered Crystal<sup>1</sup>

BY A. A. MARADUDIN

RECEIVED APRIL 12, 1964

Starting from the Kubo expression for thermal conductivity a calculation of the lattice thermal conductivity of an isotopically disordered cubic Bravais crystal is carried out to lowest order in the concentration of the minority constituent (the impurities). It is shown that to this order in the concentration the expression for the conductivity has the form predicted by simple kinetic theory arguments, in the case that the impurity atoms are heavier than the atoms of the host crystal. The reciprocal of the phonon lifetime in this case has a resonance character of the type discussed recently by Brout and Visscher.

#### 1. Introduction

In 1914, in the published proceedings of the Wolfskehl Conferences of the preceding year, Debye<sup>2</sup> suggested that anharmonic terms in the expansion of the potential energy of a crystal in powers of the displacements of the atoms from their equilibrium positions would lead to the exchange of energy between the normal modes of the harmonic approximation, and therefore provided a mechanism which could explain the thermal resistance of insulators. Fifteen years later Peierls<sup>3</sup> derived a quantum mechanical transport equation for the phonon distribution function for a crystal possessing cubic anharmonicities, from the solution of which the lattice thermal conductivity could be calculated. The next major contribution to the theory of lattice thermal conductivity is to be found in the work of Klemens<sup>4</sup> who first emphasized the importance of the scattering of phonons by crystalline defects as a mechanism giving rise to thermal resistance. In the succeeding years the theory of thermal resistance due to point defects has been discussed by a number of authors.<sup>5</sup> All of these authors have based their treatments on the Peierls transport equation.<sup>3</sup>

In 1957 a new approach to the calculation of transport coefficients was presented by Kubo and his co-

workers.<sup>6</sup> The starting point of this approach is an expression for the desired transport coefficient as a Fourier transform of the two time correlation function of the current operators which appear in the macroscopic equations by which the coefficient is defined. It was hoped that the use of such correlation function expressions for the calculation of transport coefficients would yield results which the conventional approach *via* a transport equation could not reproduce.

Recent experimental results<sup>7</sup> for the thermal conductivity of ionic crystals containing point defects can be explained rather well if it is assumed that the inverse relaxation time for the scattering of phonons by point defects, in terms of which the collision term in the Peierls transport equation is usually approximated, has a resonance character in its dependence on the frequency of the phonon impinging on the defect. The subsequent demonstration by Brout and Visscher<sup>8</sup> and by others<sup>9</sup> that a heavy mass defect in a crystal can give rise to a low frequency "resonance mode" of vibration of the perturbed crystal has led to a number of attempts to incorporate this phenomenon into calculations of lattice thermal conductivity. This is usually done<sup>10</sup> by calculating the cross section for the scattering

(1) This research was supported by the Advanced Research Projects Agency, Director for Materials Sciences, and technically monitored by the Air Force Office of Scientific Research under Contract AF 49(638)-1245.

(2) P. Debye in "Vorträge über die Kinetische Theorie der Materie," B. G. Teubner, Leipzig and Berlin, 1914.

(3) R. E. Peierls, *Ann. Physik*, **3**, 1055 (1929).

(4) P. G. Klemens, *Proc. Roy. Soc. (London)*, **A208**, 108 (1951); *Proc. Phys. Soc. (London)*, **A68**, 1113 (1958).

(5) R. Berman, P. T. Nettle, F. W. Sheard, A. N. Spencer, R. W. H. Stevenson, and J. M. Ziman, *Proc. Roy. Soc. (London)*, **A253**, 403 (1959); J. Callaway, *Phys. Rev.*, **113**, 1046 (1959); P. Carruthers, *Rev. Mod. Phys.*, **33**, 92 (1961); H. Bross, *Phys. Status Solidi*, **2**, 481 (1962); P. G. Klemens, *Phys. Rev.*, **119**, 507 (1960); P. G. Klemens, G. K. White, and R. J. Tainsh, *Phil. Mag.*, **7**, 1323 (1962).

(6) R. Kubo, M. Yokota, and S. Nakajima, *J. Phys. Soc. Japan*, **12**, 1203 (1957). In this paper a quantum mechanical derivation of formal expressions for kinetic coefficients is presented. A classical derivation of these expressions had been given several years earlier by M. S. Green, *J. Chem. Phys.*, **22**, 398 (1954).

(7) R. O. Pohl, *Phys. Rev. Letters*, **8**, 481 (1962); C. T. Walker and R. O. Pohl, *Phys. Rev.*, **131**, 1433 (1963).

(8) R. Brout and W. Visscher, *Phys. Rev. Letters*, **9**, 54 (1962).

(9) S. Takeno, *Progr. Theoret. Phys. (Kyoto)*, **29**, 191 (1963); *ibid.*, **29**, 328 (1963); Yu. M. Kagan and Ya. A. Iosilevskii, *Zh. Eksperim. i Teor. Fiz.*, **42**, 259 (1962); *Soviet Phys. JETP*, **15**, 182 (1962).

(10) M. V. Klein, *Phys. Rev.*, **131**, 1500 (1963); J. Krumhansl, Proceedings of the 1963 International Conference on Lattice Dynamics, Pergamon Press, London, to be published; J. Callaway, *Nuovo Cimento*, **29**, 883 (1963); S. Takeno, *Progr. Theoret. Phys. (Kyoto)*, **30**, 144 (1963).

of phonons by a point defect not in the Born approximation but by the use of the T-matrix of generalized scattering theory.<sup>11</sup> A relaxation time is then calculated from the scattering cross section and used in the relaxation time approximation to the Peierls transport equation.

In the present paper we calculate the lattice thermal conductivity of a disordered crystal starting from a correlation function expression for the thermal conductivity. We consider for simplicity an arbitrary cubic Bravais crystal a fraction  $(1 - p)$  of whose lattice sites are occupied by atoms of mass  $M$ , while a fraction  $p$  ( $\ll 1$ ) are occupied randomly by atoms of mass  $M'$ . We neglect here any changes in the interatomic force constants of the crystal which result from the introduction of the small concentration of impurity atoms of mass  $M'$ . In practice it is more convenient to modify the statistical hypothesis underlying our work by stating that each lattice site of our crystal is occupied by an atom of mass  $M$  with probability  $1 - p$ , or by an atom of mass  $M'$  with probability  $p$ . In the limit as  $N$ , the number of atoms in the crystal, becomes large, the two ways of looking at the statistical side of our problem yield the same result.

Recently, and independently of the present work, Woll and Langer<sup>12</sup> have also calculated the lattice thermal conductivity of an isotopically disordered crystal. Their work differs from that reported here in at least two respects. They have devised a clever matrix propagator method for calculating the Fourier transform of the heat current correlation function, while the present calculation proceeds along more conventional lines. More importantly, their calculation was carried out for a nearest neighbor model of a disordered linear chain. Such a crystal model does not sustain a low frequency resonance mode when one of its atoms is replaced by a heavy impurity atom. Consequently, one of the more interesting features of the three-dimensional calculation is absent from the one-dimensional result. In addition, as we will see in section 3, the heat current operator for a three-dimensional crystal has a contribution, not present for a nearest-neighbor model of a linear chain, whose consequences so far have not been studied within the framework of conventional transport theory but which can be determined by the methods used in the present paper.

It should also be said from the outset that one cannot expect to obtain a finite thermal conductivity from the present model, and we will find that our final expression for the conductivity is a sum over all allowed phonon wave vectors inside a unit cell of the reciprocal lattice which diverges at long wave lengths. Physically, this divergence is associated with the fact that the long wave length lattice waves in an isotopically disordered crystal do not feel the microscopic fluctuations in the mass density of the crystal: they see a homogeneous medium whose density is the mean density of the crystal.<sup>13</sup> In a harmonic crystal these waves propagate without being attenuated, and hence give rise to an infinite conductivity. In a real crystal anharmonic forces as well as the boundaries of the crystal scatter phonons

more effectively than do point defects, and suppress the divergence. If we desire, we can impose a long wave length cutoff on the sum over phonon wave vectors with the justification that for longer wave lengths another mechanism, *viz.*, boundary scattering, will be dominant in determining the thermal conductivity.

We conclude these introductory remarks by expressing the crystal Hamiltonian in a form well suited to the calculations of the following sections.

The Hamiltonian for our disordered crystal can be written as

$$H = \sum_{l\alpha} \frac{p_\alpha^2(l)}{2M_l} + \frac{1}{2} \sum_{l\alpha} \sum_{l'\beta} \Phi_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l') \quad (1.1)$$

In this expression  $p_\alpha(l)$  and  $u_\alpha(l)$  are the  $\alpha$ -Cartesian components of the momentum and displacement of the  $l$ th atom, respectively;  $M_l$  is the mass of the  $l$ th atom; and the  $\{\Phi_{\alpha\beta}(ll')\}$  are the atomic force constants for the crystal. We rewrite eq. 1.1 in the form

$$H = \sum_{l\alpha} \frac{p_\alpha^2(l)}{2M} + \frac{1}{2} \sum_{l\alpha} \sum_{l'\beta} \Phi_{\alpha\beta}(ll') u_\alpha(l) u_\beta(l') + \sum_{l\alpha} \left( \frac{1}{2M_l} - \frac{1}{2M} \right) p_\alpha^2(l) \quad (1.2)$$

and we will treat the last term of this expression as a perturbation on the remainder. We next carry out the normal coordinate transformation which diagonalizes the unperturbed Hamiltonian

$$u_\alpha(l) = \left( \frac{\hbar}{2NM} \right)^{1/2} \sum_{\mathbf{k}j} \frac{e_\alpha(\mathbf{k}j)}{(\omega_j(\mathbf{k}))^{1/2}} e^{2\pi i \mathbf{k} \cdot \mathbf{x}(l)} A_{\mathbf{k}j} \quad (1.3a)$$

$$p_\alpha(l) = \frac{1}{i} \left( \frac{\hbar M}{2N} \right)^{1/2} \sum_{\mathbf{k}j} e_\alpha(\mathbf{k}j) (\omega_j(\mathbf{k}))^{1/2} e^{2\pi i \mathbf{k} \cdot \mathbf{x}(l)} B_{\mathbf{k}j} \quad (1.3b)$$

Here  $\omega_j(\mathbf{k})$  is the frequency of the normal mode of the unperturbed crystal described by the wave vector  $\mathbf{k}$  and branch index  $j$ , while  $\mathbf{e}(\mathbf{k}j)$  is the associated unit polarization vector.  $\mathbf{x}(l)$  is the equilibrium position of the  $l$ th atom, and  $A_{\mathbf{k}j}$  and  $B_{\mathbf{k}j}$  are phonon operators which are defined in terms of the usual phonon creation and destruction operators  $a_{\mathbf{k}j}^+$  and  $a_{\mathbf{k}j}$  by

$$A_{\mathbf{k}j} = a_{\mathbf{k}j} + a_{-\mathbf{k}j}^+ = A_{-\mathbf{k}j}^- \quad (1.4a)$$

$$B_{\mathbf{k}j} = a_{\mathbf{k}j} - a_{-\mathbf{k}j}^+ = -B_{-\mathbf{k}j}^+ \quad (1.4b)$$

In terms of these new operators the crystal Hamiltonian becomes

$$H = H_0 + H_D \quad (1.5a)$$

$$H_0 = \frac{1}{4} \sum_{\mathbf{k}j} \hbar \omega_j(\mathbf{k}) [A_{\mathbf{k}j}^+ A_{\mathbf{k}j} + B_{\mathbf{k}j}^+ B_{\mathbf{k}j}] \quad (1.5b)$$

$$H_D = - \sum_{\mathbf{k}_1j_1} \sum_{\mathbf{k}_2j_2} V(\mathbf{k}_1j_1; \mathbf{k}_2j_2) B_{\mathbf{k}_1j_1} B_{\mathbf{k}_2j_2} \quad (1.5c)$$

where

$$V(\mathbf{k}_1j_1; \mathbf{k}_2j_2) = \frac{\hbar}{4N} (\omega_{j_1}(\mathbf{k}_1) \omega_{j_2}(\mathbf{k}_2))^{1/2} (\mathbf{e}(\mathbf{k}_1j_1) \mathbf{e}(\mathbf{k}_2j_2)) \times \sum_l \left( \frac{M}{M_l} - 1 \right) e^{2\pi i (\mathbf{k}_1 + \mathbf{k}_2) \cdot \mathbf{x}(l)} \quad (1.5d)$$

(11) B. A. Lippmann and J. Schwinger, *Phys. Rev.*, **79**, 469 (1950).

(12) E. J. Woll, Jr., *Bull. Am. Phys. Soc.*, [2] **9**, 14 (1964).

(13) A. A. Maradudin and G. H. Weiss, *J. Chem. Phys.*, **29**, 631 (1958).

C. Domb, A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Phys. Rev.*, **115**, 24 (1959).

We now turn to the problem of calculating the lattice thermal conductivity of a disordered crystal described by this Hamiltonian.

**2. Transformation of the Kubo Formula for Lattice Thermal Conductivity**

The starting point for our calculation of lattice thermal conductivity is the Kubo expression

$$\kappa = -\frac{1}{\Omega T} \frac{2}{3\hbar} \text{Im} \lim_{\epsilon \rightarrow 0} \int_0^\infty dt e^{-\epsilon t} \langle \mathbf{S}(t) \cdot \mathbf{S}(0) \rangle \quad (2.1)$$

in the form which applies to cubic or isotropic crystals. Here  $\Omega$  is the volume of the crystal and  $\mathbf{S}(t)$  is the Heisenberg representation operator for the heat current operator

$$\mathbf{S}(t) = e^{i(t/\hbar)H} \mathbf{S}(0) e^{-i(t/\hbar)H} \quad (2.2)$$

and  $H$  is the crystal Hamiltonian. The angular brackets in eq. 2.1 denote an average in the canonical ensemble described by the Hamiltonian  $H$

$$\langle O \rangle = \frac{\text{Tr} e^{-\beta H} O}{\text{Tr} e^{-\beta H}} = \frac{1}{Z} \sum_n e^{-\beta E_n} \langle n | O | n \rangle \quad (2.3)$$

In eq. 2.3  $E_n$  is the energy of the (exact) eigenstate  $|n\rangle$  of  $H$ . We do not derive or justify the formula 2.1 here, and refer the interested reader to the extensive literature on this problem<sup>14</sup> for a derivation.

If we expand the average in eq. 2.1 in terms of the eigenstates of  $H$ , we can carry out the time integration exactly to obtain

$$\kappa = \frac{1}{\Omega T} \frac{2\pi}{3\hbar} \frac{1}{Z} \sum_{mn} e^{-\beta E_m} |\langle m | \mathbf{S}(0) | n \rangle|^2 \delta' \left( \frac{1}{\hbar} (E_m - E_n) \right) \quad (2.4)$$

For computational purposes it is convenient to re-express eq. 2.4 as

$$\kappa = -\frac{1}{\Omega T} \frac{2\pi}{3\hbar} \frac{d}{d\nu} \rho(\nu) \Big|_{\nu=0} \quad (2.5)$$

where

$$\rho(\nu) = \frac{1}{Z} \sum_{mn} e^{-\beta E_m} |\langle m | \mathbf{S}(0) | n \rangle|^2 \delta \left( \frac{1}{\hbar} (E_m - E_n) - \nu \right) \quad (2.6)$$

If in this expression we replace  $\nu$  by  $-\nu$ , and then relabel the dummy summation variables  $m$  and  $n$  as  $n$  and  $m$ , respectively, we obtain the result that

$$\rho(-\nu) = e^{\beta\hbar\nu} \rho(\nu) \quad (2.7)$$

Therefore, because we can write the derivative of  $\rho(\nu)$  at  $\nu = 0$  as

$$\frac{d\rho(\nu)}{d\nu} \Big|_{\nu=0} = \lim_{\nu \rightarrow 0^+} \frac{\rho(\nu) - \rho(-\nu)}{2\nu} \quad (2.8)$$

(14) H. Mori, *Phys. Rev.*, **112**, 1829 (1958); *ibid.*, **115**, 298 (1959); J. A. McLennan, *ibid.*, **115**, 1405 (1959); M. I. Klinger, *Zh. Tekh. Fiz.*, **27**, 2780 (1957); *Soviet Phys. Tech. Phys.*, **2**, 2578 (1957); D. N. Zubarev, *Dokl. Akad. Nauk SSSR*, **140**, 92 (1961); *Soviet Phys. Dokl.*, **6**, 776 (1961); R. Kubo, "Boulder Lectures in Theoretical Physics," Vol. 1, Academic Press, New York, N. Y., 1958, p. 120; H. Mori, I. Oppenheim, and J. Ross in "Studies in Statistical Mechanics," Vol. I, J. DeBoer and G. E. Uhlenbeck, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, pp. 271-298; R. J. Hardy, Ph.D. Thesis, Lehigh University, 1962, unpublished; G. V. Chester, *Rept. Progr. Phys.*, **26**, 411 (1963).

we can express  $\kappa$  in the form

$$\kappa = \frac{1}{\Omega T} \frac{\pi}{3\hbar} \lim_{\nu \rightarrow 0^+} \frac{(e^{\beta\hbar\nu} - 1)\rho(\nu)}{\nu} \quad (2.9)$$

The function  $\rho(\nu)$  can be written in a form better suited for its evaluation as

$$\rho(\nu) = \frac{\beta\hbar}{e^{\beta\hbar\nu} - 1} \frac{f(\nu + i0) - f(\nu - i0)}{2\pi i} = \frac{\beta\hbar}{e^{\beta\hbar\nu} - 1} f(\nu) \quad (2.10)$$

where  $f(z)$  is the continuation to the complex  $z$  plane of the Fourier series coefficient

$$f(i\omega_l) = \frac{1}{\beta} \int_0^\beta du e^{-i\omega_l u} F(u) \quad \omega_l = \frac{2\pi l}{\beta\hbar} \quad (2.11)$$

of the correlation function

$$F(u) = \langle T_u e^{uH} \mathbf{S}(0) e^{-uH} \cdot \mathbf{S}(0) \rangle \quad -\beta \leq u \leq \beta \quad (2.12)$$

In eq. 2.12  $T_u$  is the  $u$  ordering operator which orders a product of operators from right to left in order of increasing arguments. Conditions which ensure that the function  $f(z)$  is in fact the desired continuation to arbitrary complex argument of the function  $f(i\omega_l)$ , which is defined only at a discrete set of points, have been established by Baym and Mermin.<sup>15</sup> Combining eq. 2.9 and 2.10 we obtain

$$\kappa = \frac{1}{\Omega k T^2} \frac{\pi}{3} \lim_{\nu \rightarrow 0^+} \frac{f(\nu)}{\nu} \quad (2.13)$$

As it stands, this expression gives the thermal conductivity corresponding to a particular configuration of the two kinds of atoms over the lattice sites of the crystal. However, we have no knowledge of the atomic configuration in any given case; all we know are the concentrations  $p$  and  $1 - p$  of the two constituents. We express our ignorance by averaging the result given by eq. 2.13 over all possible atomic configurations compatible with the statistical hypothesis of the preceding section. The expression that is the basis for the remainder of this paper is

$$\langle \kappa \rangle_A = \frac{1}{\Omega k T^2} \frac{\pi}{3} \left\langle \lim_{\nu \rightarrow 0^+} \frac{f(\nu)}{\nu} \right\rangle_A \quad (2.14)$$

where  $\langle \dots \rangle_A$  denotes the configuration average.

**3. The Heat Current Operator**

Before we can use eq. 2.14 to calculate the thermal conductivity we must have an expression for the heat current operator  $\mathbf{S}$ . In a recent note<sup>16</sup> the author has derived the following simple expression for this operator

$$S_\mu = \sum_l x_\mu(l) \dot{H}(l) \quad (3.1)$$

where  $x_\mu(l)$  is the  $\mu$ -Cartesian component of the position vector of the  $l$ th atom in the crystal, and  $H(l)$  is the part of the crystal Hamiltonian which is associated with the  $l$ th lattice site. The expression given by eq. 3.1 is not exact. An exact expression for  $S_\mu$  has been obtained by Hardy,<sup>14,17</sup> but the differences between the

(15) G. Baym and N. D. Mermin, *J. Math. Phys.*, **2**, 232 (1961).

(16) A. A. Maradudin, Westinghouse Research Laboratories Scientific Paper 63-129-103-P1, 1963, unpublished.

(17) R. J. Hardy, *Phys. Rev.*, **132**, 168 (1963).

results obtained on the basis of his expression and those obtained through the use of eq. 3.1 appear to be significant only at temperatures of the order of or even higher than the melting temperature of the crystal.

The expression for  $H(l)$  applicable to the present problem is<sup>16</sup>

$$H(l) = \sum_{\alpha} \frac{\dot{p}_{\alpha}^2(l)}{2M_l} + \frac{1}{2} \sum_{l'\alpha\beta} \Phi_{\alpha\beta}(ll') u_{\alpha}(l) u_{\beta}(l') \quad (3.2)$$

The time derivative of  $H(l)$  is

$$\dot{H}(l) = \frac{1}{i\hbar} [H(l), H] = \frac{1}{2} \sum_{l'\alpha\beta} \Phi_{\alpha\beta}(ll') \times \left[ \frac{u_{\alpha}(l) \dot{p}_{\beta}(l')}{M_{l'}} - \frac{u_{\beta}(l') \dot{p}_{\alpha}(l)}{M_l} \right] \quad (3.3)$$

Combining eq. 3.1 and 3.3 we obtain

$$S_{\mu} = \frac{1}{2} \sum_{i\alpha} \sum_{l'\beta} x_{\mu}(\bar{l}) \Phi_{\alpha\beta}(\bar{l}) \frac{u_{\alpha}(\bar{l}+l') \dot{p}_{\beta}(l')}{M_{l'}} \quad (3.4)$$

In writing this equation we have introduced the variable  $\bar{l} = l - l'$ , and have used the fact that  $\Phi_{\alpha\beta}(ll')$  depends on  $l$  and  $l'$  only through their difference.

We now carry out the normal coordinate transformation given by eq. 1.3 in eq. 3.4 and obtain

$$S_{\mu} = \frac{\hbar}{2N} \sum_{\mathbf{k}j} \sum_{\mathbf{k}'j'} (\omega_j(\mathbf{k}) \omega_{j'}(\mathbf{k}'))^{1/2} v_{\mu}(\mathbf{k}j; \mathbf{k}'j') A_{\mathbf{k}j} B_{\mathbf{k}'j'} \times \left\{ N \Delta(\mathbf{k} + \mathbf{k}') + \sum_{l'} \left( \frac{M}{M_{l'}} - 1 \right) e^{2\pi i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{x}(l')} \right\} \quad (3.5)$$

where  $\Delta(\mathbf{k})$  equals unity when  $\mathbf{k}$  is a translation vector of the reciprocal lattice and vanishes otherwise, and where

$$v_{\mu}(\mathbf{k}j, \mathbf{k}'j') = \frac{1}{2\omega_j(\mathbf{k})} \sum_l e_{\alpha}(\mathbf{k}j) \left\{ x_{\mu}(\bar{l}) \frac{\Phi_{\alpha\beta}(\bar{l})}{M} \times \sin 2\pi \mathbf{k} \cdot \mathbf{x}(\bar{l}) \right\} \times e_{\beta}(\mathbf{k}'j') \quad (3.6)$$

Thus, we obtain a separation of the heat current operator into a part which is independent of the disorder and a part which depends on the disorder

$$S_{\mu} = S_{\mu}^{(a)} + S_{\mu}^{(d)} \quad (3.7)$$

where  $S_{\mu}^{(a)}$  gives the heat current operator for the perfect host crystal, while  $S_{\mu}^{(d)}$  is the contribution to the heat current from the interaction terms in the crystal Hamiltonian

$$S_{\mu}^{(a)} = \frac{\hbar}{2} \sum_{\mathbf{k}jj'} (\omega_j(\mathbf{k}) \omega_{j'}(\mathbf{k}'))^{1/2} v_{\mu}(\mathbf{k}j; -\mathbf{k}'j') A_{\mathbf{k}j} B_{-\mathbf{k}'j'} \quad (3.8)$$

$$S_{\mu}^{(d)} = \frac{\hbar}{2N} \sum_{\mathbf{k}j} \sum_{\mathbf{k}'j'} \sum_l (\omega_j(\mathbf{k}) \omega_{j'}(\mathbf{k}'))^{1/2} \times v_{\mu}(\mathbf{k}j; \mathbf{k}'j') \left( \frac{M}{M_l} - 1 \right) e^{2\pi i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{x}(l)} A_{\mathbf{k}j} B_{\mathbf{k}'j'} \quad (3.9)$$

Let us look at  $S_{\mu}^{(a)}$  more closely.

We can simplify the expression for  $v_{\mu}(\mathbf{k}j; -\mathbf{k}'j')$  given by eq. 3.6 if we introduce the eigenvalue equation for the normal mode frequencies of the unperturbed crystal

$$\sum_{\beta} D_{\alpha\beta}(\mathbf{k}) e_{\beta}(\mathbf{k}j) = \omega_j^2(\mathbf{k}) e_{\alpha}(\mathbf{k}j) \quad (3.10)$$

$$D_{\alpha\beta}(\mathbf{k}) = \frac{1}{M} \sum_l \Phi_{\alpha\beta}(\bar{l}) e^{-2\pi i \mathbf{k} \cdot \mathbf{x}(l)} \quad (3.11)$$

together with the orthogonality condition on the eigenvectors

$$\sum_{\alpha} e_{\alpha}(\mathbf{k}j) e_{\alpha}(\mathbf{k}'j') = \delta_{jj'} \quad (3.12)$$

It follows from eq. 3.6 and 3.10-3.12 that  $v_{\mu}(\mathbf{k}j; -\mathbf{k}'j')$  can be written in the form

$$v_{\mu}(\mathbf{k}j; -\mathbf{k}'j') = -\delta_{jj'} v_{\mu}(\mathbf{k}j) - v_{\mu}(\mathbf{k}'j') \quad (3.13)$$

where  $v_{\mu}(\mathbf{k}j)$  is the  $\mu$ -component of the group velocity of the phonon  $(\mathbf{k}j)$

$$v_{\mu}(\mathbf{k}j) = \frac{1}{2\pi} \frac{\partial \omega_j(\mathbf{k})}{\partial \mathbf{k}_{\mu}} \quad (3.14)$$

and

$$v_{\mu}(\mathbf{k}jj') = \frac{[\omega_j^2(\mathbf{k}) - \omega_{j'}^2(\mathbf{k}')]}{4\pi \omega_j(\mathbf{k})} \sum_{\alpha} \frac{\partial e_{\alpha}(\mathbf{k}j)}{\partial \mathbf{k}_{\mu}} e_{\alpha}(\mathbf{k}'j') \quad (3.15)$$

It should be pointed out that the analog of  $v_{\mu}(\mathbf{k}jj')$  for a monatomic linear chain vanishes because the eigenvector  $\mathbf{e}(\mathbf{k}j)$  is a constant independent of  $\mathbf{k}$ .

Both  $v_{\mu}(\mathbf{k}j)$  and  $v_{\mu}(\mathbf{k}'j')$  are odd functions of the wave vector  $\mathbf{k}$ . In view of eq. 3.13 we can write  $S_{\mu}^{(a)}$  as the sum of a term which is diagonal in the phonon branch indices and a term which is not

$$S_{\mu}^{(a)} = S_{\mu}^{(aa)} + S_{\mu}^{(a1)} \quad (3.16)$$

where

$$S_{\mu}^{(aa)} = \frac{\hbar}{2} \sum_{\mathbf{k}j} \omega_j(\mathbf{k}) v_{\mu}(\mathbf{k}j) A_{\mathbf{k}j} B_{\mathbf{k}j} \quad (3.17)$$

$$= \sum_{\mathbf{k}j} \hbar \omega_j(\mathbf{k}) v_{\mu}(\mathbf{k}j) a_{\mathbf{k}j} + a_{\mathbf{k}j} \quad (3.18)$$

$$S_{\mu}^{(a1)} = \frac{\hbar}{2} \sum_{\mathbf{k}jj'} (\omega_j(\mathbf{k}) \omega_{j'}(\mathbf{k}'))^{1/2} v_{\mu}(\mathbf{k}jj') A_{\mathbf{k}j} B_{\mathbf{k}'j'} \quad (3.19)$$

The existence of the nondiagonal contribution to the heat current operator has been demonstrated previously by Hardy<sup>14,17</sup> and Choquard.<sup>18</sup>

The contribution  $S_{\mu}^{(aa)}$  is the expression which is commonly written down for the phonon heat current operator in a harmonic crystal. We see, however, that there are at least two other contributions to the heat current operator in the harmonic approximation, *viz.*,  $S_{\mu}^{(a1)}$  and  $S_{\mu}^{(d)}$ . In the calculations of the next section, however, we retain only the contributions  $S_{\mu}^{(aa)}$  and  $S_{\mu}^{(a1)}$  to the heat current operator and neglect the contribution associated with  $S_{\mu}^{(d)}$ . The motivation for this approximation lies in the fact that since  $S_{\mu}^{(d)}$  is, roughly speaking, proportional to the interaction term in the crystal Hamiltonian, when we evaluate the configuration average of the product of two phonon

(18) Ph. Choquard, Preliminary Report, Battelle Memorial Institute, Geneva, Switzerland, 1962. unpublished.

Green's functions in the next section the terms involving  $S_\mu^{(d)}$  in the spectral densities obtained from these averages will be of at least one higher order in  $p$  than those which do not involve  $S_\mu^{(d)}$ .

For convenience in what follows we express the heat current operator as

$$S_\mu = \sum_{\mathbf{k}j j'} S_\mu(\mathbf{k}j j') A_{\mathbf{k}j} B_{\mathbf{k}j'}^+ \quad (3.20a)$$

where

$$S_\mu(\mathbf{k}j j') = \delta_{j j'} \frac{\hbar}{2} \omega_j(\mathbf{k}) v_\mu(\mathbf{k}j) + \frac{\hbar}{2} (\omega(\mathbf{k}) \omega_{j'}(\mathbf{k}))^{1/2} v_\mu(\mathbf{k}j j') \quad (3.20b)$$

The results we obtain in this approximation already go beyond what is obtainable from the usual treatment of lattice thermal conductivity on the basis of the Peierls transport equation since the latter makes no provision for the nondiagonal contribution to the heat current operator,  $S_\mu^{(01)}$ .

It is useful to note that  $v_\mu(\mathbf{k}j j')$  obeys the symmetry relation

$$\omega_j(\mathbf{k}) v_\mu(\mathbf{k}j j') = \omega_{j'}(\mathbf{k}) v_\mu(\mathbf{k}j' j) \quad (3.21)$$

as a consequence of which we see that

$$\omega_j(\mathbf{k}) S_\mu(\mathbf{k}j j') = \omega_{j'}(\mathbf{k}) S_\mu(\mathbf{k}j' j) \quad (3.22)$$

#### 4. The Thermal Conductivity

In this section we obtain the Fourier coefficient  $f(i\omega_l)$  of the heat current correlation function  $F(u)$ , which is defined by eq. 2.12, and from it the thermal conductivity. According to eq. 2.12 and 3.20 the explicit expression for  $F(u)$  is

$$F(u) = \sum_\mu \sum_{\mathbf{k}j_1 j_2} \sum_{\mathbf{k}'j_3 j_4} S_\mu(\mathbf{k}j_1 j_2) S_\mu(\mathbf{k}'j_3 j_4) \times \langle T A_{\mathbf{k}j_1}(u) B_{\mathbf{k}j_2}^+(u) A_{\mathbf{k}'j_3}(0) B_{\mathbf{k}'j_4}^+(0) \rangle \quad (4.1)$$

It will be convenient later on to recall that  $S_\mu(\mathbf{k}j j')$  is an odd function of  $\mathbf{k}$ .

The calculation of the correlation function  $\langle T A_{\mathbf{k}j_1}(u) B_{\mathbf{k}j_2}^+(u) A_{\mathbf{k}'j_3}(0) B_{\mathbf{k}'j_4}^+(0) \rangle$  is greatly simplified by the circumstance that for the present problem the perturbation Hamiltonian is a quadratic function of the phonon creation and destruction operators, *i.e.*, of the operators  $\{B_{\mathbf{k}j}\}$ . Since only two phonon vertices occur in this problem we are led to the result that the correlation function  $F(u)$  can be written in the factored form

$$F(u) = \sum_\mu \sum_{\mathbf{k}j_1 j_2} \sum_{\mathbf{k}'j_3 j_4} S_\mu(\mathbf{k}j_1 j_2) S_\mu(\mathbf{k}'j_3 j_4) \times \{ \mathfrak{D}^{++}(\mathbf{k}j_1, \mathbf{k}'j_3; u) \mathfrak{D}^{--}(\mathbf{k}j_2, \mathbf{k}'j_4; u) + \mathfrak{D}^{+-}(\mathbf{k}j_1, \mathbf{k}'j_4; u) \mathfrak{D}^{-+}(\mathbf{k}j_2, \mathbf{k}'j_3; u) \} \quad (4.2)$$

where we have introduced the phonon Green's functions

$$\mathfrak{D}^{++}(\mathbf{k}j, \mathbf{k}'j'; u) = \langle T_u A_{\mathbf{k}j}(u) A_{\mathbf{k}'j'}(0) \rangle \quad (4.3a)$$

$$\mathfrak{D}^{--}(\mathbf{k}j, \mathbf{k}'j'; u) = \langle T_u B_{\mathbf{k}j}^+(u) B_{\mathbf{k}'j'}^+(0) \rangle \quad (4.3b)$$

$$\mathfrak{D}^{+-}(\mathbf{k}j, \mathbf{k}'j'; u) = \langle T_u A_{\mathbf{k}j}(u) B_{\mathbf{k}'j'}^+(0) \rangle \quad (4.3c)$$

$$\mathfrak{D}^{-+}(\mathbf{k}j, \mathbf{k}'j'; u) = \langle T_u B_{\mathbf{k}j}^+(u) A_{\mathbf{k}'j'}(0) \rangle \quad (4.3d)$$

The evaluation of  $\mathfrak{D}^{++}(\mathbf{k}j, \mathbf{k}'j'; u)$  has been carried out in ref. 19. The evaluation of the remaining Green's functions can be carried out in the same way.

The Green's functions  $\mathfrak{D}^{\pm\pm}(\mathbf{k}j, \mathbf{k}'j'; u)$  can be expanded in Fourier series for  $u$  in the interval  $(-\beta, \beta)$

$$\mathfrak{D}^{\pm\pm}(\mathbf{k}j, \mathbf{k}'j'; u) = \sum_{l=-\infty}^{\infty} \mathfrak{D}^{\pm\pm}(\mathbf{k}j, \mathbf{k}'j'; i\omega_l) e^{i\omega_l u} \quad (4.4)$$

where  $\omega_l = 2\pi l/\beta\hbar$ . From eq. 4.2 and 4.4, we see that we can write  $f(i\omega_l)$ , the Fourier coefficient of  $F(u)$ , as

$$f(i\omega_l) = \sum_{\mathbf{k}j_1 j_2} \sum_{\mathbf{k}'j_3 j_4} \sum_{l_1=-\infty}^{\infty} \mathbf{S}(\mathbf{k}j_1 j_2) \cdot \mathbf{S}(\mathbf{k}'j_3 j_4) \times \{ \mathfrak{D}^{++}(\mathbf{k}j_1, \mathbf{k}'j_3; i\omega_{l_1}) \mathfrak{D}^{--}(\mathbf{k}j_2, \mathbf{k}'j_4; i\omega_l - i\omega_{l_1}) + \mathfrak{D}^{+-}(\mathbf{k}j_1, \mathbf{k}'j_4; i\omega_{l_1}) \mathfrak{D}^{-+}(\mathbf{k}j_2, \mathbf{k}'j_3; i\omega_l - i\omega_{l_1}) \} \quad (4.5)$$

The Fourier coefficients  $\mathfrak{D}^{\pm\pm}(\mathbf{k}j, \mathbf{k}'j'; i\omega_l)$  are readily obtained by the methods described in ref. 19 with the results that

$$\mathfrak{D}^{++}(\mathbf{k}j, \mathbf{k}'j'; i\omega_l) = \alpha(\mathbf{k}j, i\omega_l) \Delta(\mathbf{k} + \mathbf{k}') \delta_{j j'} + \beta(\mathbf{k}j, i\omega_l) M(\mathbf{k}j, -\mathbf{k}'j'; i\omega_l) \beta(\mathbf{k}'j', i\omega_l) \quad (4.6a)$$

$$\mathfrak{D}^{--}(\mathbf{k}j, \mathbf{k}'j'; i\omega_l) = -\alpha(\mathbf{k}j, i\omega_l) \Delta(\mathbf{k} + \mathbf{k}') \delta_{j j'} - \alpha(\mathbf{k}j, i\omega_l) M(-\mathbf{k}j, \mathbf{k}'j'; i\omega_l) \alpha(\mathbf{k}'j', i\omega_l) \quad (4.6b)$$

$$\mathfrak{D}^{+-}(\mathbf{k}j, \mathbf{k}'j'; i\omega_l) = -\beta(\mathbf{k}j, i\omega_l) \Delta(\mathbf{k} - \mathbf{k}') \delta_{j j'} - \beta(\mathbf{k}j, i\omega_l) M(\mathbf{k}j, \mathbf{k}'j'; i\omega_l) \alpha(\mathbf{k}'j', i\omega_l) \quad (4.6c)$$

$$\mathfrak{D}^{-+}(\mathbf{k}j, \mathbf{k}'j'; i\omega_l) = \beta(\mathbf{k}j, i\omega_l) \Delta(\mathbf{k} - \mathbf{k}') \delta_{j j'} + \alpha(\mathbf{k}j, i\omega_l) M(-\mathbf{k}j, -\mathbf{k}'j'; i\omega_l) \beta(\mathbf{k}'j', i\omega_l) \quad (4.6d)$$

The various functions appearing in these expressions are given by

$$M(\mathbf{k}j, \mathbf{k}'j'; i\omega_l) = -2\beta V(-\mathbf{k}j, \mathbf{k}'j') + (2\beta)^2 \sum_{\mathbf{k}_1 j_1} V(-\mathbf{k}j, \mathbf{k}_1 j_1) \alpha(\mathbf{k}_1 j_1, i\omega_l) V(-\mathbf{k}_1 j_1, \mathbf{k}'j') -$$

$$(2\beta)^3 \sum_{\mathbf{k}_1 j_1} \sum_{\mathbf{k}_2 j_2} V(-\mathbf{k}j, \mathbf{k}_1 j_1) \alpha(\mathbf{k}_1 j_1, i\omega_l) V(-\mathbf{k}_1 j_1, \mathbf{k}_2 j_2) \times \alpha(\mathbf{k}_2 j_2, i\omega_l) V(-\mathbf{k}_2 j_2, \mathbf{k}'j') + \dots =$$

$$M(-\mathbf{k}'j', -\mathbf{k}j; i\omega_l) \quad (4.7)$$

$$\alpha(\mathbf{k}j, i\omega_l) = \frac{2\omega_j(\mathbf{k})}{\beta\hbar} \frac{1}{\omega_j^2(\mathbf{k}) + \omega_l^2} \quad (4.8a)$$

$$\beta(\mathbf{k}j, i\omega_l) = \frac{2i\omega_l}{\beta\hbar} \frac{1}{\omega_j^2(\mathbf{k}) + \omega_l^2} \quad (4.8b)$$

All of the random features of the disordered crystal are contained in the function  $M(\mathbf{k}j, \mathbf{k}'j'; i\omega_l)$ .

When we multiply two propagators together in the manner specified by eq. 4.5, and take the configuration average of the product, we see that we have two distinct averages to evaluate, namely

$$\langle M(\mathbf{k}j, \mathbf{k}'j'; i\omega_l) \rangle_A$$

and

$$\langle M(-\mathbf{k}j_1, -\mathbf{k}'j_2; i\omega_l) M(\mathbf{k}j_3, \mathbf{k}'j_4; i\omega_l) \rangle_A$$

In the approximation in which the repeated scattering of a phonon from one and the same impurity is taken

(19) A. A. Maradudin in "Astrophysics and the Many-Body Problem," W. A. Benjamin, Inc., New York, N. Y., 1963, p. 107.

into account exactly, while the scattering of a phonon from two or more different impurities is neglected, it has been shown<sup>19,20</sup> that for a cubic Bravais host crystal the former average is given by

$$\langle M(\mathbf{k}j; \mathbf{k}'j'; i\omega_l) \rangle_A = \Delta(\mathbf{k} - \mathbf{k}')\delta_{jj'}C(\mathbf{k}j; i\omega_l) \quad (4.9a)$$

where the function  $C(\mathbf{k}j; i\omega_l)$  is

$$C(\mathbf{k}j; i\omega_l) = -\epsilon p \frac{\beta \hbar \omega_j(\mathbf{k})}{2} \times \frac{(\omega_j^2(\mathbf{k}) + \omega_l^2)F^{-1}(i\omega_l)}{\omega_j^2(\mathbf{k}) + \omega_l^2 + \epsilon p \omega_j^2(\mathbf{k})F^{-1}(i\omega_l)} \quad (4.9b)$$

with

$$F(i\omega_l) = 1 - \frac{\epsilon \omega_l^2}{3N} \sum_{\mathbf{k}j} \frac{1}{\omega_j^2(\mathbf{k}) + \omega_l^2} \quad (4.9c)$$

$$\epsilon = 1 - \frac{M'}{M} \quad (4.9d)$$

The latter average can always be written as

$$\begin{aligned} \langle M(-\mathbf{k}j_1; -\mathbf{k}'j_2; i\omega_l)M(\mathbf{k}j_3; \mathbf{k}'j_4; i\omega_l) \rangle_A = \\ \langle M(-\mathbf{k}j_1; -\mathbf{k}'j_2; i\omega_l) \rangle_A \langle M(\mathbf{k}j_3; \mathbf{k}'j_4; i\omega_l) \rangle_A + \\ \langle M(-\mathbf{k}j_1; -\mathbf{k}'j_2; i\omega_l)M(\mathbf{k}j_3; \mathbf{k}'j_4; i\omega_l) \rangle_{A, \text{correlated}} \end{aligned} \quad (4.10a)$$

where the second term on the right side of this equation gives those terms which arise from the interference between the two factors when the configuration average of their product is taken. In the approximation represented by eq. 4.9a, we can substitute the result given by eq. 4.9a into the first term on the right side of eq. 4.10a. A detailed analysis,<sup>20</sup> which we will not reproduce here, shows that to the same approximation the correlated part of the average 4.10a is given by the product of an even function of  $\mathbf{k}$  alone and an even function of  $\mathbf{k}'$  alone. When this term is substituted into the configuration average of eq. 4.5, it yields a vanishing contribution to the thermal conductivity because of the oddness of  $\mathbf{S}(\mathbf{k}j_1j_2)$  and  $\mathbf{S}(\mathbf{k}'j_3j_4)$  in  $\mathbf{k}$  and  $\mathbf{k}'$ , respectively. As a result, for the purposes of the present paper we may write

$$\langle M(-\mathbf{k}j_1; -\mathbf{k}'j_2; i\omega_l)M(\mathbf{k}j_3; \mathbf{k}'j_4; i\omega_l) \rangle_A = \Delta(\mathbf{k} - \mathbf{k}')\delta_{j_1j_2}\delta_{j_3j_4}C(\mathbf{k}j_1; i\omega_l)C(\mathbf{k}j_3; i\omega_l) \quad (4.10b)$$

It is an immediate consequence of the results expressed by eq. 4.9 and 4.10 that in taking the configuration average of both sides of eq. 4.5 we can replace the average of the product of two propagators by the product of the averages

$$\begin{aligned} \langle f(i\omega_l) \rangle_A = \sum_{\mathbf{k}j_1j_2} \sum_{\mathbf{k}'j_3j_4} \sum_{l=-\infty}^{\infty} \mathbf{S}(\mathbf{k}j_1j_2)\mathbf{S}(\mathbf{k}'j_3j_4) \times \\ \{ \langle \mathcal{D}^{++}(\mathbf{k}j_1; \mathbf{k}'j_3; i\omega_l) \rangle_A \langle \mathcal{D}^{--}(\mathbf{k}j_2; \mathbf{k}'j_4; i\omega_l - i\omega_l) \rangle_A + \\ \langle \mathcal{D}^{+-}(\mathbf{k}j_1; \mathbf{k}'j_4; i\omega_l) \rangle_A \langle \mathcal{D}^{-+}(\mathbf{k}j_2; \mathbf{k}'j_3; i\omega_l - i\omega_l) \rangle_A \} \end{aligned} \quad (4.11)$$

The Fourier coefficients  $\mathcal{D}^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; i\omega_l)$  possess spectral representations which we write in the form

(20) A. A. Maradudin, Westinghouse Research Laboratories Scientific Paper 64-929-100-P4, January 29, 1964. A result equivalent to that given by eq. 4.10b is also obtained by Woll and Langer, ref. 12.

$$\mathcal{D}^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; i\omega_l) = \int_{-\infty}^{\infty} d\nu \frac{\Delta^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; \nu)}{\nu - i\omega_l} \quad (4.12)$$

The spectral density  $\Delta^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; \nu)$  can be obtained from the Fourier coefficient  $\mathcal{D}^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; i\omega_l)$  if in the latter we replace  $i\omega_l$  by the continuous, complex, variable  $z$ . We then see that

$$\Delta^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; \nu) = \frac{1}{2\pi i} \{ \mathcal{D}^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; \nu + i0) - \mathcal{D}^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; \nu - i0) \} \quad (4.13)$$

When the spectral representations (4.12) are substituted into eq. 4.11, the sum over  $l$  can be carried out directly, and the functions  $f(z)$  and therefore  $f(\nu)$  constructed. Combining the result of these steps with eq. 2.14, we obtain for the thermal conductivity

$$\begin{aligned} \langle \kappa \rangle_A = -\frac{1}{\Omega k T^2} \frac{\pi}{3} \frac{\beta^2 \hbar^2}{4} \sum_{\mathbf{k}j_1j_2} \sum_{\mathbf{k}'j_3j_4} \mathbf{S}(\mathbf{k}j_1j_2) \cdot \mathbf{S}(\mathbf{k}'j_3j_4) \times \\ \int_{-\infty}^{\infty} d\nu \operatorname{csch}^2 \frac{\beta \hbar \nu}{2} \{ \langle \Delta^{++}(\mathbf{k}j_1; \mathbf{k}'j_3; \nu) \rangle_A \times \\ \langle \Delta^{--}(\mathbf{k}j_2; \mathbf{k}'j_4; -\nu) \rangle_A + \langle \Delta^{+-}(\mathbf{k}j_1; \mathbf{k}'j_4; \nu) \rangle_A \times \\ \langle \Delta^{-+}(\mathbf{k}j_2; \mathbf{k}'j_3; -\nu) \rangle_A \} \end{aligned} \quad (4.14)$$

This result is correct to the lowest order in  $p$ .

Combining eq. 4.6, 4.7, 4.9, and 4.10 we can write the configuration averages of the Fourier coefficients  $\mathcal{D}^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; i\omega_l)$  as

$$\langle \mathcal{D}^{++}(\mathbf{k}j; \mathbf{k}'j'; i\omega_l) \rangle_A = \Delta(\mathbf{k} + \mathbf{k}')\delta_{jj'} \times \frac{2\omega_j(\mathbf{k})}{\beta \hbar} \frac{1 + \epsilon p F^{-1}(i\omega_l)}{\omega_j^2(\mathbf{k}) + \omega_l^2 + \epsilon p \omega_j^2(\mathbf{k})F^{-1}(i\omega_l)} \quad (4.15a)$$

$$\langle \mathcal{D}^{--}(\mathbf{k}j; \mathbf{k}'j'; i\omega_l) \rangle_A = -\Delta(\mathbf{k} + \mathbf{k}')\delta_{jj'} \times \frac{2\omega_j(\mathbf{k})}{\beta \hbar} \frac{1}{\omega_j^2(\mathbf{k}) + \omega_l^2 + \epsilon p \omega_j^2(\mathbf{k})F^{-1}(i\omega_l)} \quad (4.15b)$$

$$\langle \mathcal{D}^{+-}(\mathbf{k}j; \mathbf{k}'j'; i\omega_l) \rangle_A = -\Delta(\mathbf{k} - \mathbf{k}')\delta_{jj'} \times \frac{2i\omega_l}{\beta \hbar} \frac{1}{\omega_j^2(\mathbf{k}) + \omega_l^2 + \epsilon p \omega_j^2(\mathbf{k})F^{-1}(i\omega_l)} \quad (4.15c)$$

$$\langle \mathcal{D}^{-+}(\mathbf{k}j; \mathbf{k}'j'; i\omega_l) \rangle_A = -\langle \mathcal{D}^{+-}(\mathbf{k}j; \mathbf{k}'j'; i\omega_l) \rangle_A \quad (4.15d)$$

From these results and eq. 4.13 we obtain for the configuration average of the spectral densities of these propagators

$$\langle \Delta^{++}(\mathbf{k}j; \mathbf{k}'j'; \nu) \rangle_A = \Delta(\mathbf{k} + \mathbf{k}')\delta_{jj'} \times \frac{2\omega_j(\mathbf{k})}{\pi \beta \hbar} \frac{\epsilon p \nu^2 b(\nu)}{D(\mathbf{k}j; \nu)} \quad (4.16a)$$

$$\langle \Delta^{--}(\mathbf{k}j; \mathbf{k}'j'; \nu) \rangle_A = -\Delta(\mathbf{k} + \mathbf{k}')\delta_{jj'} \times \frac{2\omega_j(\mathbf{k})}{\pi \beta \hbar} \frac{\epsilon p \omega_j^2(\mathbf{k}) b(\nu)}{D(\mathbf{k}j; \nu)} \quad (4.16b)$$

$$\langle \Delta^{+-}(\mathbf{k}j; \mathbf{k}'j'; \nu) \rangle_A = -\Delta(\mathbf{k} - \mathbf{k}')\delta_{jj'} \times \frac{2\nu}{\beta \hbar} \frac{\epsilon p \omega_j^2(\mathbf{k}) b(\nu)}{D(\mathbf{k}j; \nu)} \quad (4.16c)$$

$$\langle \Delta^{-+}(\mathbf{k}j; \mathbf{k}'j'; \nu) \rangle_A = -\langle \Delta^{+-}(\mathbf{k}j; \mathbf{k}'j'; \nu) \rangle_A \quad (4.16d)$$

The various functions appearing in these expressions are defined by

$$D(\mathbf{k}j; \nu) = [\omega_j^2(\mathbf{k}) - \nu^2 + \epsilon p \omega_j^2(\mathbf{k}) a(\nu)]^2 + \epsilon^2 p^2 \omega_j^4(\mathbf{k}) b^2(\nu) \quad (4.17)$$

$$a(\nu) = \frac{1 - \epsilon \nu^2 \tilde{G}_o(\nu^2)}{[1 - \epsilon \nu^2 \tilde{G}_o(\nu^2)]^2 + \pi^2 \epsilon^2 \nu^4 G_o^2(\nu^2)} \quad (4.18)$$

$$b(\nu) = \frac{\text{sgn } \nu \pi \epsilon \nu^2 G_o(\nu^2)}{[1 - \epsilon \nu^2 \tilde{G}_o(\nu^2)]^2 + \pi^2 \epsilon^2 \nu^4 G_o^2(\nu^2)} \quad (4.19)$$

$$G_o(\nu^2) = \frac{1}{3N} \sum_{\mathbf{k}j} \delta(\nu^2 - \omega_j^2(\mathbf{k})) \quad (4.20)$$

$$\tilde{G}_o(\nu^2) = \frac{1}{3N} \sum_{\mathbf{k}j} \frac{1}{(\nu^2 - \omega_j^2(\mathbf{k}))_P} \quad (4.21)$$

The function  $G_o(\nu^2)$  is the distribution function for the squares of the normal mode frequencies of the perfect host crystal, while  $\tilde{G}_o(\nu^2)$  is its Hilbert transform.

In obtaining the results for the spectral densities given by eq. 4.16 we have assumed that the impurity atoms do not give rise to localized vibration modes. This is because the approximation to the configuration average of the propagators  $\mathcal{D}^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; i\omega)$  that we use here yields a  $\delta$ -function contribution to the corresponding averaged spectral densities associated with the localized modes, if any are present. In the case of a cubic Bravais crystal where the localized mode is triply degenerate,<sup>19</sup> the product of the  $\delta$ -functions which would arise from this source in the product of the spectral densities in eq. 4.14 is nonintegrable. Physically, this is due to the fact that in this approximation heat is conducted by the localized modes as if they are noninteracting, and thus with zero resistance. A more sophisticated treatment of the impurity problem is required to overcome this undesirable feature of the present calculation. One possibility is to use self-consistent forms of the phonon propagators.<sup>21</sup> In this approximation the pole of  $\langle \mathcal{D}^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; z) \rangle_A$  in the neighborhood of the localized mode frequency, which gives rise to the  $\delta$ -function in the spectral density  $\langle \Delta^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; \nu) \rangle_A$ , is spread out into a branch cut. The spectral density loses its  $\delta$ -function character and the integral over  $\nu$  in eq. 4.14 is no longer singular. Inclusion of the anharmonicity of the interatomic forces in the present theory would also have the same beneficial consequences for the spectral densities. It should be emphasized, however, that no difficulties of the kind just described arise when the expressions for the spectral densities given by eq. 4.16 are used in the case that the impurities are heavier than the atoms they replace. Since this situation displays a number of features which are of current interest in the theory of thermal resistivity due to point defects, the fact that in all that follows we consider only heavy impurities or impurities which are not light enough to give rise to localized modes does not render our results overly restrictive.

When we substitute the spectral densities given by eq. 4.16 and the explicit expression for  $\mathbf{S}(\mathbf{k}j_1 j_2)$  given by eq. 3.20b into eq. 4.14, we obtain

$$\langle \kappa \rangle_A = \kappa^{(0)} + \kappa^{(1)} \quad (4.22a)$$

(21) J. S. Langer and R. W. Davies, *Bull. Am. Phys. Soc.*, [2] **8**, 15 (1963).

where

$$\kappa^{(0)} = \frac{2\epsilon^2 p^2}{3\pi} \sum_{\mathbf{k}j} \omega_j^6(\mathbf{k}) v^2(\mathbf{k}j) \times \int_{-\infty}^{\infty} d\nu c_v(\nu, T) \frac{b^2(\nu)}{D^2(\mathbf{k}j; \nu)} \quad (4.22b)$$

$$\kappa^{(1)} = \frac{\epsilon^2 p^2}{3\pi} \sum_{\mathbf{k}j_1 j_2} \omega_{j_1}^2(\mathbf{k}) \omega_{j_2}^2(\mathbf{k}) [\omega_{j_1}^2(\mathbf{k}) + \omega_{j_2}^2(\mathbf{k})] v^2(\mathbf{k}j_1 j_2) \times \int_{-\infty}^{\infty} d\nu c_v(\nu, T) \frac{b^2(\nu)}{D(\mathbf{k}j_1; \nu) D(\mathbf{k}j_2; \nu)} \quad (4.22c)$$

where we have put

$$c_v(\nu, T) = \frac{k}{\Omega} \frac{(1/2\beta\hbar\nu)^2}{\sinh^2 1/2\beta\hbar\nu} \quad (4.23)$$

Let us study each of these contributions in turn.

As it stands, the result given by eq. 4.22b is sufficiently complicated that it is not easy to see even its qualitative features. Accordingly, we make some approximations on the functions which enter into it which lead to a result which can be readily understood. Let us first define a frequency  $\nu_o(\mathbf{k}j)$  by the equation

$$\omega_j^2(\mathbf{k}) - \nu_o^2 + \epsilon p \omega_j^2(\mathbf{k}) a(\nu_o) = 0 \quad (4.24)$$

If we then assume that  $b(\nu)$  is slowly varying for  $\nu$  in the neighborhood of  $\nu_o(\mathbf{k}j)$ , so that we can replace it by its value at  $\nu_o$ , and in addition is small, we can make the "quasi-particle" approximation

$$D^{-2}(\mathbf{k}j; \nu) \cong N(\mathbf{k}j) [\delta(\nu - \nu_o) + \delta(\nu + \nu_o)] \quad (4.25a)$$

where the coefficient  $N(\mathbf{k}j)$  is found to be

$$N(\mathbf{k}j) = \frac{\pi}{2} \frac{1}{|2\nu_o - \epsilon p \omega_j^2(\mathbf{k}) a'(\nu_o)|} \times \frac{1}{\epsilon^3 p^3 \omega_j^5(\mathbf{k}) b^3(\nu_o)} \quad (4.25b)$$

With this simple approximation for  $D^{-2}(\mathbf{k}j; \nu)$  the integral over  $\nu$  in eq. 4.22b becomes trivial, and we obtain

$$\kappa^{(0)} = \frac{1}{3} \epsilon^2 p^2 \sum_{\mathbf{k}j} \frac{\omega_j^6(\mathbf{k}) v^2(\mathbf{k}j) c_v(\nu_o, T)}{|2\nu_o - \epsilon p \omega_j^2(\mathbf{k}) a'(\nu_o)|} \times \frac{2}{\epsilon^3 p^3 \omega_j^5(\mathbf{k}) b^3(\nu_o)} \quad (4.26)$$

From eq. 4.16 and 4.17 and the kind of argument that led to eq. 4.25 we see that the spectral densities of the phonon propagators  $\langle \Delta^{\pm\pm}(\mathbf{k}j; \mathbf{k}'j'; \nu) \rangle_A$  have a resonance form, centered at  $\nu = \pm\nu_o$ . The width of this resonance at half-maximum, which we denote by  $2\Gamma(\mathbf{k}j)$ , gives the decay rate for the probability (rather than for the probability amplitude) of finding a phonon in the mode  $(\mathbf{k}j)$  at time  $t$  if it is present in this mode at time  $t = 0$ . We call the reciprocal of this width the phonon lifetime, and from eq. 4.16 obtain the result

$$\tau^{-1}(\mathbf{k}j) = 2\Gamma(\mathbf{k}j) = \frac{2\epsilon p \omega_j^2(\mathbf{k}) b(\nu_o)}{2\nu_o - \epsilon p \omega_j^2(\mathbf{k}) a'(\nu_o)} \quad (4.27)$$

Finally, if we make the approximation of replacing  $\nu_o$  by  $\omega_j(\mathbf{k})$  and neglecting  $\epsilon p \omega_j^2(\mathbf{k}) a'(\nu_o)$  compared with

$\omega_j(\mathbf{k})$ , because it gives a contribution of higher order in  $p$  than we consider here, we obtain

$$\kappa^{(0)} = \frac{1}{3} \sum_{\mathbf{kj}} c_v(\omega_j(\mathbf{k}), T) v^2(\mathbf{kj}) \tau(\mathbf{kj}) \quad (4.28a)$$

$$= \frac{1}{3} \sum_{\mathbf{kj}} c_v(\omega_j(\mathbf{k}), T) v(\mathbf{kj}) l(\mathbf{kj}) \quad (4.28b)$$

where  $l(\mathbf{kj}) = v(\mathbf{kj})\tau(\mathbf{kj})$  is the mean free path of the phonon  $(\mathbf{kj})$ . The result given by eq. 4.28 is just the result given by the kinetic theory applied to a phonon gas. It must be kept in mind that eq. 4.28 is only an approximation to the expression given by eq. 4.22b which results when we neglect the shift in the frequency of the phonon  $(\mathbf{kj})$  given by  $\nu_o(\mathbf{kj}) - \omega_j(\mathbf{k})$ , and when the width  $2\Gamma(\mathbf{kj})$  is small.

To the approximation represented by eq. 4.28, the reciprocal of the phonon lifetime is given by

$$\tau^{-1}(\mathbf{kj}) = \pi p \epsilon^2 \times \frac{\omega_j^3(\mathbf{k}) G_o(\omega_j^2(\mathbf{k}))}{[1 - \epsilon \omega_j^2(\mathbf{k}) \tilde{G}_o(\omega_j^2(\mathbf{k}))]^2 + \pi^2 \epsilon^2 \omega_j^4(\mathbf{k}) G_o^2(\omega_j^2(\mathbf{k}))} \quad (4.29)$$

In the long wave length limit, *i.e.*, for small  $\omega_j(\mathbf{k})$ ,  $G_o(\omega_j^2(\mathbf{k}))$  is proportional to  $\omega_j(\mathbf{k})$ , so that the inverse lifetime is proportional to  $\omega_j^4(\mathbf{k})$ , or to  $k^4$ . We see therefore from eq. (4.28a) that the sum over  $\mathbf{k}$  diverges at long wave lengths like  $\Sigma k^{-2}$ . However, we can argue that by the time that the phonon wave lengths become so long that the sum begins to diverge, the scattering of phonons by the external boundaries of the crystal begins to dominate, and a finite result for the conductivity is recovered. We may, therefore, impose a long wave length cutoff on the sums in eq. 4.28, but we will not indicate this explicitly in any of the results which follow.

Expressions of the type given by the right side of eq. 4.29 have received a great deal of study recently in connection with the theory of the Mössbauer effect for an impurity nucleus<sup>19,22</sup> lattice thermal conductivity,<sup>10</sup> and the thermal properties of crystals.<sup>23</sup> From the standpoint of the present paper, the most interesting feature of this expression is the resonance character it possesses when  $\epsilon$  is large and negative, *i.e.*, when the substitutional impurity is a heavy atom. In this case it can be shown<sup>8,22</sup> that the equation

$$1 = -|\epsilon| \omega^2 \tilde{G}_o(\omega^2) \quad (4.30)$$

always has a solution  $\omega_r^2$  which tends to zero as  $|\epsilon|$  increases indefinitely. In the neighborhood of this frequency the reciprocal lifetime  $\tau^{-1}(\mathbf{kj})$  has the form

$$\tau^{-1}(\mathbf{kj}) \cong \frac{\pi p}{4B^2(\omega_r^2)} \frac{\omega_r G_o(\omega_r^2)}{(\omega_j(\mathbf{k}) - \omega_r)^2 + \frac{1}{4}(\gamma_r^2)} \quad (4.31)$$

where

$$B(\omega_r^2) = \frac{1}{3N} \sum_{\mathbf{kj}} \frac{\omega_j^2(\mathbf{k})}{(\omega_r^2 - \omega_j^2(\mathbf{k}))^2} \quad (4.32)$$

(22) W. M. Visscher, *Phys. Rev.*, **129**, 28 (1963); A. A. Maradudin, Westinghouse Research Laboratories Scientific Paper 63-129-103-P9, 1963, unpublished.

(23) G. W. Lehman and R. E. DeWames, *Phys. Rev.*, **131**, 1008 (1963); Yu. M. Kagan and Ya. A. Iosilevskii, *Zh. Eksperim. i. Teor. Fiz.*, **45**, 819 (1963).

$$\gamma_r = \pi \frac{\omega_r G_o(\omega_r^2)}{B(\omega_r^2)} \quad (4.33)$$

The functional form for  $\tau^{-1}(\mathbf{kj})$  given by eq. 4.29 is that assumed by Pohl<sup>7</sup> to explain experimental results for the low temperature thermal conductivity of KCl with a small number of nitrite ions introduced substitutionally into the chloride sublattice. The origin of the resonance form for the inverse lifetime in that case is more likely due to the internal degrees of freedom in the nitrite ion<sup>24</sup> than to any approximation of this ion as a pure mass defect.

Qualitative and quantitative results for the thermal conductivity of a disordered crystal have been obtained by Callaway<sup>10</sup> and Takeno<sup>10</sup> on the basis of an inverse phonon lifetime of the form given by eq. 4.29, and we do not consider this aspect of the problem any further here.

It may be worth pointing out that it is because the function  $\tilde{G}_o(\omega^2)$  vanishes identically for  $|\omega| < \omega_L$  for a nearest neighbor model of a linear chain that this model is incapable of yielding a resonance form for  $\tau^{-1}(\mathbf{kj})$ .

We come finally to the contribution  $\kappa^{(1)}$  to the thermal conductivity. If we make use of eq. 3.15 we see that we can rewrite the expression for  $\kappa^{(1)}$  in the more symmetric form.

$$\kappa^{(1)} = \frac{\epsilon^2 p^2}{6\pi} \sum_{\mathbf{kj}_1 j_2} [\omega_{j_1}^2(\mathbf{k}) - \omega_{j_2}^2(\mathbf{k})]^2 u^2(\mathbf{kj}_1 j_2) \times \int_{-\infty}^{\infty} d\nu c_v(\nu, T) \frac{b^2(\nu)}{D(\mathbf{kj}_1; \nu) D(\mathbf{kj}_2; \nu)} \quad (4.34)$$

where the components of the vector  $\mathbf{u}(\mathbf{kj}j')$  are given by

$$u_\mu(\mathbf{kj}j') = \frac{1}{4\pi} \sum_{\alpha} \frac{\partial e_\alpha(\mathbf{kj})}{\partial k_\mu} e_\alpha(\mathbf{kj}') \quad (4.35)$$

From the form of eq. 4.34 we see that in the approximation which yielded eq. 4.28, *i.e.*, replacement of  $D^{-1}(\mathbf{kj}_1; i\nu)$  and  $D^{-1}(\mathbf{kj}_2; \nu)$  by normalized  $\delta$ -functions, the integral over  $\nu$  is nonvanishing only if  $\omega_{j_1}(\mathbf{k}) = \omega_{j_2}(\mathbf{k})$ , but when this is the case the sum over  $\mathbf{k}$ ,  $j_1$ , and  $j_2$  vanishes because of the factor  $[\omega_{j_1}^2(\mathbf{k}) - \omega_{j_2}^2(\mathbf{k})]^2$ . To obtain a nonvanishing result for  $\kappa^{(1)}$  we would have to keep  $\Gamma(\mathbf{kj})$  finite in our calculations. Put another way, the contribution  $\kappa^{(1)}$  is of higher order in  $p$  than  $\kappa^{(0)}$ .

In summary, we have evaluated the Kubo formula for thermal conductivity for an isotopically disordered cubic Bravais crystal to lowest order in the concentration of the minority species. When the impurity atoms are heavier than the atoms they replace, the result has the form given by kinetic theory. However, it is not necessary to introduce a phenomenological phonon lifetime in an *ad hoc* way to obtain this result.<sup>25</sup> The lifetime which appears in our result arises in a natural way from the analysis. The inverse of the phonon lifetime has a resonance character when the impurity atom mass is much heavier than the mass of the host atom, in qualitative agreement with experimental data on lattice thermal conductivity in impure crystals.<sup>7</sup> Finally,

(24) M. Wagner, *Phys. Rev.*, **133**, A750 (1964).

(25) W. C. Schieve and R. L. Peterson, *ibid.*, **126**, 1458 (1962).



although the expression for the conductivity diverges at long wave lengths, arguments can be made for the introduction of a long wave length cutoff on the sums.

**Acknowledgment.**—The author is grateful to Professor J. S. Langer and Dr. E. J. Woll, Jr., for discussions of their work on the problem discussed in this paper.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF CALIFORNIA AT SAN DIEGO, LA JOLLA, CALIFORNIA]

## Contribution to the Theory of Brownian Motion

BY ROBERT J. RUBIN<sup>1</sup>

RECEIVED APRIL 14, 1964

The statistical dynamical behavior of a large spherical particle in an  $n$ -dimensional harmonic crystal is studied. This Brownian sphere is formed by constraining the particles inside a large spherical region of the crystal to move as a single particle. Effective equations of motion for the Brownian sphere are derived. For the one-dimensional and three-dimensional crystals, these equations are identical with the Langevin equation for a free particle and a harmonic oscillator, respectively. For the Brownian sphere in a two-dimensional crystal, a generalized Langevin equation is derived which is a non-Markoffian linear integro-differential equation. These results for the Brownian sphere are compared with the results obtained by Hemmer and Rubin for a different crystal lattice model.

### Introduction

The physical concepts and ideas which have evolved in the study of Brownian motion phenomena have pervaded many areas of physics, chemistry, astronomy, and mathematics.<sup>2,3</sup> In this paper, we continue a line of investigation<sup>4-7</sup> whose purpose is to gain some insight into the nature of the assumptions made in developing a theory of Brownian motion. These basic assumptions are best illustrated in the Langevin equation<sup>2a</sup>

$$M\ddot{X} + \beta\dot{X} - K(X) = A(t)$$

which has been used as a starting point for developing the theory. The Langevin equation is the equation of motion of a Brownian particle of mass  $M$  in an external force field  $K(X)$ . It is assumed in writing such an equation that the influence of the surrounding medium on the Brownian particle can be represented as the sum of two terms:  $\beta\dot{X}$  a dynamical friction or viscous resistance proportional to particle velocity, and  $A(t)$  a rapidly fluctuating random force whose intensity is related to the temperature of the medium. Starting from the Langevin equation, a complete description of the state of the Brownian particle is obtained in the form of a conditional probability distribution function (c.p.d.f.). The c.p.d.f.  $W(\dot{X}_2, X_2, t_2 | \dot{X}_1, X_1, t_1)$  is the conditional probability that the velocity and position are  $\dot{X}_2$  and  $X_2$  at time  $t_2$  when they were  $\dot{X}_1$  and  $X_1$  at the earlier time  $t_1$ .

In this paper, as in earlier work,<sup>4-7</sup> we consider a modification of a perfect harmonic  $n$ -dimensional crystal with nearest-neighbor central and noncentral forces. The effect of the modification is to introduce a Brownian particle into the crystal. These modified harmonic oscillator systems have the important feature

(1) (a) National Science Foundation Senior Postdoctoral Fellow; (b) address correspondence to National Bureau of Standards, Washington 25, D. C.

(2) (a) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943); (b) M. C. Wang and G. E. Uhlenbeck, *ibid.*, **17**, 323 (1945).

(3) J. L. Doob, "Stochastic Processes," John Wiley and Sons, Inc., New York, N. Y., 1953.

(4) R. J. Rubin, "Proceedings of the International Symposium on Transport Processes in Statistical Mechanics, Brussels, August, 1956," I. Prigogine, Ed., Interscience Publishers, Inc., New York, N. Y., 1958, p. 155.

(5) P. C. Hemmer, Thesis, *Det Fysiske Seminar i Trondheim*, 2 (1959).

(6) R. J. Rubin, *J. Math. Phys.*, **1**, 309 (1960).

(7) R. J. Rubin, *ibid.*, **2**, 373 (1961).

that explicit exact expressions for the c.p.d.f. of the Brownian particle can be obtained directly from the equations of motion. The only assumption made is that the system is initially in thermal equilibrium. Once an explicit form of the c.p.d.f. has been obtained, the form of the associated Langevin equation (or generalized Langevin equation) can be inferred. Hemmer<sup>5</sup> and Rubin<sup>4,6,7</sup> modified the crystal by increasing the mass of one of the lattice particles to a very large value. In this paper we consider a different modification of the crystal in which the particles inside a large spherical region are assumed to be rigidly connected. This large spherical aggregate, which we will call a Brownian sphere, is treated as a single particle.

In the earlier work, it has been shown that for a very heavy particle in the one-dimensional crystal<sup>5-7</sup> the heavy particle behaves like a free Brownian particle. The Langevin equation, which is consistent with the c.p.d.f., has the form<sup>2a</sup>

$$M\ddot{X} + \beta_1\dot{X} = A(t)$$

where the friction constant  $\beta_1$  is given in terms of lattice parameters. For the three-dimensional crystal,<sup>7</sup> again in the limit of a very heavy particle, the particle behaves like a Brownian oscillator. The Langevin equation which is consistent with the c.p.d.f. in this case has the form<sup>2a</sup>

$$M\ddot{X} + \beta_3\dot{X} + kX = A(t)$$

where  $\beta_3$  and  $k$  are given in terms of lattice parameters. For the two-dimensional crystal, the results are less complete. It is shown<sup>7</sup> that the position and velocity of the heavy particle are non-Markoffian random variables<sup>8</sup> in contrast to the case of the one- and three-dimensional crystals where the position and velocity are shown to be Markoffian random variables. This is the extent of the results which have been obtained previously.

In studying the properties of the Brownian sphere, we shall need several results which have been estab-

(8) A pair (or more) of random variables is said to be Markoffian if for  $t_3 > t_2 > t_1$  the conditional probability distribution function  $W(\dot{X}_3, X_3, t_3 | \dot{X}_2, X_2, t_2; \dot{X}_1, X_1, t_1)$  is independent of the values of  $\dot{X}$  and  $X$  at time  $t_1$ , i.e., if  $W(\dot{X}_3, X_3, t_3 | \dot{X}_2, X_2, t_2; \dot{X}_1, X_1, t_1) = W(\dot{X}_3, X_3, t_3 | \dot{X}_2, X_2, t_2)$ ; otherwise the variables are said to be non-Markoffian.