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Thermal conductivity of disordered harmonic solids

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As a crystal is disordered, a point may be reached where the typical mean free path of phonons is so short that the wavelength and mean free path are no longer sharp concepts, and the textbook phonon-gas model for thermal conductivity breaks down. This paper proposes an alternate theory for the disordered regime, and the subsequent paper implements the theory for a realistic model of amorphous silicon. The idea is that the dominant scattering is correctly described by a harmonic Hamiltonian, which is, in principle, transformable into a one-body problem of decoupled oscillators. From this the thermal conductivity can be exactly calculated by an analog of the Kubo-Greenwood formula for electrical conductivity of disordered metals. Anderson localization is correctly contained in this theory; localized states contribute no currents in harmonic approximation. What is required is an atomistic model with a large unit cell and periodic boundary conditions (to avoid undesired surface effects). The linear size of the model should be larger than the mean free paths of the dominant phonons. A Kubo formula and then a Kubo-Greenwood-type formula are derived for this problem. A "mode diffusivity" D_i for the ith exact oscillator state is defined. The heat is carried by off-diagonal elements of the heat current operator, which have a nonzero contribution because the temperature gradient introduces nonzero off-diagonal elements of the density matrix $\langle a_i^\dagger a_j \rangle$. An effort is made to interpret these results physically. Schemes for implementing this formalism are discussed.

I. INTRODUCTION

In semiconductors and insulators, lattice vibrations are the carriers of heat currents. This can give very high thermal conductivities, as in diamond, or fairly low thermal conductivities, as in glasses. The high thermal conductivity of crystals like diamond was explained by Peierls[1] using the idea of a weakly interacting phonon gas. Peierls wrote down the appropriate Boltzmann equation for this problem. Kittel[2] noticed that glasses had thermal conductivities that could be modeled as phonon "liquids" with very short phonon mean free paths, $l \approx a$ where a is comparable to an interatomic spacing. The Peierls-Boltzmann theory no longer applies in this regime, because if $l \approx a$ then the "phonon" does not propagate far enough to sample the periodicity of the medium, and it is not possible to assign with any accuracy a wave vector or group velocity (or mean free path) to the vibrational eigenstates. Currently it is common to associate the condition $l \approx a$ with the "Ioffe-Regel criterion"[3] and to presume that therefore the vibrational eigenstates are at the margin of Anderson localization.[4] This has motivated efforts to explain the thermal conductivity of glasses as a type of hopping of vibrational energy between localized vibrational eigenstates.[5]

The present paper formulates a theory which applies in an intermediate regime, where disorder is sufficient that vibrations do not propagate, but insufficient to cause all the states to localize. Also it is necessary that the material be stiff enough or the temperature low enough that the harmonic approximation is applicable. The Hamiltonian then, in principle, can be transformed into $3N$ decoupled oscillators, and all properties can be calculated (again in principle) from the eigenvectors and eigenvalues of the harmonic problem. In this model, localized states contribute no heat current (anharmonic terms are needed to permit hopping). Nevertheless, significant heat currents are carried by modes that are neither localized nor propagating.

The mechanism by which this heat is carried is subtle, and we attempt to illuminate this. The basic idea is that the heat current operator has off-diagonal matrix elements $\mathbf{S}_{ij}$ between the decoupled harmonic eigenstates i and j. The diagonal elements $\mathbf{S}_{ii}$ are zero, which just confirms that they are nonpropagating. The temperature gradient ensures that there are off-diagonal elements of the density operator, i.e., $\langle a_i^\dagger a_j \rangle \neq 0$. This allows the off-diagonal elements of $\mathbf{S}$ to carry heat. These aspects of heat conduction are explained in Sec. III and the appendices where the heat current operator and Kubo formula are derived, and in Sec. VI, which is devoted to interpretation.

The companion paper,[6] denoted FKAW, implements this formulation for a realistic model of glassy silicon. Nearly all of the vibrational modes of this model turn out to be delocalized but nonpropagating, and the calculated thermal conductivity agrees well in magnitude with experiment. We believe that this situation is generic in dense glasses, failing only for foamy glasses. Similar behavior occurs in strongly disordered but crystalline

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solid solutions, like $KBr_x(CN)_{1-x}$,[7] and also in certain weakly disordered crystals with very complicated unit cells, like YB_{68}.[8] A preliminary report of this work was given in Ref. 9.

Flicker and Leath[10] have developed the coherent potential approximation for lattice thermal conductivity. Our method is akin to theirs, except that rather than making a self-consistent approximation to the lattice Green's function, we use an exact representation for a large but finite-size system. This has the disadvantage of requiring an even larger computer calculation, but has two advantages: (1) the only errors are from the finite size of the model system, limited by the computational cost and (2) there are no restrictions on what kind of disorder can be studied, unlike the coherent potential approximation (CPA) which can only easily handle mass disorder.

II. PEIERLS-BOLTZMANN THEORY

The heat current in the phonon gas model is

$$\mathbf{J}=\frac{1}{V}\sum_i \mathbf{v}_i \hbar\omega_i \delta N_i \ , \tag{1}$$

where i stands for phonon quantum numbers $(\mathbf{Q},n)$, $\mathbf{v}_i$ is the group velocity $\partial\omega_i/\partial\mathbf{Q}$, and δN_i is the deviation of the distribution function from the equilibrium Bose-Einstein value $n_i=(e^{\beta\hbar\omega_i}-1)^{-1}$. In the next section we shall derive a formula for the heat current operator **S** which gives the heat current, i.e., $\mathbf{J}=\mathrm{tr}\rho\mathbf{S}$. An explicit formula is worked out in Appendix A. Keeping only the parts of **S** which are consistent with our use of the harmonic approximation, the operator **S** has the form

$$S=\sum_{ij} S_{ij} a_i^\dagger a_j \ . \tag{2}$$

Even a harmonic Hamiltonian generates terms in **S** which are third order in the operators $(a,a^\dagger)$. However, these contribute a measurable heat current which is smaller by $(u/a)^2$ than the contribution of the quadratic part of **S** of Eq. (2) and thus of the same size as the neglected anharmonic contributions. To be consistent with Eq. (1), δN_i must be the deviation of $\langle a_i^\dagger a_i\rangle$ from equilibrium, the off-diagonal density matrix elements $\langle a_i^\dagger a_j\rangle$ must vanish, and the diagonal form of the heat current must be $S_{ii}=\hbar\omega_i v_i/V$. This is verified in Appendix A. Even in the phonon-gas model, **S** has nonzero off-diagonal elements, but for weak disorder they are unimportant because the density matrix is diagonal.[11] The Peierls-Boltzmann[1] kinetic equation determines δN_i. In particular, in steady state to first order in the temperature gradient ∇T, δN_i has the form

$$\delta N_i=\sum_j Q_{ij}^{-1}\left[\omega_j\left[\frac{\partial n_j}{\partial\omega_j}\right]\mathbf{v}_j\cdot\frac{\nabla T}{T}\right] , \tag{3}$$

where Q_{ij} is the linearized scattering operator. Commonly one approximates Q_{ij} by δ_{ij}/τ_i where τ_i is a suitable relaxation time for mode i. Since the heat capacity has the form $C=\sum_i C_i$, where

$$C_i=\left[\frac{\hbar\omega_i^2}{VT}\right]\left[-\frac{\partial n_i}{\partial\omega_i}\right] , \tag{4}$$

therefore the thermal conductivity $\kappa_{\alpha\beta}\equiv-\partial J_\alpha/\partial(\nabla_\beta T)$ is approximately

$$\kappa_{\alpha\beta}=\sum_i v_{i\alpha}v_{i\beta}\tau_i C_i \ , \tag{5}$$

$$\kappa_{\alpha\beta}=\tfrac{1}{3}Cvl\delta_{\alpha\beta} \ . \tag{6}$$

Equation (6) holds for cubic symmetry, and the mean sound velocity v and mean free path $l=v\tau$ are defined by comparing (5) and (6).

This gas model is very successful for crystalline matter. For example, Pettersson[12] has shown that careful microscopic calculations for alkali halides agree with experiment, and Sham[13] has derived the Peierls-Boltzmann equation from the rigorous Kubo formula (derived in the next section), assuming the existence of quasiparticle states. For disturbances varying slowly[14] in space and time, the only known limitation of the Boltzmann approach is either (a) that each phonon i should have a sufficiently long mean free path $l_i=|\mathbf{v}_i|\tau_i$ that its wave vector **Q** can be defined, i.e., $l_i \gg \lambda_i=2\pi/|\mathbf{Q}|$, or alternately (b) if the wave vector **Q** is impressed externally, then the resulting oscillation should have a long enough lifetime (or dephasing time) τ_i that its frequency ω_i is well defined, i.e., $\tau_i \gg T_i=2\pi/\omega_i$. For acoustic modes the two criteria are the same, but for the optic branches (where group velocity v_i is often much smaller than phase velocity $\omega_i/|\mathbf{Q}|$) the second criterion is less restrictive. Probably the less restrictive criterion is sufficient; optic phonons, when they satisfy (b) but not (a), are not contributing much to κ anyway. Amorphous materials have relatively few phonons which satisfy either criterion (only very long wavelength acoustic modes). It is, therefore, unrealistic to expect a phonon-gas model to apply, and transport properties can be expected to be more liquid than gaslike. Nevertheless, equations like (5) and (6) continue to be surprisingly useful for semiquantitative purposes. Slack[15] (following Kittel[2]) made an analysis of both crystals and glasses and proposed that l_i for each propagating mode in Eq. (5) could be replaced by its wavelength, in the limit where scattering is strong. The resulting formula for κ represents a hypothetical "minimum thermal conductivity" in the spirit of Ioffe and Regel[3] and Mott.[16] One of our aims is to test the robustness of the minimum thermal conductivity concept.

III. KUBO FORMULA AND HEAT CURRENT OPERATOR

Parallel to the well-known Kubo formula[17] relating the electrical conductivity to the (electrical) current-current correlation function, there is a Kubo formula[18] relating the thermal conductivity to the (heat) current-current correlation function. This second Kubo formula seems to inspire less confidence than the first. The reason is that in the electrical case there is a term in the Hamiltonian,

$-\int d^3x\, \mathbf{j}\cdot\mathbf{A}/c$, which drives the electrical current. The electrical Kubo formula follows from standard perturbation theory. No similar term involving the temperature gradient is available in the Hamiltonian to drive a heat current. Thus the thermal Kubo formula requires an additional statistical hypothesis. Several derivations[19] exist in the literature. We sketch below one of the proofs,[20] because it illuminates the otherwise somewhat obscure mechanism of heat conduction that holds for delocalized but nonpropagating states. The statistical hypothesis is that a system in steady state has a local space-dependent temperature $T(x)=[k_B\beta(x)]^{-1}$ described by a local equilibrium density matrix

$$\rho=\exp\left[-\int d^3x\,\beta(x)h(x)\right]\Big/Z\ , \tag{7}$$

where $h(x)$ is the Hamiltonian density operator, and the Hamiltonian is $H=\int d^3x\, h(x)$. In harmonic approximation, the Hamiltonian is

$$H=\sum_l \frac{p_l^2}{2m_l}+\sum_{l,m}\frac{1}{2}\frac{\partial^2 E}{\partial u_l \partial u_m}u_l u_m\ . \tag{8}$$

Atom l of mass m_l is located at position $r_l=R_l+u_l$ where R_l is the average position and u_l is the displacement. E is the Born-Oppenheimer energy, and only the lowest interesting term in powers of the atomic displacements u is kept. In a nonrelativistic theory such as this, the local energy density $h(x)$ is not defined uniquely, but we can make a reasonable choice that at each site l there is a local energy h_l given by

$$h_l=t_l+V(R_l)=\frac{p_l^2}{2m_l}+\sum_m \frac{1}{2}\frac{\partial^2 E}{\partial u_l \partial u_m}u_l u_m\ . \tag{9}$$

The kinetic energy t_l is automatically local, but the potential energy V has no unique spatial location. This model takes second derivatives of the energy, and assigns the unmixed ($l=m$) terms all to the atom l (regardless of the fact that the source of this energy is mostly interactions with other atoms). Mixed terms are assigned half to atom l and half to atom m. The Hamiltonian density $h(x)$ is then

$$h(x)=\sum_l h_l\delta(x-R_l)\ . \tag{10}$$

For slowly varying temperatures, the inherent ambiguity in $h(x)$ is eliminated by averaging over distances larger than interatomic interaction lengths.

A heat current density operator $\mathbf{S}(x)$ and a total heat current operator $\mathbf{S}$ are now defined by the condition of local energy conservation,

$$\frac{\partial h(x)}{\partial t}+\nabla\cdot\mathbf{S}(x)=0\ , \tag{11}$$

$$\mathbf{S}=\frac{1}{V}\int d^3x\,\mathbf{S}(x)\ . \tag{12}$$

Hardy[21] has shown that these requirements lead to the following choice for the heat current operator:

$$\mathbf{S}=\frac{1}{2V}\sum_l\left[\frac{\mathbf{p}_l}{m_l}\left[\frac{p_l^2}{2m_l}+V(R_l)\right]+\text{H.c.}\right]+\frac{1}{2i\hbar V}\sum_{lm}\left\{(\mathbf{R}_l-\mathbf{R}_m)\left[\frac{p_l^2}{2m_l},V(R_m)\right]+\text{H.c.}\right\}\ , \tag{13}$$

where H.c. means Hermitian conjugate. The first term of 13 has the obvious meaning that the local energy at R_l moves with the local atomic velocity p_l/m_l. This carries nearly all the heat in a gas, but very little in a solid. The second term can be interpreted as a rate at which atom m is doing work on atom l, multiplied by the distance R_l-R_m over which this energy is transferred. This term carries essentially all the heat in a solid (either crystalline or glassy).

The measured heat current $\mathbf{J}=\text{tr}\rho\mathbf{S}$ vanishes in equilibrium [when $\beta(x)$ is constant]. If the temperature modulation $\delta T(x)$ is weak, $\beta(x)$ can be written as $\beta[1-\delta T(x)/T]$, where $(k_B\beta)^{-1}$ is the average temperature T. Then Eq. (7) is

$$\rho=\exp[-\beta(H+H')]/Z\ , \tag{14}$$

$$\begin{aligned}H'&=-\frac{1}{T}\int d^3x\,\delta T(x)h(x)\\&=\frac{1}{T}\int_{-\infty}^{0}dt\int d^3x\,\delta T(x)\nabla\cdot\mathbf{S}(x,t)\\&=-\frac{1}{T}\int_{-\infty}^{0}dt\int d^3x\,\nabla T(x)\cdot\mathbf{S}(x,t)\ .\end{aligned} \tag{15}$$

Here we have used the integrated form of Eq. (11), and performed an integration by parts. The temperature gradient $\nabla T(x)$ can now be taken to be spatially constant and removed from the integral, and $\int d^3x\,\mathbf{S}(x)$ can be replaced by $V\mathbf{S}$. The operator H' formally plays the role of a perturbation. Just like the case of electrical conduction, the driving term of H' involves the current operator. The density matrix Eq. (14) can be expanded in powers of the perturbation:

$$e^{-\beta(H+H')}=e^{-\beta H}\left[1+\int_0^\beta d\lambda\, e^{\lambda H}H'e^{-\lambda H}+\cdots\right]\ . \tag{16}$$

Evaluating the heat current, $\text{tr}\rho_0\mathbf{S}$ is still zero, but the first correction from Eq. (16) is not, and this term is identified as $-\kappa\cdot\nabla T$, giving

$$\kappa_{\mu\nu}=\frac{V}{T}\int_0^\beta d\lambda\int_{-\infty}^{0}dt\langle e^{\lambda H}S_\mu(t)e^{-\lambda H}S_\nu(0)\rangle\ . \tag{17}$$

Now we can time shift the time integral, and define $e^{\lambda H}Se^{-\lambda H}=S(-i\hbar\lambda)$, which yields the Kubo formula

$$\kappa_{\mu\nu}(\omega)=\frac{V}{T}\int_0^\beta d\lambda\int_0^\infty dt\, e^{i(\omega+i\eta)t}\langle S_\mu(-i\hbar\lambda)S_\nu(t)\rangle\ . \tag{18}$$

Here ω represents the frequency of an ac applied temperature gradient. The experimental case corresponds to $\omega=0$, but it is useful theoretically—both to the formalism and to the numerical evaluation—to consider the ac generalization. Further interpretation of this formula will be made in Sec. V.

IV. THERMAL CONDUCTIVITY FORMULAS

For a disordered harmonic solid the exact many-body states are simply the various ways of occupying the $3N$ harmonic-oscillator states. Postponing the question of whether these states can be realistically calculated, we now assume that we know these exact eigenfrequencies ω_i and polarization eigenvectors $e_\alpha(l,i)$ for all $3N$ modes i at all N atoms l and three Cartesian directions α. The Hamiltonian operator is

$$H=\sum_i \hbar\omega_i(a_i^\dagger a_i+\tfrac{1}{2}) . \tag{19}$$

Then we can write the heat current operator Eq. (13) in terms of these oscillator states. Consistent with the harmonic approximation, the heat current operator has the general form given in Eq. (2). The specific form of the matrix element S_{ij} is worked out in Appendix A. Using these harmonic results, the Kubo formula Eq. (18) can be evaluated. The result is[9]

$$\kappa_{\mu\nu}(\omega)=\frac{\pi V}{T}\sum_{i,j}\frac{n_i-n_j}{\hbar(\omega_i-\omega_j)}(S_\mu)_{ij}(S_\nu)_{ji}\delta(\omega_i-\omega_j-\omega) , \tag{20}$$

where n_i is the equilibrium (Bose-Einstein) occupation of the ith exact oscillator mode. This result is explained in Appendix B.

A special case of the harmonic solid is a perfectly ordered harmonic crystal, with eigenvectors e which are also eigenvectors of the translation operator, labeled by $k=(\mathbf{Q},n)$. These states carry currents, which are the diagonal matrix elements S_{kk} of the heat current and have the form $\hbar\omega_k v_k/V$, as shown in Appendix A. Examining Eq. (20), we see that the value at $\omega=0$ is infinite, corresponding to a perfect heat conductor. As soon as there is any disorder, finite values of $\kappa_{\mu\nu}$ must occur, which can only happen if the diagonal matrix elements of $\mathbf{S}$ are zero. Then the heat must be carried by off-diagonal elements of $\mathbf{S}$. The interpretation of this result is discussed further in Sec. V.

When disorder or interactions are weak, perturbation theory carried to infinite order with the help of diagrams can be used to evaluate Eq. (18). The lowest-order "conserving" approximation (which includes the "ladder diagrams") gives the Peierls-Boltzmann equation,[13] and higher-order perturbation theory has not proved tractable, in general, although special limits (e.g., "weak localization" effects[22]) have been explored. The principal point of the present paper is to argue that Eq. (20) is useful for model calculations in glasses or highly disordered crystals. This is the phonon analog of the "Kubo-Greenwood"[23] approach for electrical conductivity of disordered metals.

Examination of Eq. (5) suggests another way to write the formula for κ. In the limit $\omega\rightarrow 0$, because of the δ function in (20), the factor $(n_j-n_i)/(\omega_i-\omega_j)$ becomes $(-\partial n/\partial\omega_i)$. Equation (4) related this to the specific heat C_i of the ith mode. The result is

$$\kappa=\frac{1}{V}\sum_i C_i(T)D_i \tag{21}$$

$$D_i=\frac{\pi V^2}{3\hbar^2\omega_i^2}\sum_j^{\neq i}|S_{ij}|^2\delta(\omega_i-\omega_j) . \tag{22}$$

For a harmonic disordered sample, Eq. (22) provides a microscopic, temperature-independent definition of the "mode diffusivity" D_i. It is an intrinsic property of the ith normal mode, and provides an unambiguous criterion for localization. Localized modes have $D_i=0$ and make no contribution to κ. Of course, once inelastic (anharmonic) processes are included, a nonzero contribution to κ will occur by a mechanism analogous to electron hopping.

For actual calculations on periodically repeated clusters, the delta function in (22) must be broadened (to a Lorentzian of width $\eta >$ level spacing). Numerical calculations of D_i are given in FKAW and clear evidence for a mobility edge is shown.

V. INTERPRETATION OF RESULT

Now we pause to interpret our formula (20). The basic assumption is that if the two ends of a system are coupled to heat baths at two different temperatures, the system evolves to a steady state with a local temperature $T(x)$ which smoothly interpolates. In order to achieve this local equilibrium, there must presumably be some inelastic (anharmonic) processes which redistribute vibrational energies among the states i. Just as in the standard phonon-gas theory of specific heats, we assume that these anharmonic interactions can be neglected apart from their role in achieving the steady state.

Next we ask how can heat be transported by decoupled harmonic eigenstates which do not themselves carry heat. In the corresponding Kubo-Greenwood treatment of electrical conductivity, it is the external E field which couples the states (via the current operator) and permits an electrical current. In a different way, the temperature gradient also effectively couples the different harmonic eigenstates (via the heat current operator). This is apparent mathematically from Eqs. (15) and (16), but the physical reason is not so obvious. We should ask what sort of vibrational wave function would represent a system with a temperature gradient. All possible vibrational wave functions can be represented by linear combinations of of harmonic states with different occupation numbers. If vibrational eigenstates were all localized, it would be easy to construct states with a temperature gradient, simply by having states localized near the hot end be more populated than states near the cold end. Such a state has a purely diagonal density matrix, and no heat current, because $\mathbf{S}$ has vanishing diagonal matrix elements. If the states are delocalized, then in order to have greater vibrational amplitude at the hot end than the cold end, it is necessary to use nonstationary localized states (like wave packets) which are superpositions of the harmonic vibrational eigenstates. Then the density matrix will have nonzero off-diagonal matrix elements between the different vibrational eigenstates contained in the localized superposition state, and trρ**S** will no longer be zero. This provides an interpretation of what Eqs. (15) and (16) are accomplishing.

VI. SIZE EFFECTS

Two subtle issues need discussion. One is the question of limits ($V\rightarrow\infty,\eta\rightarrow 0$) which occur in the formulas for κ. This issue plays a role in numerical calculations and is discussed in this section with care, if not with rigor. The other is the apparent discontinuity between the phonon-gas picture involving "diagonal currents" carried by approximate Bloch-wave eigenstates, and the present picture involving "off-diagonal currents" carried by exact nonpropagating states. The discussion in this section provides at least a partial connection between these pictures.

It is convenient to split Eq. (20) into two parts,

$$\kappa=\kappa^{\mathrm{I}}+\kappa^{\mathrm{II}}\ , \tag{23}$$

$$\kappa^{\mathrm{I}}(\omega)=\frac{iV}{T}\sum_{i\neq j}\frac{n_i-n_j}{\hbar(\omega_i-\omega_j)}\frac{|S_{ij}|^2}{\omega_i-\omega_j-\omega-i\eta}\ , \tag{24}$$

$$\kappa^{\mathrm{II}}(\omega)=\frac{iV}{\hbar T}\frac{1}{\omega+i\eta}\sum_i\left[-\frac{\partial n_i}{\partial\omega_i}\right]S_{ii}^2\ . \tag{25}$$

The full complex ω-dependent equations are given, rather than just the real part which is shown in Eq. (20). A limiting process, first $V\rightarrow\infty$, then $\eta\rightarrow 0$, is implied. Then for the real parts of κ^{I} and κ^{II}, one gets δ functions in place of energy denominators. The formulas should be interpreted as having a subscript like $\mu=x$, i.e., $S_{ij}=S_{xij}$ and $\kappa=\kappa_{xx}$. Off-diagonal formulas (κ_{xy}) can be easily guessed.

There are three cases to contrast: (a) a perfect infinite crystal; (b) our hypothetical object of interest, an infinite imperfect solid or glass; (c) our actual object of study, a computationally useful model for (b) consisting of an N atom disordered cluster with periodic (or other) boundary conditions applied. In case (a), state labels i and j in Eqs. (24) and (25) are $(\mathbf{Q},n)$ and $(\mathbf{Q},n')$ and S_{ij} vanishes unless the wave vector is conserved. The part κ^{I} [Eq. (13)] is the interband conductivity, and κ^{II} is the intraband conductivity. In this case Eq. (25) can be written

$$\kappa^{\mathrm{II}}=\frac{1}{1+i\omega\tau}\sum_i v_{ix}^2\tau C_i\ . \tag{26}$$

The infinitesimal η has been written as $1/\tau$ in recognition of the fact that collisions (left out of the model) will broaden the response. This is the thermal analog of the Drude response of a metal. At $\omega=0$ Eq. (26) becomes just Eq. (5).

In case (b), an infinite but imperfect solid, the exact eigenstates are nonpropagating, i.e., $S_{ii}=0$. Only strict periodicity (Bloch's theorem) permits $S_{ii}\neq 0$. Thus $\kappa^{\mathrm{II}}=0$ and $\kappa(\omega)=\kappa^{\mathrm{I}}$. When the exact eigenstates are delocalized (as is true for most states in glasses, we believe) then κ^{I} gives a nonzero dc conductivity. It is important to let $V\rightarrow\infty$ before $\eta\rightarrow 0$. If the reverse is done, then κ^{I} consists only of isolated delta functions, and $\kappa^{\mathrm{I}}(0)=0$. We now argue that Eq. (24) also applies in case (c), except for a correction which goes to zero as $V\rightarrow\infty$. The correction is numerically significant for 10^3 atom clusters and can be understood from case (a).

In case (c) we have a cluster of N atoms, which is repeated periodically to fill all space. N is of order 10^3, i.e., small enough to permit exact diagonalization of the harmonic Hamiltonian, but big enough to capture the physics of a disordered solid or glass. The reason for periodic repetition is to avoid surfaces and the resulting contamination of κ.

There are two basic ways to calculate κ. Either (A) use periodic boundary conditions [$\mathbf{e}(r+L,i)=\mathbf{e}(r,i)$ for each polarization vector **e**] and evaluate Eq. (24) [Eq. (25) gives zero] keeping η larger than the mean level spacing, or (B) treat the system as an infinite crystal with an N-atom unit cell, use Bloch's theorem [$\mathbf{e}(r+L,i)=e^{iQL}\mathbf{e}(r,i)$], and evaluate both Eqs. (24) and (25) by summing over all **Q**'s in the small Brillouin zone which corresponds to the large unit cell. Neither procedure goes to the true $V\rightarrow\infty$ limit of case (b) as smoothly as one would like. Procedure (B) retains in principal the property of perfect crystallinity (although with a large, disorderly unit cell) so that $\kappa(\omega)$ will contain a term $\kappa^{\mathrm{II}}\propto\delta(\omega)$ and a term κ^{I} which will get small as $\omega\rightarrow 0$. The amount of spectral weight in κ^{II} goes to zero as $N\rightarrow\infty$, probably as $1/N$. The argument is that there are of order N narrow bands which repel each other, making band widths and velocities on average of order $1/N$. Procedure (A) is coarser because only the $Q=0$ (periodically repeated) eigenstates are used. For these states (and also zone boundary states with antiperiodic boundary conditions) $S_{ii}=0$ so the $\sim O(1/N)$ contribution from $\kappa^{\mathrm{II}}(\omega)$ is missing. We see this effect very clearly in our numerical studies in the subsequent paper; the $\kappa(\omega)$ results have a small, Lorentzian-shaped dip centered at $\omega=0$ which reflects the missing κ^{II} part. We speed the convergence of our calculations by adding an appropriately adjusted Lorentzian such that the extrapolation of $\kappa(\omega)$ to $\omega=0$ is smooth and monotonic. Another way of seeing this is from the following one-dimensional example. If we double the periodic cell size (by introducing further disorder) we gain twice as many energy bands and therefore increase the contributions to Eq. (24) (illustrated in Fig. 1) while simultaneously decreasing the contribution to Eq. (25) because $S_Q\rightarrow 0$ at the new zone boundaries. However, the new contribution to Eq. (24) is approximately the same as contributions to Eq. (25) in the smaller cell originating from the zone boundary. (This is because $S_{QQ'}\rightarrow S_Q$ in the limit $Q'\rightarrow Q$ as demonstrated by Hardy.[21])

For actual calculations using a periodic cluster [case (c)], we have successfully used procedure (A) (keeping η greater than the level spacing) and found it appropriate to add a Lorentzian piece to make up for the missing κ^{II} contribution that would have emerged in procedure (B). Thus, for actual implementation, Eq. (24) is used with a delta function broadened into a Lorentzian, of width η, chosen to exceed the mean level spacing, and an extrapolation from $\omega>\eta$ down to $\omega=0$.

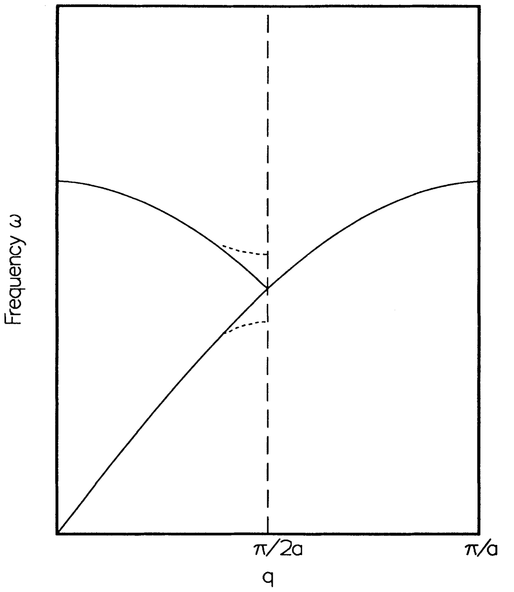

Fig. 1. One-dimensional illustration of how crystal symmetry breaking (in this case, dimerization) converts intraband processes into interband processes.

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APPENDIX A: HEAT CURRENT OPERATOR

In order to calculate, it is necessary to have formulas for the matrix elements S_{ij} of the heat current operator. In implementing the general theory, Hardy[21] considered only a Bravais lattice. Here we extend Hardy's result to the case of a supercell with more than one type of atom, such as a periodic model for amorphous Si/Ge alloys.

The leading term of Eq. (13) is quadratic and higher-order (anharmonic) terms are smaller by powers of u/a (≈ 0.03 at room temperature) where a is an interatomic spacing, so we neglect them. Ranninger[24] has written down expressions for the anharmonic terms in the heat current operator to all orders, but no one to our knowledge has evaluated these contributions to the thermal conductivity. Only the second term in the heat-current-density operator Eq. (13) is second order in the vibrational coordinates:

$$\mathbf{S}=\frac{1}{2V}\sum_{l,m}\sum_{\alpha,\beta}(\mathbf{R}_l-\mathbf{R}_m)\frac{p_{l\alpha}}{m_l}\frac{\partial^2 E}{\partial u(l\alpha)\partial u(m\beta)}u(m\beta) . \tag{A1}$$

We now consider $\mathbf{S}$ for a periodic system of N cells, with n atoms per cell, labeled by $\kappa=1,\ldots,n$:

$$\mathbf{S}=-\frac{1}{2V}\sum_{l,m}\sum_{\kappa,\kappa'=1}^{n}\sum_{\alpha,\beta=1}^{3}(\mathbf{R}_{l\kappa}-\mathbf{R}_{m\kappa'})\times\frac{p_{l\kappa\alpha}}{m_\kappa}\Phi_{\alpha\beta}^{\kappa\kappa'}(0,m-l)u_{m\kappa'\beta} , \tag{A2}$$

where l and $m=1,\ldots,N$ label the cell; $\Phi^{\kappa\kappa'}(0,m-l)$ is the force constant tensor between atoms $l\kappa$ and $m\kappa'$. Thus we consider atoms with all values of l at this stage, not only those within the single cell that represents the disorderly array of atoms in the amorphous system; this is helpful for implementing periodic boundary conditions. Next we make a normal mode transformation similar to that of a crystal. Unlike the case of a crystal, however, we consider only a single wave vector $\mathbf{K}$, which is chosen to be zero or else a special point on the supercell's first Brillouin-zone boundary. Therefore, the polarization vector, $\mathbf{e}(\kappa;\mathbf{K},j)$, can be taken to be real and the factor $e^{i\mathbf{K}\cdot\mathbf{r}_l}$ is ± 1. Vibrational coordinates (p_i,q_i) are now transformed to normal mode coordinates $(P(\mathbf{K},j),Q(\mathbf{K},j))$:

$$u_{l\kappa\alpha}=\frac{1}{\sqrt{m_\kappa}}\sum_j e_\alpha(\kappa;\mathbf{K},j)Q(\mathbf{K},j)e^{i\mathbf{K}\cdot\mathbf{R}_l} , \tag{A3}$$

$$p_{l\kappa\alpha}=\sqrt{m_\kappa}\sum_j e_\alpha(\kappa;\mathbf{K},j)P(\mathbf{K},j)e^{i\mathbf{K}\cdot\mathbf{R}_l} . \tag{A4}$$

Substituting these expressions into Eq. (A2) gives

$$\mathbf{S}=-\frac{1}{2V}\sum_{j,j'}\sum_{\alpha\beta}\sum_{m,\kappa,\kappa'}P(\mathbf{K},j)Q(-\mathbf{K},j')e_\alpha(\kappa;\mathbf{K},j)\times e_\beta(\kappa';\mathbf{K},j')D_{\beta\alpha}^{\kappa'\kappa}(0,m)\times(\mathbf{R}_m+\mathbf{R}_{\kappa\kappa'})e^{i\mathbf{K}\cdot\mathbf{R}_m} , \tag{A5}$$

where the Hermitian force constants $D_{\beta\alpha}^{\kappa'\kappa}(0,m)$ are mass-scaled versions of the non-Hermitian force constants Φ, namely

$$\Phi_{\beta\alpha}^{\kappa'\kappa}(0,m)/(m_\kappa m_{\kappa'})^{1/2} .$$

The expression for a crystal is the same except the wave vector $\mathbf{K}$ is not fixed but summed over the Brillouin zone. In Eqs. (A3)–(A5) $\mathbf{K}$ is chosen to be at either the center or corner of the Brillouin zone. The former choice yields periodic and the latter choice antiperiodic boundary conditions, i.e., $u(x_l)=-u(x_l+L)$, where L is either $\mathbf{A}$, $\mathbf{B}$, or $\mathbf{C}$, the supercell lattice vectors. Equation (A5) can also be written in terms of phonon creation and annihilation operators:

$$\mathbf{S}=\sum_{i,j}\mathbf{S}_{ij}a_i^\dagger a_j , \tag{A6}$$

$$\mathbf{S}_{ij}=\frac{\hbar}{2V}\mathbf{v}_{\mathbf{K}ij}(\omega_{\mathbf{K}i}+\omega_{\mathbf{K}j}) , \tag{A7}$$

$$\mathbf{v}_{\mathbf{K}ij}=\frac{i}{2\sqrt{\omega_{\mathbf{K}i}\omega_{\mathbf{K}j}}}\sum_{\alpha,\beta}\sum_{m,\kappa,\kappa'}e_\alpha(\kappa;\mathbf{K},i)D_{\beta\alpha}^{\kappa'\kappa}(0,m)\times(\mathbf{R}_m+\mathbf{R}_{\kappa\kappa'})e^{i\mathbf{K}\cdot\mathbf{R}_m}\times e_\beta(\kappa';\mathbf{K},j) . \tag{A8}$$

Quadratic terms like $a_i a_j$ or $a_i^\dagger a_j^\dagger$ are neglected in our treatment as they contribute nothing in the $\omega \to 0$ limit. The crystalline analog of Eq. (A8) has diagonal $(i=j)$ terms which are just the phonon group velocity $\mathbf{v}_{\mathbf{k}j}$. In our noncrystalline implementation, this is still true except that **K** is always a zone center or boundary point where the corresponding group velocity is zero. Thus the diagonal elements vanish as required in our case.

APPENDIX B: DERIVATION OF EQ. (20)

We present here details of the derivation of Eq. (20). The starting point is the Kubo expression, Eq. (18), which can be written in the Lehman representation:

$$\kappa_{\alpha\beta}(\omega)=\frac{V}{T}\int_0^\beta d\lambda \int_0^\infty dt\, e^{i(\omega+i\eta)t}\sum_{m,n}\frac{e^{-\beta E_n}}{Z}\langle n|e^{\lambda H}S_\alpha e^{-\lambda H}|m\rangle\langle m|e^{iHt/\hbar}S_\beta e^{-iHt/\hbar}|n\rangle\ , \tag{B1}$$

$$\mathrm{Re}\kappa_{\alpha\beta}(\omega)=\frac{\pi\hbar V}{ZT}\sum_{m,n}e^{-\beta E_m}\left[\frac{e^{\beta E_{n,m}}-1}{E_{n,m}}\right]\langle n|S_\alpha|m\rangle\langle m|S_\beta|n\rangle\delta(E_{n,m}-\hbar\omega)\ , \tag{B2}$$

where $E_{n,m}=E_n-E_m$. Using the harmonic approximation of Eqs. (17) and (18) we calculate $\mathrm{Re}\kappa_{xx}$ (denoted as κ; S_x denoted as S)

$$\kappa(\omega)=\frac{\pi\hbar V}{T}\sum_n\frac{e^{-\beta E_n}}{Z}\sum_m\frac{e^{\beta E_{n,m}}-1}{E_{n,m}}\sum_{i,j,k,l}\langle n|a_k^\dagger a_l|m\rangle\langle m|a_j^\dagger a_i|n\rangle S_{kl}S_{ji}\delta(E_{n,m}-\hbar\omega)\ . \tag{B3}$$

The exact state $|m\rangle$ is the unique state which couples to $a_j^\dagger a_i|n\rangle$, denoted as $|n_{ij}\rangle$. We use the standard expressions

$$\langle m|a_j^\dagger a_i|n\rangle=\sqrt{(n_j+1)n_i}\,\delta_{m,n_{ij}}\ , \tag{B4}$$

$$\langle n|a_k^\dagger a_l|n_{ij}\rangle=\sqrt{(n_j+1)n_i}\,\delta_{l,j}\delta_{k,i}\ , \tag{B5}$$

$$\langle m|a_i^\dagger a_i|n\rangle=n_i\delta_{m,n}\ . \tag{B6}$$

In terms of the normal mode frequencies, $E_{n,m}$ becomes $\hbar(\omega_i-\omega_j)$. There are two parts to κ, $\kappa^{\mathrm{I}}(\omega)$ containing the pieces with $n\neq m$, and therefore $i\neq j$ $(k=i, l=j)$, $\kappa^{\mathrm{II}}(\omega)$ with $n=m$ and therefore $i=j$ $(k=l)$. In particular, κ^{I} is

$$\kappa^{\mathrm{I}}(\omega)=\frac{\pi}{VT}\sum_n\frac{e^{-\beta E_n}}{Z}\sum_{i\neq j}\left[\frac{e^{\beta\hbar\omega_{ij}}-1}{\hbar\omega_{ij}}\right](n_j+1)\times n_i|S_{ij}|^2\delta(\omega_{ij}-\omega)\ . \tag{B7}$$

Now since $i\neq j$, we can write

$$\begin{aligned}\sum_n\frac{e^{-\beta E_n}}{Z}n_i(n_j+1)&=\langle n_i(n_j+1)\rangle\\ &=\langle n_i\rangle(\langle n_j\rangle+1)\end{aligned} \tag{B8}$$

and there is an identity

$$(e^{\beta\omega_{ij}}-1)(\langle n_j\rangle+1)\langle n_i\rangle=\langle n_j\rangle-\langle n_i\rangle\ . \tag{B9}$$

The expression (B7) then becomes our central result, Eq. (24):

$$\kappa^{\mathrm{I}}(\omega)=\frac{\pi}{VT}\sum_{i\neq j}\left[\frac{\langle n_j\rangle-\langle n_i\rangle}{\hbar\omega_{ij}}\right]|S_{ij}|^2\delta(\omega_{ij}-\omega)\ . \tag{B10}$$

In the text we have designated the Bose factor $\langle n_i\rangle$ by n_i for simplicity.

In the case of $\mathrm{Re}\kappa^{\mathrm{II}}(\omega)$ we shall replace the delta function in expression (A3) by $\mathrm{Re}[i/(\omega+i/\tau)]$ to obtain

$$\kappa^{\mathrm{II}}(\omega)=\frac{\beta}{VT}\mathrm{Re}\left[\frac{1}{\omega+i/\tau}\right]\sum_{i,j}\langle n_i n_j\rangle S_{ii}S_{jj}\ . \tag{B11}$$

The factor $\langle n_i n_j\rangle$ can be written as $\langle n_i\rangle\langle n_j\rangle$ plus a correction $\langle n_i^2\rangle-\langle n_i\rangle^2$ when $i=j$. Therefore, we get

$$\begin{aligned}\kappa^{\mathrm{II}}(\omega)&=\frac{\beta}{VT}\mathrm{Re}\left[\frac{\tau}{1-i\omega\tau}\right]J\ ,\\ J&=\left[\sum_i\langle n_i\rangle S_{ii}\right]^2+\sum_i(\langle n_i^2\rangle-\langle n_i\rangle^2)S_{ii}^2\ .\end{aligned} \tag{B12}$$

Since the average energy current must be zero in equilibrium the first term in J must be zero. The term which remains reduces to Eq. (24) after using the identity

$$\begin{aligned}\langle n_i^2\rangle-\langle n_i\rangle^2&=\langle n_i\rangle(\langle n_i\rangle+1)\\ &=-k_B T\frac{\partial\langle n_i\rangle}{\partial(\hbar\omega_i)}\ .\end{aligned} \tag{B13}$$

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