Role of nonpairwise interactions on phonon thermal transport

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(Received 5 October 2002; revised manuscript received 13 January 2003; published 29 April 2003)

In this paper, the phonon system for a perfect silicon lattice is obtained by means of a model considering a phenomenological potential that includes both two- and three-body contributions. Phonon dispersions are discussed, and anharmonic contributions to the phonon Hamiltonian are evaluated. The model is compared with a model involving a pairwise potential, previously used by the author in the calculation of silicon thermal conductivity. The equation of motion is solved for both models, obtaining phonon dispersions practically indistinguishable and in good agreement with the experimental data. The role of nonpairwise interactions in phonon-phonon–scattering processes, relevant for the calculation of thermal conductivity, is then discussed. The thermal conductivity obtained with the present model including two- and three-body interactions has a good agreement with the experimental data, better than the one previously achieved with the model involving a central potential.

DOI: 10.1103/PhysRevB.67.144305 PACS number(s): 66.70.+f, 63.20.Mt

I. INTRODUCTION

To obtain the phonon system of a lattice, the first step is to solve the equation of atomic motion, deriving the forces acting on the lattice sites from potential-energy (V) functions of the particle coordinates. A model of the lattice is then necessary with the potential $V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ depending on the N-lattice site positions. For certain materials, the choice of the interatomic function V required in dynamic simulations is still an open problem that calls for a large fraction of the activity done in the condensed-matter physics.

Fitting the potential on experimental data, with a parametrization of the functions that appear in its analytical form, allows to design a phonon system suitable to discuss, for instance, mechanical and thermal properties of the material. One of the more complex tasks is the determination of the phonon thermal conductivity in a perfect lattice or in a lattice with defects (pointwise or extended defects). Assuming the phonon distribution to obey the Boltzmann equation, the deviation from the equilibrium distribution caused by a thermal gradient can be obtained by means of several approaches to solve the transport problem (see, for instance Ref. 1).

The major problem that one faces in the calculation of thermal resistance is the determination of phonon-scattering probabilities. Usually, the probability rates are considered within a relaxation-time approximation,[2–5] often assuming a continuum hypothesis (such as Debye and Einstein models for acoustic- and optical-phonon branches[6]): in this framework, the interatomic potential turns out to be inessential for the development of calculations.

As proposed in Ref. 7, an iterative approach to the Boltzmann equation allows us to handle a realistic atomic model, considering in a rigorous way the three-phonon scattering processes and the phonon scattering from lattice defects. The iterative approach was applied to rare-gas crystals and to diamondlike structures (C,Si and Ge),[8,9] where a pairwise potential was introduced to obtain phonon dispersions and three-phonon–scattering probabilities.

A strong criticism to this iterative evaluation of thermal conductivity is that a pairwise potential can be inaccurate in the determination of a phonon system and a phonon anharmonicity. An approach to determine the thermal transport with a many-body potential, notwithstanding the complexity of the problem, is presented here.

The comparison of the phonon frequencies, extracted by means of equation of the motion with two different potentials (pairwise and many body), shows that the dispersion relations are practically indistinguishable and in good agreement with experimental data. The phonon-phonon–scattering probabilities with a nonpairwise interaction are then estimated and the thermal conductivity for a silicon sample evaluated.

It is then possible to give an answer to the problem of the role and accuracy of the pairwise potential in the model of a phonon system.

II. PHONON SYSTEM IN THE SILICON PERFECT LATTICE

Assuming the lattice behavior to be controlled by an interatomic potential depending on the coordinates of the atomic sites, the simplest analytical form that can be used is a sum of pairwise terms, with the energy of a pair depending on their relative distance, that is, $V_{ij}=V(|\mathbf{r}_{ij}|)$, where $\mathbf{r}_{ij}$ is the vector joining the two lattice points at the i and j sites.

Many-body forms have been proposed, for instance, the Keating potential, widely used to study elastic and static properties of covalent semiconductors and applied to the investigation of defect vibrational modes in diamondlike crystals.[10,11] The Stillinger-Weber potential was the first attempt to construct a potential for silicon[12] based on two-body and three-body terms, and depending on the site distances and angles θ between adjacent lattice bonds with a vertex at the lattice site. The structure of the potential favors the configuration where $\cos\theta=-\frac{1}{3}$, that is, a structure with angles as close as possible to that found in the diamondlike tetrahedral structure.

The Stillinger-Weber potential gives a fairly realistic de-

scription of crystalline silicon. A modified form was tested in lattice-dynamics calculations in germanium.[14] However, the built-in tetrahedral bias of the potential creates problems in the evaluation of energies of nontetrahedral polytypes found under pressure.[13] The family of potentials developed by Tersoff are based on bond orders, where the strength of a bond between two atoms depends on the local environment.[15–18]

The problem of the choice of the potential was not so relevant in the study of thermal conductivity, since the usual approach to the thermal transport determination was through the time-relaxation approximation. Now, we have at our disposal a different approach, an iterative one,[7] that takes into account the true lattice, and works with phonon dispersions and phonon-phonon interactions elaborated from a potential function. Therefore, the problem of the type of potential used in the thermal conductivity calculation becomes relevant.

Assuming a diamondlike lattice, let us denote by index i the lattice site at one of the two positions of the basis in a generic cell. Assuming a central potential $V(r)$, where r is the interatomic distance, and calling $\boldsymbol{\eta}_i$ the displacement of atom i from its average position $\mathbf{R}_i$ in the vibrating lattice, one can expand in terms of the displacements the function $V(r)=V(|\mathbf{r}_{ij}|)$:[19]

$$V_{ij}=\frac{dV}{dR^2}d(\mathbf{r}_{ij}\cdot\mathbf{r}_{ij})+\frac{1}{2}\frac{d^2V}{d(R^2)^2}[d(\mathbf{r}_{ij}\cdot\mathbf{r}_{ij})]^2+\ \ldots, \quad (1)$$

where $\mathbf{r}_{ij}=\mathbf{R}_j+\boldsymbol{\eta}_j-\mathbf{R}_i-\boldsymbol{\eta}_i=\mathbf{R}_{ij}+\boldsymbol{\eta}_j-\boldsymbol{\eta}_i$, $R=|\mathbf{R}_{ij}|$, and $d(\mathbf{r}_{ij}\cdot\mathbf{r}_{ij})$ is the square of the distance variation due to the displacement field. In this way, one obtains the following expression for the second-order term of the potential energy of interaction between i and j atoms:

$$V_{ij}^{(2)}=\frac{1}{2}\{\Gamma[\boldsymbol{\eta}_j-\boldsymbol{\eta}_i]\cdot[\boldsymbol{\eta}_j-\boldsymbol{\eta}_i]+B[\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)]^2\}, \quad (2)$$

where

$$\Gamma=\frac{1}{R}\frac{dV}{dR};\quad B=\frac{1}{R}\frac{d}{dR}\left[\frac{1}{R}\frac{dV}{dR}\right]. \quad (3)$$

The coefficients Γ and B depend on the equilibrium lattice site distance. The force acting on site i can be obtained by the total potential energy $V^{(2)}=\Sigma_j V_{ij}^{(2)}$ of the reticular centers; consequently the equation of motion can be written in the form

$$M\ddot{\boldsymbol{\eta}}_i=-\nabla_{\boldsymbol{\eta}_i}V^{(2)}=\sum_j\{\Gamma(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)+B\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)\mathbf{R}_{ij}\} \quad (4)$$

where M is the atomic mass.

An elementary excitation of the crystal in the harmonic approximation will be represented by a phonon with wave vector $\mathbf{q}$, polarization index p, and polarization vector $\mathbf{e}_{\mathbf{q}p}$. The phonon frequency will be indicated by $\omega_{\mathbf{q}p}$. The representation here used for calculations can be found in Ref. 9 or in Ref. 1.

The aim of the work reported in Ref. 9 was to solve the phonon Boltzmann equation[20] for a solid having the structure and the vibrational (harmonic and anharmonic) properties of the real lattice. The model of the solid with a discrete reticular lattice and a pair potential proposed in Ref. 9 gave good phonon-dispersion relations and reliable information on the weight of the various scattering mechanisms contributing to thermal resistance; in particular, it was possible to evaluate the role of optical phonons in the scattering processes as a function of temperature.

However, the choice of a pair potential to obtain the phonon system can be open to criticism. It is then necessary to face the problem of the thermal conductivity estimation in the framework of a more general potential, including nonpairwise interactions.

Here, the subject of the paper is to develop an approach able to manage the phonon system with nonpairwise interactions and to discuss its anharmonicity.

Let us now introduce the new phonon assembly, where the pairwise potential is replaced by a many-body potential, having in mind the well-known Stillinger-Weber and Tersoff forms, that is, introducing in the potential energy a three-body interaction, with an explicit dependence on angle θ_{ijk} between bonds i-j and i-k with vertex i. The potential assumes the following analytic form:

$$V_{ij}(r_{ij})=[af_1(r_{ij})+b_{ij}f_2(r_{ij})]f_c(r_{ij}), \quad (5)$$

where

$$b_{ij}=\sum_{k\neq i,j}^{Z-1}b(r_{ij},r_{ik},g(\cos\theta_{ijk}))f_c(r_{ij})f_c(r_{ik}), \quad (6)$$

with Z the site coordination number. f_1 and f_2 are suitable functions depending on the site distances; f_c is a cutoff function truncating the potential at a point between the nearest-neighbor (nn) and next-nearest-neighbor (nnn) distances for the diamondlike lattice, as in the Stillinger-Weber and Tersoff potentials. Developing the potential with respect to distances r_{ij}, r_{ik} and angle θ_{ijk}, and retaining only the low-order terms, one obtains

$$V_{ij}=\frac{\partial V}{\partial(R^2)}d(\mathbf{r}_{ij}\cdot\mathbf{r}_{ij})+\frac{1}{2}\frac{\partial^2V}{\partial(R^2)^2}[d(\mathbf{r}_{ij}\cdot\mathbf{r}_{ij})]^2+\sum_k\frac{\partial V}{\partial g}d[g(\theta_{ijk})]+\cdots, \quad (7)$$

where derivatives are evaluated at lattice equilibrium positions. The function $g(\theta_{ijk})$ is taken with the same structure appearing in the Stillinger-Weber potential:

$$g(\theta_{ijk})=(\cos\theta_{ijk}+\tfrac{1}{3})^2. \quad (8)$$

The first and the second terms in Eq. (7) have been already found in Eq. (2), since they refer to distance variations and are coming from the central part of the potential. The third term in Eq. (7) now describes the role of an angular variation when the lattice moves from the equilibrium position. The variation $d[g(\theta_{ijk})]$ is due to the displacement field of three adjacent lattice positions $\boldsymbol{\eta}_i$, $\boldsymbol{\eta}_j$, and $\boldsymbol{\eta}_k$. As we shall see

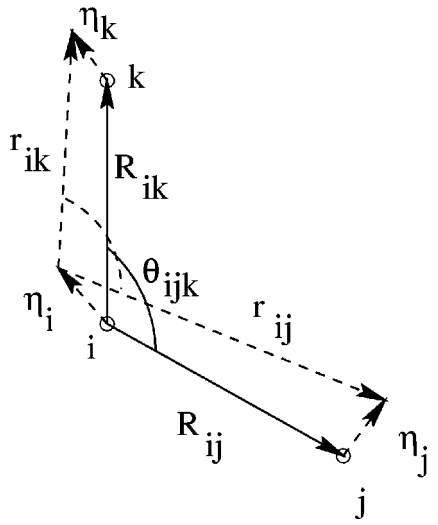

FIG. 1. Vectors $\mathbf{r}_{ij}, \mathbf{r}_{ik}, \mathbf{R}_{ij}, \mathbf{R}_{ik}$ join the actual positions and the equilibrium positions of the lattice sites. $\boldsymbol{\eta}_i, \boldsymbol{\eta}_j, \boldsymbol{\eta}_k$ represent the lattice displacement field at the i, j, and k sites. Note the angle with a vertex in the site i: it is changing according to the atomic position variations. The equilibrium position is giving a value $\cos\theta_{ijk} = -1/3$.

later, the third term gives harmonic and anharmonic contributions to the potential interaction.

To handle the calculation in an easy way, the notation

$$\boldsymbol{\eta}_j - \boldsymbol{\eta}_i = \mathbf{d}_{ij}; \quad \boldsymbol{\eta}_k - \boldsymbol{\eta}_i = \mathbf{d}_{ik} \tag{9}$$

is used. Vectors $\mathbf{r}_{ij}, \mathbf{r}_{ik}, \mathbf{R}_{ij}, \mathbf{R}_{ik}, \boldsymbol{\eta}_i, \boldsymbol{\eta}_j, \boldsymbol{\eta}_k$ are shown in Fig. 1. The angle with a vertex in site i changes according to the atomic position variations around the equilibrium position $\cos\theta_{ijk} = -1/3$.

An obvious definition of cosine is

$$\cos\theta_{ijk} = \frac{(\mathbf{R}_{ij} + \mathbf{d}_{ij}) \cdot (\mathbf{R}_{ik} + \mathbf{d}_{ik})}{|\mathbf{r}_{ij}||\mathbf{r}_{ik}|}. \tag{10}$$

If in this formula, the denominator $|\mathbf{r}_{ij}||\mathbf{r}_{ik}|$ is put equal to R^2, terms that are relevant to obtain a proper phonon dispersion evaluation are lost.

The variation due to the angular change $d[g(\theta_{ikj})]$ at the harmonic order is then given by

$$\begin{aligned} R^4 d[g(\theta_{ijk})] &= (\mathbf{d}_{ij}\cdot\mathbf{R}_{ik})^2 + (\mathbf{d}_{ik}\cdot\mathbf{R}_{ij})^2 + 2(\mathbf{d}_{ij}\cdot\mathbf{R}_{ik})(\mathbf{d}_{ik}\cdot\mathbf{R}_{ij}) \\ &+ 2/3(\mathbf{d}_{ij}\cdot\mathbf{R}_{ij})(\mathbf{d}_{ij}\cdot\mathbf{R}_{ik}) + 2/3(\mathbf{d}_{ij}\cdot\mathbf{R}_{ij})(\mathbf{d}_{ik}\cdot\mathbf{R}_{ij}) \\ &+ 2/3(\mathbf{d}_{ik}\cdot\mathbf{R}_{ik})(\mathbf{d}_{ij}\cdot\mathbf{R}_{ik}) + 2/3(\mathbf{d}_{ik}\cdot\mathbf{R}_{ik})(\mathbf{d}_{ik}\cdot\mathbf{R}_{ij}) \\ &+ 1/9(\mathbf{d}_{ij}\cdot\mathbf{R}_{ij})^2 + 1/9(\mathbf{d}_{ik}\cdot\mathbf{R}_{ik})^2 \\ &+ 2/9(\mathbf{d}_{ij}\cdot\mathbf{R}_{ij})(\mathbf{d}_{ik}\cdot\mathbf{R}_{ik}). \end{aligned} \tag{11}$$

In Eq. (11) there are two terms of the form $(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij})^2 = [\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j - \boldsymbol{\eta}_i)]^2$ already found in Eq. (2), meaning a redistribution of energy among the various contributions. The last three terms in Eq. (11) are the most relevant terms to obtain transverse-acoustic modes in good agreement with the experimental data, and are exactly the terms disappearing from the development of Eq. (10), where in the denominator it is considered that $|\mathbf{r}_{ij}||\mathbf{r}_{ik}| = R^2$.

The equation of motion becomes

$$\begin{aligned} M\ddot{\boldsymbol{\eta}}_i = -\nabla_{\boldsymbol{\eta}_i} V_i &= \Gamma \sum_{j\neq i} (\boldsymbol{\eta}_j - \boldsymbol{\eta}_i) + B \sum_{j\neq i} \mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j - \boldsymbol{\eta}_i)\mathbf{R}_{ij} \\ &+ \frac{\Xi}{2} \sum_{j\neq i} \sum_{k\neq i,j} \left[\frac{8}{9}\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j - \boldsymbol{\eta}_i)\mathbf{R}_{ij} \right. \\ &+ \frac{8}{9}\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j - \boldsymbol{\eta}_i)\mathbf{R}_{ik} + \frac{8}{3}\mathbf{R}_{ik}\cdot(\boldsymbol{\eta}_j - \boldsymbol{\eta}_i)\mathbf{R}_{ik} \\ &+ \left. \frac{8}{3}\mathbf{R}_{ik}\cdot(\boldsymbol{\eta}_j - \boldsymbol{\eta}_i)\mathbf{R}_{ij} \right] \end{aligned} \tag{12}$$

with a new coupling constant

$$\Xi = \frac{1}{R^4}\frac{\partial V}{\partial g}. \tag{13}$$

If only nn lattice site interactions are included, only three coupling constants Γ, B, and Ξ are involved in the equation of motion.

Before solving the equation and investigating the role of the new terms appearing in Eq. (12), let us remember that in Eq. (11) only harmonic contributions have been considered. Anharmonic terms also come from the angular variation but they are not shown in Eq. (11): obviously, they must be involved in the thermal conductivity calculations. Other anharmonic contributions can come from the mixed variation $d[\mathbf{r}_{ij}\cdot\mathbf{r}_{ij}]d[\cos\theta_{ijk} + 1/3]^2$, but they are terms of the fourth order, usually not considered in the evaluation of thermal transport.

The new harmonic contributions can be easily inserted in the framework of the calculation previously used in Ref. 9. The equation of motion is transformed into a linear homogeneous system of equations of the form

$$\sum_{\beta=1}^{6} a_{\alpha\beta} e_\beta + \overline{\omega}^2 e_\alpha = 0, \tag{14}$$

where $\overline{\omega}$ is the phonon reduced frequency and e_α are the spatial components of the polarization vector related to the two atomic sites of the cell basis (three for each site of the basis). The coefficients of the Hermitian matrix $a_{\alpha\beta}$ for the central potential are given in Table I of Ref. 9, here called $a^{old}_{\alpha\beta}$. These coefficients must be modified to include the contribution of the angular variations. The matrix coefficients become

$$a_{\alpha\beta} = a^{old}_{\alpha\beta} + b_{\alpha\beta}, \tag{15}$$

with

$$b_{\alpha\beta} = \xi_1 N^+_{\alpha\beta} + \xi_2 M^+_{\alpha\beta} \quad \text{for} \quad \alpha = 1,2,3 \quad \text{and} \quad \beta = 1,2,3;$$

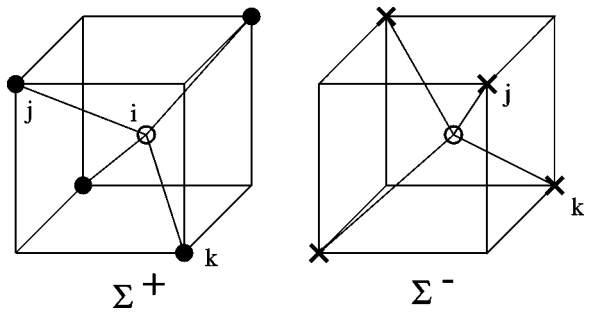

FIG. 2. Lattice sites around the lattice position i on which the sums $\Sigma^{\pm}$ in Eq. (17) are evaluated to obtain functions $N^{\pm}$ and $P^{\pm}$ mixing coordinates of i,j, and k sites. When the sum is denoted by Σ^{+}, the sites to consider are denoted by dots, and when the sum is Σ^{-}, the sites are crosses.

$$b_{\alpha\beta}=\xi_1 N^{-}_{\alpha'\beta'}+\xi_2 M^{-}_{\alpha'\beta'} \quad \text{for} \quad \alpha=4,5,6 \quad \text{and} \quad \beta=4,5,6;$$

$$b_{\alpha\beta}=\xi_1 P^{+}_{\alpha\beta'}+\xi_2 Q^{+}_{\alpha\beta'} \quad \text{for} \quad \alpha=1,2,3 \quad \text{and} \quad \beta=4,5,6;$$

$$b_{\alpha\beta}=\xi_1 P^{-}_{\alpha'\beta}+\xi_2 Q^{-}_{\alpha'\beta} \quad \text{for} \quad \alpha=4,5,6 \quad \text{and} \quad \beta=1,2,3; \tag{16}$$

with $\alpha'=\alpha-3;\beta'=\beta-3$, and

$$N^{\pm}_{\alpha\beta}=\sum_t {}^{\pm}\left(x_{t\alpha}\pm\frac{1}{2}\right)\left(x_{t\beta}\pm\frac{1}{2}\right),$$

$$M^{\pm}_{\alpha\beta}=\sum_t {}^{\pm}\sum_{t'\neq t} {}^{\pm}\left(x_{t\alpha}\pm\frac{1}{2}\right)\left(x_{t'\beta}\pm\frac{1}{2}\right),$$

$$P^{\pm}_{\alpha\beta}=\sum_t {}^{\pm}\sum_{t'\neq t} {}^{\pm}\left(x_{t\alpha}\pm\frac{1}{2}\right)\left(x_{t\beta}\pm\frac{1}{2}\right)\exp(i\mathbf{x}_{t'}\cdot\mathbf{q}),$$

$$Q^{\pm}_{\alpha\beta}=\sum_t {}^{\pm}\sum_{t'\neq t} {}^{\pm}\left(x_{t\alpha}\pm\frac{1}{2}\right)\left(x_{t'\beta}\pm\frac{1}{2}\right)\exp(i\mathbf{x}_{t}\cdot\mathbf{q}). \tag{17}$$

Here $\mathbf{x}_t$ are vectors identifying four lattice points around the lattice site under consideration, shown in Fig. 2: where the sum is denoted by Σ^{+}, the sites are those denoted by dots, and for the Σ^{-} the sites to be considered are crosses. Functions $N^{\pm}$ and $P^{\pm}$ are mixing coordinates of j and k sites. The coefficients in Eq. (21) are

$$\xi_1=\frac{8}{3}\frac{\Xi}{B^*}; \quad \xi_2=\frac{32}{9}\frac{\Xi}{B^*}; \quad B^*=B\left(1+\Xi\frac{8}{9}\right). \tag{18}$$

The parameters Γ,B, and Ξ can be used to fit the phonon-dispersion curves solving Eq. (14) with the experimental data in Fig. 3, the phonon dispersions obtained by the present calculation (continuous lines) are shown in comparison with those (dotted lines) already proposed in Ref. 9 and used to determine the thermal conductivity of Si with the central potential. The figure also reports the experimental data (diamonds).[21,22] A good agreement is obtained for both sets of curves. The value of the parameters involved in the present calculation and in the previous one are shown in

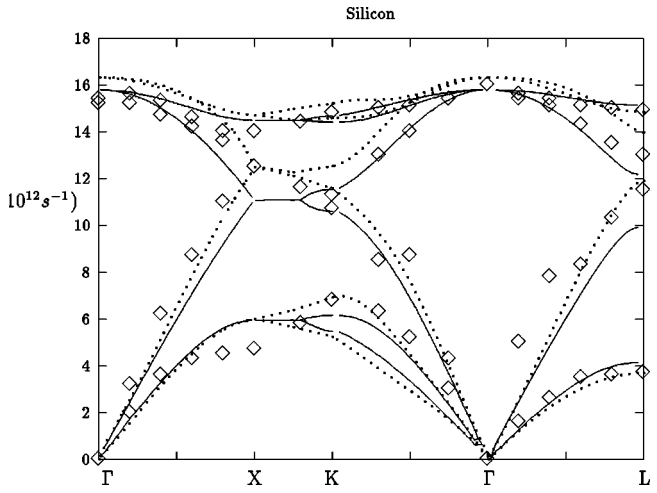

FIG. 3. Theoretical phonon-dispersion curves (continuous lines) for silicon, in comparison with experimental data (Refs. 21 and 22). The phonon dispersions obtained by the present calculation are represented by continuous lines, and those already proposed in Ref. 9 and used to calculate the thermal conductivity of Si by dotted lines. The values of parameters used for calculations are shown in Table I.

Table I. The calculation done here needs only two parameters instead of the four used for the model with the central potential. In fact, in the present work, the interaction between nnn sites is assumed to be zero: it can be thought that the nnn interactions are included to a certain extent in the angular variation, where three atoms are involved and two of them are at the nnn site distance.

In Fig. 3, it is possible to see that the agreement of the present calculation with the experimental dispersion data is good for optical branches. A little discrepancy is observed for the longitudinal phonon dispersion at points X and L of the Brilloiun zone.

It is interesting to compare the roles of the various terms in equation of motion. As shown in Table I, in the new calculation, one of the old parameters Γ/B can be put equal to zero, since its role is played by the new parameter Ξ. In the case where Γ/B and Ξ were both equal to zero, the transverse-acoustic modes disappear. The nnn terms of the model with a central potential, giving coefficients B' and Γ'/B, are able to adjust the phonon dispersion at the boundary of the Brillouin zone, giving a better longitudinal mode in X and L. In fact, if we consider the pairwise potential with only nn interactions, that is, with coefficients B' and Γ'/B equal to zero, the longitudinal modes turn out to be practically indistinguishable from the logitudinal modes of the present model.

A last comment must be devoted to the role of ξ_1 and ξ_2 used in the $b_{\alpha,\beta}$ coefficients. As previously mentioned, in considering the angular variation, the denominator in Eq. (10) is assumed to be dependent on the displacement field. If the denominator were put equal to R^2, ξ_1 turns to be equal to zero. Inserting in the dynamical matrix $\xi_1=0$ and, for instance, $\xi_2=32\ \Xi/9B^*$, the transverse acoustic (TA)-mode has a frequency much lower than the observed experimental

value. In particular, the TA frequency at the point X on the Brillouin zone is strongly reduced, passing from $6.0 \times 10^{12}\mathrm{s}^{-1}$ to $1.5\times 10^{12}\mathrm{s}^{-1}$.

III. ANHARMONICITY AND THERMAL CONDUCTIVITY

The third-order contribution to the interaction energy between the two reticular centers at i and j sites, coming from a pairwise potential was previously given in Ref. 9, and it is

$$V_{ij}^{(3)}=\frac{1}{6}A[\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)]^3+\frac{1}{2}B\ [\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)] \times[(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)], \tag{19}$$

where

$$A=\frac{1}{R}\frac{d}{dR}\left[\frac{1}{R}\frac{d}{dR}\left(\frac{1}{R}\frac{dV}{dR}\right)\right]. \tag{20}$$

In the evaluation of the angular variation, to obtain the phonon-dispersion relations, the development was stopped in Eq. (10) to the harmonic contributions: anharmonic terms are of course present and give further contributions to $V_{ij}^{(3)}$, modifying the scattering matrix of the three-phonon processes. The terms of the third order, coming from the development of Eq. (10), have the same structure as those of in Eq. (19), but contain vectors $\mathbf{R}_{ik}$ and $(\boldsymbol{\eta}_k-\boldsymbol{\eta}_i)$ too. The full list of all the terms is given in the Appendix. Among these contributions, Eqs. (A1) and (A7) are of the same form as those of appearing in Eq. (19), and are going to renormalize the A and B coefficients.

No other contributions at the third-order can come from a further development of the interaction energy.

A lot of new third-order terms then appear: let us estimate their weight in the thermal transport of the material.

In the numerical analysis, it is useful to introduce the adimensional anharmonic parameter $\epsilon=-8R^2A/3B$, describing the ratio between A and B. Using the experimental data of the Grüneisen constant, as done in Ref. 9 an estimate of the parameter ϵ is possible, obtaining a value ~ 26 in silicon.

All the new terms of the third order, Eqs. (A1)–(A12), are multiplied by the factor Ξ that is evaluated from the phonon-dispersion experimental data. Introducing the adimensional ratio $\nu=\Xi/B$, we have a new anharmonic parameter ν that is completely known: its value is very low (~ 0.04). Due to this fact, and assuming that in terms (A1)–(A6) the role played by the displacement field is almost the same, the sum of these six terms is introduced in Eq. (19) estimating a new contribution of the form

$$(2/9+4/3+2)[\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)][(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)]. \tag{21}$$

The same for terms (A7)–(A12), giving

$$(5/9+11/3+10)[\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)]^3. \tag{22}$$

Instead of Eq. (19), the following equation is used to evaluate the phonon-scattering probability:

$$V_{ij}^{(3)}=-\frac{1}{6}\left(\frac{3\epsilon B}{8R^2}+\frac{128}{9}\frac{Z}{2}\frac{\nu B}{R^2}\right)[\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)]^3 +\frac{1}{2}\left(B+\frac{32}{9}\frac{Z}{2}\nu B\right) \times[\mathbf{R}_{ij}\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)][(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)\cdot(\boldsymbol{\eta}_j-\boldsymbol{\eta}_i)]. \tag{23}$$

A factor 1/2 is inserted to avoid summing two times the same contribution. For $\nu=\Xi/B=0.04$, the first coefficient changes by 12% and the second by 30%: the variations are small enough to justify the use of Eqs. (21) and (22). It is then easy to insert them in the iterative numerical procedure for the calculation of thermal conductivity κ, the phonon system here obtained with the two- and three-body interactions, and the anharmonicity described in Eq. (23).

For the evaluation of κ proposed in the present paper, only three parameters are necessary: two of them (ν,B) are evaluated from the phonon-dispersion data, that is independent of the value of thermal conductivity, and the third is the anharmonic parameter ϵ. The low number of parameters is due to the fact that only nn site interactions are considered, whereas in the previous calculation,[9] four harmonic and two anharmonic parameters ϵ,ϵ' were being used, with nnn sites involved, too. Under the approximation given in this section, the thermal conductivity for silicon is here evaluated in a temperature range between 6 K and 250 K. In Fig. 4, the results of the present calculation with the anharmonicity given by Eq. (23) are shown. The upper continuous curve represents the thermal conductivity evaluated for an isotopically pure silicon crystal, whereas the lower curve shows the behavior of a sample with the natural isotopic composition. The value of ϵ is assumed to be 22, to have a good agreement at 250 K, between the theoretical calculation and the experimental data in the case of an isotopically pure silicon sample.

Relaxation-time approximation is avoided for the three-phonon scatterings, but is introduced for boundary scattering in the form of $\tau_p=L/s_p$, where L represents the characteristic length in the sample,[20] and s_p is the velocity of sound for a phonon with polarization index p.

The role of the isotope effect is considered here, as in Ref. 9. The isotope effect on the thermal conductivity is due to point defects, with a mass difference in the lattice position where the defect is placed, giving a scattering probability rate of a phonon $\mathbf{q}p$ into a phonon $\mathbf{q}'p'$ of the form

TABLE I. Values of the coefficients describing the interaction between nearest neighbors and next-nearest neighbors $(B,\Gamma/B,\Gamma'/B,B')$ for the model with a pairwise potential and values of the coefficients for the nearest-neighbor interaction in the model with two- and three-body interactions $(B,\Xi/B)$. The values of B and B' are given in units of $10^{20}\mathrm{g\,cm^{-2}\,s^{-2}}$.

	B	B′	Γ/B	Γ'/B	Ξ/B
(two body)	2.2	4.5×10^{-2}	0.06	−0.0075	0.00
(two body and three body)	2.4	0.0	0.00	0.0	0.04

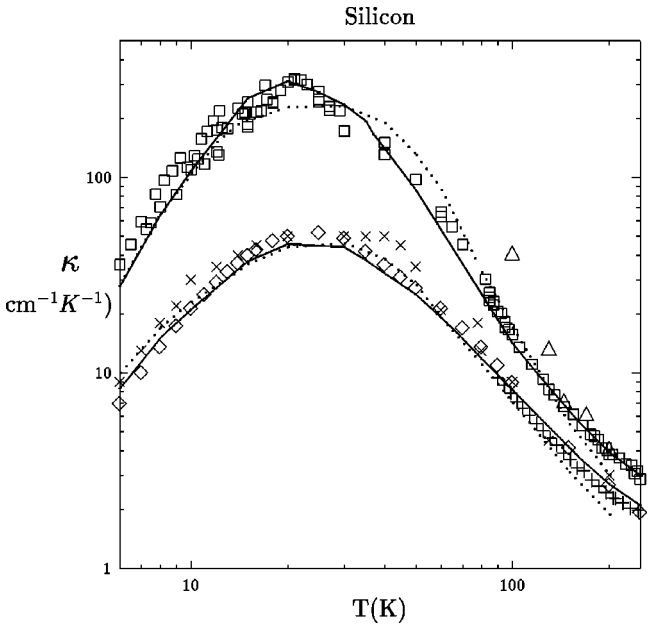

FIG. 4. Thermal conductivity as a function of the temperature for silicon, obtained with scattering probabilities coming from Eq. (23). The upper continuous curve represents the thermal conductivity evaluated for an isotopically pure silicon crystal, whereas the lower curve shows the behavior of a sample with a natural isotopic composition. The experimental data are obtained from Refs. 23–25. The dotted lines represent thermal conductivities evaluated with the central potential as in Ref. 8.

$$\mathcal{P}^{\mathbf{q}'p'}_{\mathbf{q}p} = \frac{\pi}{2}\left(\frac{\Delta M}{M}\right)^2 \frac{1}{N^2}\omega_{\mathbf{q}p}\omega_{\mathbf{q}'p'}|\mathbf{e}_{\mathbf{q}p}\cdot\mathbf{e}_{\mathbf{q}'p'}|^2 \times \delta(\omega_{\mathbf{q}p}-\omega_{\mathbf{q}'p'})n^o_{\mathbf{q}p}(1+n^o_{\mathbf{q}'p'}), \tag{24}$$

where ΔM is the mass variation and $n^o_{\mathbf{q}p}$ the equilibrium phonon distribution. If the defects are assumed to be present in a fraction f_i of the crystal sites, there will be Nf_i centers producing an elastic scattering. These defects are moreover considered statistically distributed in both sites of the lattice basis.

The agreement with experimental data[23–25] is good.

It is now possible to compare the results of the present calculations with the data obtained in the previous paper,[8] analyzing a phonon system with a central potential. In Ref. 8, the theoretical thermal conductivity at temperatures higher than 100 K seems to deviate from the experimental data, and in both cases (pure silicon and silicon with isotopic defects) it is lower than the experimental data. Here, we can see a better agreement with the experimental data, obtained with only three (two harmonic and one anharmonic) parameters inserted in calculations, instead of six used with the central potential.

As a conclusion, the paper shows that pairwise and non-pairwise potentials give the same phonon dispersions, but the number of parameters required to fit the experimental data is one-half for the model with a non-pairwise potential. In the thermal conductivity evaluation, the renormalization of the anharmonic coefficients (23), used in the phonon-phonon–scattering probability, is able to give a better agreement with experimental data, in the case of isotopically pure and natural silicon. Then, the use of a nonpairwise potential can give, for certain materials, an improvement in the thermal conductivity evaluation.

ACKNOWLEDGMENTS

The author is indebted to Professor C. Y. Fong for the useful discussions.

APPENDIX

Terms of the third order, coming from the development of Eq. (10) are

$$1/9(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij})(\mathbf{d}_{ij}\cdot\mathbf{d}_{ij}), \tag{A1}$$

$$1/9(\mathbf{R}_{ik}\cdot\mathbf{d}_{ik})(\mathbf{d}_{ij}\cdot\mathbf{d}_{ij}), \tag{A2}$$

$$1/3(\mathbf{R}_{ik}\cdot\mathbf{d}_{ij})(\mathbf{d}_{ij}\cdot\mathbf{d}_{ij}), \tag{A3}$$

$$1/3(\mathbf{R}_{ij}\cdot\mathbf{d}_{ik})(\mathbf{d}_{ij}\cdot\mathbf{d}_{ij}), \tag{A4}$$

$$2/3(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij})(\mathbf{d}_{ij}\cdot\mathbf{d}_{ik}), \tag{A5}$$

$$2(\mathbf{R}_{ij}\cdot\mathbf{d}_{ik})(\mathbf{d}_{ij}\cdot\mathbf{d}_{ik}), \tag{A6}$$

$$-1/3(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij})^3, \tag{A7}$$

$$-5/9(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij})^2(\mathbf{R}_{ik}\cdot\mathbf{d}_{ik}), \tag{A8}$$

$$-5/3(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij})^2(\mathbf{R}_{ij}\cdot\mathbf{d}_{ik}), \tag{A9}$$

$$-5/3(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij})^2(\mathbf{R}_{ik}\cdot\mathbf{d}_{ij}), \tag{A10}$$

$$-2(\mathbf{R}_{ij}\cdot\mathbf{d}_{ik})^2(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij}), \tag{A11}$$

$$-2(\mathbf{R}_{ij}\cdot\mathbf{d}_{ik})^2(\mathbf{R}_{ik}\cdot\mathbf{d}_{ik}), \tag{A12}$$

$$-2(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij})(\mathbf{R}_{ik}\cdot\mathbf{d}_{ik})(\mathbf{R}_{ij}\cdot\mathbf{d}_{ik}), \tag{A13}$$

$$-4(\mathbf{R}_{ij}\cdot\mathbf{d}_{ij})(\mathbf{R}_{ik}\cdot\mathbf{d}_{ij})(\mathbf{R}_{ij}\cdot\mathbf{d}_{ik}). \tag{A14}$$

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