Thermal Conductivity of Glasses: Theory and Application to Amorphous Si

Philip B. Allen
Department of Physics, State University of New York, Stony Brook, New York 11794-3800

Joseph L. Feldman
Condensed Matter Physics Branch, Naval Research Laboratory, Washington, D.C. 20375-5000

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Vibrations of amorphous Si are represented by the network model of Wooten, Winer, and Weaire and the forces of Stillinger and Weber. It is shown how the Kubo formula for thermal conductivity can be evaluated "exactly" assuming harmonic vibrations, making only finite-system-size errors. The results support a "shunt-resistor model" which fits data for glasses very well.

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In a recent review,[1] Freeman and Anderson claim with only slight exaggeration, "the thermal conductivity of an amorphous solid is not understood in any temperature range." There are three characteristic temperature intervals: (a) low T (≤ 1 K), where $\kappa(T)\approx T^{1.8-2.0}$ has a reasonably good explanation[2,3] as (Boltzmann-type) transport by propagation of long-wavelength vibrational modes scattered occasionally by localized two-level systems; (b) intermediate T ($4\text{ K}\leq T\leq 20$ K), where the "plateau" seen in many disordered systems has evoked a wide variety of explanations[4]; and (c) high T (>30 K), where $\kappa(T)$ rises smoothly to a limiting value $\kappa(\infty)$, unlike crystalline insulators where propagating short-wavelength phonons scattered by anharmonic interactions give $\kappa(T)\propto 1/T$. Regime (c) has a qualitative explanation due to Birch and Clark[5] and Kittel,[6] namely that the dominant high-energy vibrations are so strongly scattered by local disorder that one should assign the minimum sensible mean free path, $l\approx a$ where a is a typical atomic spacing, in the kinetic formula $\kappa=Cvl/3$. This paper addresses the high-T regime (c), and in the process sheds some light on regime (b).

Kittel's qualitative picture, while useful, is not satisfactory, since the kinetic formula $Cvl/3$ is applicable only in the Boltzmann regime where one can assign velocities v to propagating modes. Graebner, Golding, and Allen[4] demonstrated convincingly that beyond the edge of the plateau ($T\geq 20$ K) the dominant vibrations propagate distances shorter than the hypothetical wavelength $2\pi v/\omega$. In other words, they cannot be assigned a wavelength or a velocity. Thus, it is unclear what meaning should be given to Kittel's formula $Cva/3$. It is often suggested that the higher-frequency vibrations are localized in Anderson's[7] sense. The constant $\kappa(\infty)$ behavior at high T indicates otherwise. If the dominant modes at high T were localized, then energy could only be transported by hopping via anharmonicity, which should exhibit a characteristic T dependence.[8]

The basis for our work is the observation that the Kubo formula[9]

$$\kappa_{\mu\nu}(\omega)=\frac{1}{VT}\int_0^\beta d\lambda\int_0^\infty dt\, e^{i(\omega+i\eta)t}\times\langle S_\mu(-i\hbar\lambda)S_\nu(t)\rangle \qquad (1)$$

can be evaluated by brute force with only finite-system-size errors, provided the atoms are assumed to vibrate harmonically (i.e., anharmonic processes are assumed to have little influence compared to the effect which disorder has on the vibrations). In Eq. (1), $-\kappa_{\mu\nu}e^{-i\omega t}$ is the heat current in the μ direction which responds to an oscillatory temperature gradient $\partial T/\partial r_\nu e^{-i\omega t}$ of unit amplitude, $S(t)$ is the heat current operator[10] in the Heisenberg, picture, $\beta=1/k_BT$, V is the volume of the sample, and angular brackets denote an equilibrium ensemble average. The normal modes of harmonic vibration have eigenfrequencies ω_i and eigenvectors $|i\rangle$ where $\langle 1,\mu|i\rangle=\epsilon_i(1,\mu)$ is the polarization vector component corresponding to atom l and the μ direction. Then Eq. (1) can be reduced to[11]

$$\kappa_{xx}(\omega)=\frac{\pi}{VT}\sum_{i,j}\frac{n_j-n_i}{\hbar(\omega_i-\omega_j)}\times|\langle i|\tilde{S}_x|j\rangle|^2\delta(\omega_i-\omega_j-\omega)\,, \qquad (2)$$

where $\tilde{S}_x$ is a related matrix to the ordinary dynamical matrix and n_i is the equilibrium occupation $[\exp(\beta\hbar\omega_i)-1]^{-1}$. The electrical conductivity of metals has a Kubo formula analogous to Eq. (1). The independent electron approximation is analogous to the harmonic approximation, and the electronic analog of Eq. (2) is often known as the Kubo-Greenwood formula.[12] To make sense of the sum in Eq. (2), the δ function should be given a width η which goes to zero only after V goes to ∞. Our procedure involves "exact" evaluation of Eq. (2) for a finite sample with boundary conditions chosen to eliminate surface effects. Specifically, we use both periodic and antiperiodic boundary conditions, and average the results. The width η of $\delta(\omega)\approx\eta/\pi(\omega^2+\eta^2)$ is chosen to be ≈ 2 K, about 10^2 times greater than the minimum level spacing. Our results for κ are not sensitive to this choice.

To test theory, we need (i) a model for the coordinates $\mathbf{R}_l$ of the atoms, with periodicity in a large supercell; (ii) a model for the interatomic forces; and (iii) experimental results to compare with. The comparison, of course, tests not only Eq. (2) but also ingredients (i) and (ii) of the calculation. We chose amorphous Si because of much recent work on models[13] and forces.[14] In particu-

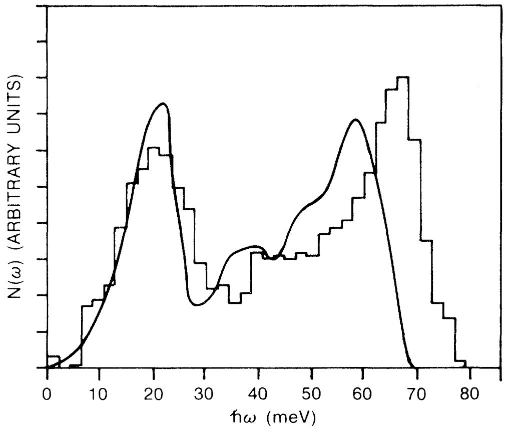

FIG. 1. Vibrational density of states for the WWW model (Ref. 15) of a-Si with use of the SW potential (Ref. 16). The continuous curve is from neutron scattering (Ref. 20). The histogram sums up 648 modes with periodic boundary conditions and an equal number with antiperiodic boundary conditions.

lar, we use the Wooten-Winer-Weaire[15] (WWW) coordinates (216 atoms in a cubic cell repeated periodically), and the Stillinger-Weber[16] (SW) two- and three-body potential, which appears to give satisfactory vibrational properties.[17] The WWW coordinates have been further relaxed to a local minimum of the SW potential.[18] Experimental results for $\kappa(T)$ in a-Si have just become available.[19] The distinction which is often made between "glasses," such as a-SiO$_2$, and "amorphous thin films," such as a-Si, seems to arise from smaller barrier heights to recrystallization in the latter case. Amorphous Si provides a good model for the glassy properties that we address. Crystalline Si is unusually harmonic; κ ($T=300$ K) exceeds that at a-Si by 10^2. Neglect of anharmonicity is then justified on the assumption that a-Si is not much more anharmonic than crystalline Si.

As shown in Fig. 1, the SW potential, together with the WWW amorphous coordinates, gives a vibrational spectrum $N(\omega)$ which agrees reasonably well with experiment.[20] The principal discrepancy, a 10% overestimate of the highest-energy peak, occurs also when the SW potential is applied to crystalline Si.[17,18] Biswas *et al.*[21] have obtained excellent agreement with experimental $N(\omega)$ from the WWW coordinates using a Keating potential.[22] Our results for the inverse participation ratio agree closely with Ref. 21; that is, we find the uppermost 2% of the eigenmodes to be localized, with all other vibrational modes well delocalized, at least on the scale of our 16-Å supercell. There are no well localized modes at lower energies, in contrast to models with dangling bonds where Ref. 21 found a small number of localized states in the lowest part of the spectrum.

Typical curves of $\kappa(\omega)$ vs ω are shown in Fig. 2. The xx, yy, and zz components of $\kappa_{\mu\nu}$ have been averaged together, as have the results from periodic and antiperiodic boundary conditions. Because of the finite system size, it is necessary to extrapolate to $\omega=0$. To understand the origin of the dip occurring near $\omega=0$ in Fig. 2, we have computed the joint density of states $J(\omega)=\sum_{ij}\delta(\omega_i-\omega_j-\omega)$ using the same broadening $\eta=2$ K in the δ function. If the term with $i=j$ is included, $J(\omega)$ is smooth, but when it is omitted, a dip occurs of exactly the size and shape seen in $\kappa(\omega)$, where the $i=j$ term is also omitted because the diagonal elements $\langle i|\tilde{S}|i\rangle$ are zero for our system. The relative size of the dip in $J(\omega)$ or $\kappa(\omega)$ vanishes in the infinite volume limit.

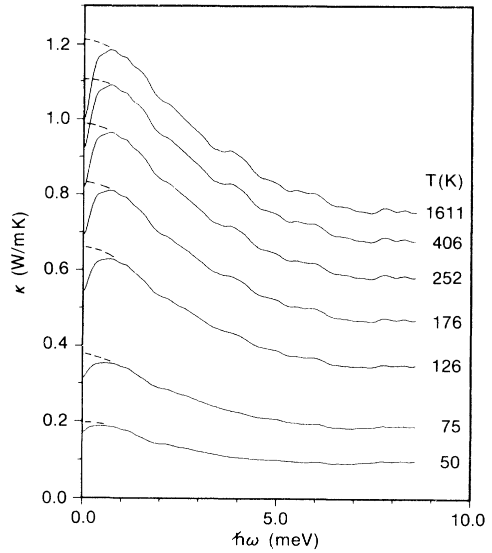

FIG. 2. $\kappa(\omega)$ evaluated with Eq. (2) and the model of Fig. 1 for vibrations of amorphous Si. The dashed line is our extrapolation to $\omega=0$.

Results for $\kappa(T)$ are shown in Fig. 3, and compared with the experiment.[19] The theory asymptotically approaches a limit of $\kappa(\infty)=1.2$ W/mK as $T=\infty$. The

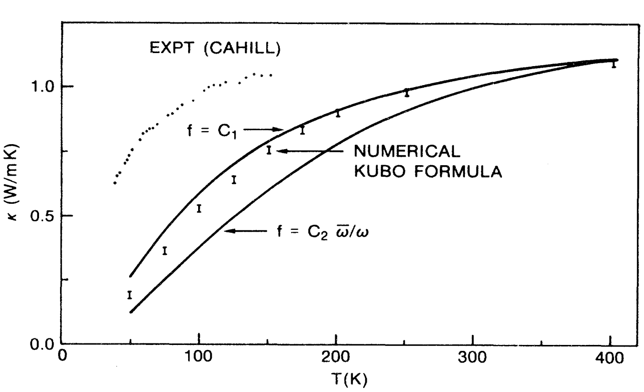

FIG. 3. The present theory for $\kappa(T)$ is represented by bars (I) indicating estimated finite-size errors in $\kappa_2(T)$. The dots are data of Ref. 19. The solid curves are from Eq. (7) with $D(\omega)=\frac{1}{3}a^2\bar{\omega}f(\omega/\bar{\omega})$.

experiment stops at $T=150$ K, but appears consistent with a high-T saturation at $\kappa(\infty)=1.1\text{-}1.3$ W/mK. At 150 K, experiment exceeds theory by a factor of 1.4, whereas at 50 K the factor is 4.0. This discrepancy is not unexpected, as will be explained below.

Let us first try to understand the shape of the calculated $\kappa(T)$ in Fig. 3. From Eq. (2) in the $\omega \rightarrow 0$ limit, we have

$$\kappa(T)=\frac{\pi}{3VT}\sum_{i,j}\left(-\frac{\partial n_i}{\partial \hbar\omega_i}\right)|\tilde{S}_{ij}|^2\delta(\omega_i-\omega_j)\,. \tag{3}$$

This can be written in terms of the contribution $C_i=(\hbar^2\omega_i^2/T)(-\partial n_i/\partial\hbar\omega_i)$ of the ith mode to the heat capacity $C(T)$ as

$$\kappa(T)=\frac{1}{V}\sum_i C_i D_i\,, \tag{4}$$

provided we define the "mode diffusivity" D_i as

$$D_i\equiv(\pi/3)\sum_j(\hbar^2\omega_i\omega_j)^{-1}|\tilde{S}_{ij}|^2\delta(\omega_i-\omega_j)\,. \tag{5}$$

To motivate the definition (5), it is not hard to show that for a perfect crystal, with eigenstates $|i\rangle$ being propagating states, the right-hand side of Eq. (5) is $v_k^2/3\eta$ where η is the width of the Lorentzian δ function. Strictly η is infinitesimal, corresponding to the infinite diffusivity and conductivity of the perfect crystal, but it is qualitatively correct for a *nearly* perfect crystal to identify η with the relaxation rate $1/\tau$.

The mode diffusivity D_i is a characteristic property of the ith eigenstate, and has not to our knowledge been defined previously. It is also useful to define average properties:

$$N(\omega)D(\omega)\equiv\sum_i D_i\delta(\omega_i-\omega)\,, \tag{6}$$

and therefore

$$\kappa(T)=\frac{1}{V}\int_0^\infty d\omega\, N(\omega)C(\omega/T)D(\omega)\,, \tag{7}$$

where $N(\omega)$ is the vibrational density of states and $C(\omega_i/T)=C_i$, and where broadened δ functions are presumed. The frequency-dependent diffusivity $D(\omega)$ was defined and discussed by John, Sompolinsky, and Stephen.[23] By dimensional analysis, $D(\omega)$ is of the form $\frac{1}{3}a^2\bar{\omega}f(\omega/\bar{\omega})$, where a and $\bar{\omega}$ are the length and frequency scales of the glass, respectively, which can be taken to be a bond length (2.35 Å) and the mean vibrational frequency (44 meV for the theory of Fig. 1). We have considered two different choices for the dimensionless function $f(\omega/\bar{\omega})$, namely, (1) a constant C_1 and (2) $f=C_2(\bar{\omega}/\omega)$. Both choices are discussed by Slack[24] in his phenomenological treatment of minimum conductivity. The first corresponds to the assignment of a propagation length which is of order a for all modes, while the second corresponds to a propagation length inversely proportional to ω as if to represent a wavelength (although no strict definition of a wavelength is possible). The solid curves of Fig. 3 represent Eq. (7) with these two choices; the constants $C_1=0.47$ and $C_2=0.33$ were used to fit to the microscopic theory at $T=400$ K. The similarity between the first choice and the microscopic theory, together with the reasonable value of C_1, provides microscopic support for the notion of minimum thermal conductivity in the form suggested by Kittel.[5,6] The physical explanation lies in the extended but nonpropagating nature of the exact eigenstates, which can diffuse because they couple to degenerate states via the heat current operator. Localized modes necessarily have $D_i=0$ because no two degenerate localized modes can overlap and the heat current operator is short ranged (if interatomic forces are short ranged).

Finally, we arrive at the problem of the enhancement of the experimental $\kappa(T)$ relative to theory in Fig. 3. It is well established[25] that propagating modes do exist in glasses at very low frequencies, and that they transport heat. Our use of periodic (or antiperiodic) boundary conditions on a 16.3-Å length scale has prohibited any low-frequency modes (our lowest vibrational eigenfrequency is 5 meV). Thus, our extrapolation of $\kappa(\omega)$ to $\omega=0$, while probably accurate for nonpropagating modes, completely omits an extra, low-frequency component consisting of heat transported ballistically by phonon quasiparticles over distances larger than the 16-Å cell size. These modes have a diffusivity $vl(\omega)/3$ (here ω is the normal mode frequency), where v is the sound velocity and $l(\omega)$, the mean free path, is large for $\omega \ll 1$ meV, but is believed[26] to fall rapidly to zero (e.g., as ω^{-4} due to Rayleigh scattering from density fluctuations) for $\omega \gtrsim 1$ meV. Thus, there are two separate pieces of Eq. (8): $\kappa_1(T)$ coming from propagating modes missed in our theory, and $\kappa_2(T)$ coming from nonpropagating modes and included. The difference between theory $[\kappa_2(T)]$ and experiment in Fig. 3 is presumably $\kappa_1(T)$. The empirical separation of $\kappa(T)$ into two pieces has been widely used[24,27] and has been called the "shunt-resistor model."[28] In Ref. 4, Graebner, Golding, and Allen show that the "plateau" in $\kappa(T)$ emerges from the shunt-resistor model in a very natural way for eight different glassy systems. We believe that we have now provided the microscopic justification for the shunt-resistor model, at least in the case where static disorder dominates and the harmonic model is appropriate. The previously mysterious $\kappa_2(T)$ has been successfully calculated from microscopic theory.

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[1] J. J. Freeman and A. C. Anderson, Phys. Rev. B **34**, 5684 (1986).

[2] R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).

[3] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972); W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

[4] Some recent papers with references to earlier work are J. E. Graebner, B. Golding, and L. C. Allen, Phys. Rev. B **34**, 5696 (1986); C. C. Yu and J. J. Freeman, Phys. Rev. B **36**, 7620 (1987); V. G. Karpov and D. A. Pashin, Zh. Eksp. Teor. Fiz. **88**, 2212 (1985) [Sov. Phys. JETP **61**, 1308 (1985)]; E. Akkermans and R. Maynard, Phys. Rev. B **32**, 7850 (1985); S. Alexander, O. Entin-Wohlman, and R. Orbach, Phys. Rev. B **34**, 2726 (1986); M. Randeria and J. P. Sethna, to be published.

[5] F. Birch and H. Clark, Am.J. Sci. **238**, 529 (1940).

[6] C. Kittel, Phys. Rev. **75**, 972 (1948).

[7] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

[8] J. Jäckle, Solid State Commun. **39**, 126 (1981).

[9] R. Kubo, M. Yokota, and S. Nakajima, J. Phys. Soc. Jpn. **12**, 1203 (1957).

[10] R. J. Hardy, Phys. Rev. **132**, 168 (1963). We slightly generalized this work to include more than one atom per unit cell.

[11] We omit certain terms in the heat current operator which give no contribution in the small-ω limit.

[12] D. A. Greenwood, Proc. Phys. Soc. (London) **71**, 585 (1960).

[13] P. C. Kelires and J. Tersoff, Phys. Rev. Lett. **61**, 562 (1988).

[14] A. M. Stoneham, V. T. B. Torres, P. M. Masri, and H. R. Schober, Philos. Mag. A **58**, 93 (1988).

[15] F. Wooten, K. Winer, and D. Weaire, Phys. Rev. Lett. **54**, 1392 (1985).

[16] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).

[17] X.-P. Li, G. Chen, P. B. Allen, and J. Q. Broughton, Phys. Rev. B **38**, 3331 (1988).

[18] J. Q. Broughton and X.-P. Li, Phys. Rev. B **35**, 9120 (1987).

[19] D. G. Cahill, H. E. Fischer, T. Klitsner, E. T. Swartz, and R. O. Pohl, J. Vac. Sci. Technol. (to be published).

[20] W. A. Kamitakahara, C. M. Soukoulis, H. R. Shanks, U. Buchenau, and G. S. Grest, Phys. Rev. B **36**, 6539 (1987).

[21] R. Biswas, A. M. Bouchard, W. A. Kamitakahara, G. S. Grest, and C. M. Soukoulis, Phys. Rev. Lett. **60**, 2280 (1988).

[22] P. N. Keating, Phys. Rev. **145**, 637 (1966).

[23] S. John, H. Sompolinsky, and M. J. Stephen, Phys. Rev. B **27**, 5592 (1983).

[24] G. A. Slack, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34, p. 1.

[25] S. Hunklinger and L. Piche, Solid State Commun. **17**, 1189 (1975); M. P. Zaitlin and A. C. Anderson, Phys. Rev. B **12**, 4475 (1975); B. Golding, J. E. Graebner, and R. J. Schutz, Phys. Rev. B **14**, 1660 (1976).

[26] See, for example, Ref. 2 and Graebner, Golding, and Allen in Ref. 4.

[27] Early uses are by Zaitlin and Anderson, Ref. 25, Eq. (3), or D. P. Jones, N. Thomas, and W. A. Phillips, Philos. Mag. B **38**, 271 (1978).

[28] A. Auerbach and P. B. Allen, Phys. Rev. B **29**, 2884 (1984).