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Energy current and thermal conductivity for Josephson-junction array models of granular superconductors

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One model of granular superconductors is based on a Josephson-junction array with capacitive, or charging, terms. As a result of having these noncommuting terms in the Hamiltonian, energy transport is possible. We have obtained an expression for the heat current for this model and have employed it in calculating the thermal conductivity κ. We find that as the temperature is lowered through the system's order-disorder phase transition, κ increases by more than one order of magnitude. Effects of having a distribution of grain sizes are also calculated.

The physics of granular superconductors (GS) has been investigated intensely for many years now.[1] It has been well established that the phase of the Ginzburg-Landau (GL) order parameter on each grain may make a contribution to the electrical conductivity,[2] the specific heat,[3] and frictional forces on vortices.[4] In this paper, we suggest that fluctuations in this phase may also contribute to the thermal conductivity. We employ a Kubo theory in the harmonic approximation, and a molecular dynamics simulation using classical Green-Kubo theory, to calculate κ for one simple model of GS. We find good agreement between the two methods, and that, although the order of magnitude of κ is low, it increases by more than one order of magnitude as T is lowered through the system's order-disorder transition, T_{c1}. We suggest that, although this system has very little entropy, there is also very little scattering, resulting in a large increase in κ below T_{c1}. Parameters appropriate to granular aluminum are used. To our knowledge, this contribution to κ has not yet been discussed.

The superconducting transition of three-dimensional (3D) GS typically takes place at a temperature $T_{c1} \ll T_{c0}$, where T_{c0} is the transition temperature of the individual grains. Near T_{c0}, the grains develop superconducting fluctuations. However, as they are of finite size and separated by the dielectric, they cannot establish long-range phase coherence. If the size of the grains is less than the bulk GL coherence length ξ_{GL}, one can associate a GL order parameter with each grain. Then, close to T_{c1}, only fluctuations in the phase of this order parameter are dominant. The grains become Josephson coupled at these temperatures, with the coupling energy given by[5] $H_J = \sum_{kk'} E_J^{(kk')}[1-\cos(\phi_{k'}-\phi_k)]/2$, where ϕ_k is the phase of the order parameter on grain k and $E_J^{(kk')}$ is the Josephson coupling energy between sites k and k'. This model has been used extensively for GS, and recently for pure high-T_c materials.[6] The thermal conductivity of these materials has received relatively little attention, although a review of κ of amorphous metals has recently been given by Löhneysen.[7] One can also include a term in the Hamiltonian to account for the charging energy associated with transferring a Cooper pair from one grain to another. This term takes the form of a kinetic energy, within the diagonal approximation to the capacitance tensor, allowing one to directly study dynamical aspects of this model such as energy transport. The charging term to be added to the Hamiltonian is written most generally as[8] $H_C = e^2 \sum_{k,k'} \hat{n}_k C^{-1}_{k,k'} \hat{n}_{k'}/2$, where $\hat{n}_k$ measures the number of Cooper pairs transferred, and $C^{-1}_{k,k'}$ is the inverse capacitance matrix. The variables ϕ_k and $\hat{n}_k$ are canonically conjugate, $[\hat{n}_k, \phi_{k'}] = -i\delta_{k,k'}$. Therefore, for $T \le T_{c0}$, the dynamics of GS may be described by the following Hamiltonian:

$$\hat{H} = \sum_k \{-E_c^{(k)}\partial^2/\partial\phi_k^2 + \tfrac{1}{2}\sum_{k'} E_J^{(kk')}[1-\cos(\phi_{k'}-\phi_k)]\} = \sum_k \hat{H}_k, \qquad (1)$$

where $E_c^{(k)} = e^2/2C$ is the charging energy which is assumed to have diagonal components only (an often-used simplifying approximation) and the other terms are as defined previously. The operator $\hat{H}_k$, the quantity in curly brackets, is a reasonable definition of a local energy operator within this model. It is often assumed, as is done here, that screening greatly reduces the effect of the long-range Coulomb interactions. Of importance to the thermal conductivity, Eq. (1) contains no cubic anharmonic terms upon expanding the potential about the ground, phase-locked state. If one considers a model with only nearest-neighbor off-diagonal components in the kinetic energy, as in Ref. 9, a canonical transformation yields a similar Hamiltonian with a diagonal kinetic energy and a cosine potential, whose argument depends on nearest and next-nearest neighbors. Therefore, one again finds no cubic anharmonic terms.

We will assume nearest-neighbor Josephson coupling and that the grains are located on a simple cubic lattice. The latter has been assumed in previous studies and can be partially justified.[10] This model is known to display an order-disorder transition[11] at $T_{c1} = 2.2E_J/k_B$. Periodic boundary conditions are used on a supercell of length NL, where L is the nearest-neighbor distance and N the number of grains along a unit cell. We wish to reason-

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ably apply classical Green-Kubo theory, and therefore require that $E_c < E_J$. Also, it must be that $T_{c1} \ll T_{c0}$, that is, the system's order-disorder transition temperature should be lower than the transition temperature of the individual grains. Although this may seem obvious, it is by no means assured by the model and places limits on the parameters. The Josephson coupling energy is defined by[12] $E_J^{(kk')} = \pi\hbar\Delta(T)/4e^2R_n$, where $\Delta(T)$ is the superconductor's energy gap and R_n is the intergranular normal state tunneling resistance between sites k and k'. The effects of dissipation are neglected in this treatment as we are only concerned with temperatures $T < T_{c0}$. It appears difficult to choose a consistent set of parameters such that (1) $T_{c1} < T_{c0}$, (2) $L < \xi_{\mathrm{GL}}$, and (3) $E_c < E_J$. The set chosen below satisfies the first two criteria, but not the third. We make use here of the result of Šimánek[14] showing that the phase transition takes place for all $E_c < 6E_J$. Using these relations, and that $\Delta(0)/k_B \approx 2$ K, a value appropriate for aluminum,[13] we find $C \approx 8.5 \times 10^{-16}$ F, or, using $C = \epsilon L$ with $\epsilon \approx 8$ (appropriate for alumina), $L \approx 9500$ Å (which is still less than ξ_{GL} for Al), $E_J \approx 3.08 \times 10^{-5}$ eV, and $\rho \approx 1.75\ \Omega$ cm. Because we have chosen $E_c = 6E_J$, quantum effects will be non-negligible in this model, tending to suppress T_{c1}; indeed $T_{\mathrm{Einstein}} = \hbar\omega_{\max}/k_B \approx 8T_{c1}$. However, the essential physics of the transition should remain, as we will discuss. We can also note that the modes responsible for carrying much of the heat are the long wavelength, low frequency ones, which effectively have a much lower T_{Einstein}. Disorder in grain sizes is always present to some extent. Therefore, disorder is introduced into the charging energies, which are taken to be $E_c^k = E_c^0(1 \pm 0.5r)$, where r is a uniformly distributed random variable between 1 and 0 and $E_c^0 = e^2/\epsilon L$. The Josephson coupling energies are assumed to be equivalent.

The expression for κ put forward by Peierls[15] is often the starting point from which an investigation into this quantity is begun. That theory is valid for weak scattering of the propagating excitations and is useful in many circumstances. In particular, it is valid for 3D structurally ordered GS well below the phase-locking transition. Since we are interested in the behavior of the disordered (thermodynamic) phase, as well as the effects of disorder in the grain sizes, we make use of the Green-Kubo theory as implemented through molecular dynamics, as well as Kubo theory. These theories require a heat current or heat current operator. Hardy[16] wrote the general form of the heat flux operator for a crystal. It depends on the local degrees of freedom, requires an assumption as to the division of energy among atoms, and can be expressed in terms of diagonal as well as off-diagonal elements with respect to the energy excitations. Allen and Feldman[17] gave a treatment for κ in the harmonic approximation within a Kubo theory using a simple extension of the Hardy expression. They applied it to amorphous silicon models and found good agreement with experiment. Ladd *et al.*[18] compared homogeneous nonequilibrium and equilibrium molecular dynamics (Green-Kubo theory), and Boltzmann-Peierls theory, in an investigation of the lattice thermal conductivity of a Lennard-Jones crystal. They found the latter two methods to be the most useful and in agreement with each other. In addition, their results showed little dependence on the size of the unit cell.

We now derive the expression for the heat current operator for this model, from which one may calculate κ. Following Hardy,[16] one takes $H(x) = \sum_k \Delta(x - q_k)\hat{H}_k$, where $\Delta(x - q_k)$ is a localizing function which is $\neq 0$ for $x \approx q_k$, and 0 otherwise. Using $\dot{H}(x) + \nabla \cdot \vec{s}(x) = 0$, and $\dot{H}(x) = [H(x), \hat{H}]/i\hbar$, we have $\nabla \cdot \vec{s}(x) = i[H(x), \hat{H}]/\hbar$, where $\vec{s}(x)$ is the local energy flux density operator, and $H(x)$ is the energy density operator. Note that $[\hat{H}, \Delta(x - q_k)] = 0$, as ϕ_k and $\partial/\partial\phi_k$ commute with all spatial variables. The consequence of this is that there is no mass transport term—the term that plays a dominant role in energy transport in the liquid state. In addition, it is worth remarking that for an ordinary liquid there may be an average mass flow which would give rise to an energy current that should not be included in the heat current. As in the ordinary solid state problem,[16] this does not occur and the energy current that we consider is equivalent to a heat current. We find for the energy (or heat) flux operator,

$$\vec{S} = \int d\Omega s(x) = \frac{L}{i\hbar}\sum_{k,l} E_J^{(k,k+l)} E_c^{(k)} \hat{n}_{k,k+l} \sin(\phi_k - \phi_{k+l})\partial/\partial\phi_k, \quad (2)$$

where $l + k$ labels a nearest neighbor of k and $\hat{n}_{k,k+l}$ is a unit vector joining nearest neighbors.

After writing $\hat{H}$ and the heat current operator in the harmonic approximation, one can write the (applied) frequency-dependent thermal conductivity as a sum over normal modes.[17] We will refer to this calculation as the lattice dynamics (LD) approach (please see Ref. 19 for details). This calculation in the high-temperature limit yields κ due only to the imposed disorder. Localization of harmonic modes is probably not an important consideration in this 3D model, although it could be of great importance in 2D ones. We have made a limited study of localization through the inverse participation function and find, as expected, that the uppermost frequency modes appear to be localized.

Our results for this model are summarized in Fig. 1, where the temperature dependence of κ is plotted for two cell sizes, $N = 6$ and $N = 9$. The parameter η in our approximation to $\delta(\omega) = \eta/\pi(\eta^2 + \omega^2)$ is taken to be 1.08×10^{-3} ps^{-1} for $N = 6$, and 3.2×10^{-4} ps^{-1} for $N = 9$. A strong size dependence is evident here. The origin of this problem is contained in the behavior of the harmonic diffusivity at low ω, which will obey a Rayleigh law, $D(\omega) \approx \omega^{-4}$. It is therefore necessary to include some additional scattering process for these modes, i.e., anharmonicity, two-level states as in glasses, or boundary scattering as in crystals, if a finite thermal conductivity is to be observed.[20]

In addition to the effect of disorder on the thermal conductivity, anharmonicity should also be considered. For this purpose, molecular dynamics (MD) is ideally suited as it can easily include anharmonicity to all orders.

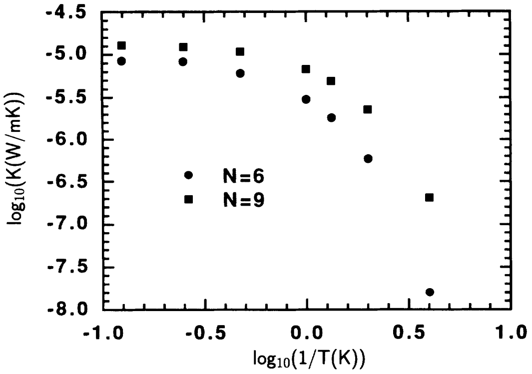

FIG. 1. Comparison of results for κ calculated using Kubo theory in the harmonic approximation for an $N = 6$ and an $N = 9$ unit cell. The finite size errors are evident in this plot and result from the longer wavelength modes available for carrying heat in the latter case.

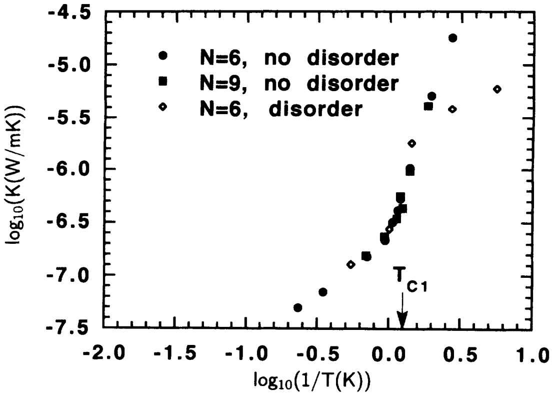

FIG. 2. $\log_{10}(\kappa)$ vs $\log_{10}(1/T)$ calculated using classical MD and Green-Kubo theory. Above T_{c1}, where $\log_{10}(1/T_{c1}) = 0.102$, the data fall onto the expected straight line. There is a weak size dependence at $T = T_{c1}$ which is too small to be seen on this plot.

Also, we may observe the effect of the phase transition in this way. Next, we present results of MD calculations of the thermal conductivity for the Hamiltonian shown in Eq. (1) using Green-Kubo theory, both with and without disorder. The classical equations of motion are written using the canonical momentum, $p_i = m_i\dot{\phi}_i$, and "mass," $m_i = \hbar^2 C/4e^2$. The average heat current in the classical limit for our problem can be extracted from Ref. 21 as well as from the classical analog of our previous discussion, and is $\vec{S}^{\rm cl}(t) = \sum_{m>n} F_{mn}(v_m + v_n)\vec{r}_{mn}/2$, where $F_{mn} = E_J^{(mn)} \sin(\phi_m - \phi_n)$, $v_m = \dot{\phi}_m$, and $\vec{r}_{mn} = L\hat{n}_{mn}$ for m, n nearest neighbors and 0 otherwise. The thermal conductivity is then given by[22] $\kappa_{\alpha,\beta}(\omega)Vk_BT^2 = \int_0^\infty \langle S_\alpha^{\rm cl}(t)S_\beta^{\rm cl}(0)\rangle \cos(\omega t)dt$.

Standard classical molecular dynamics methods have been used. We have averaged all results presented here over two sets of independent, random, initial conditions, as well as over the three Cartesian coordinates. The time step chosen was $t_0/100$, where t_0 is a typical oscillation time. We used a minimum of 50 000 time steps for thermalization, and then an additional 180 000 time steps during which the correlation functions were calculated. The accuracy was chosen so that the variation in energy over the time of the simulation was $\langle(\Delta E)^2\rangle^{1/2} \lesssim 1 \times 10^{-6} E_{\rm av}$.

In Fig. 2 we summarize the results of the simulations. The logarithm of κ is plotted vs $\log_{10}(1/T)$ both with and without disorder in the charging energies, and for the cell sizes $N = 6$ and $N = 9$. Two observations may be made immediately. First, the size effect is significantly reduced here. The anharmonicity dominates over the disorder at these temperatures, and renders the long wavelength modes ineffective carriers of heat. The second observation is that the disorder does not affect the thermal conductivity above the order-disorder phase transition. For temperatures below T_{c1}, however, the effects of disorder can clearly be seen in the reduction in κ. In this phase-locked regime, the anharmonicity plays a less dominant role, the disorder now contributing noticeably to the thermal resistance. Note that the charging energies used here are the same as those used in the lattice dynamics calculations.

The different temperature dependences observed in Figs. 1 and 2 are the result of the scattering mechanisms being considered in the two calculations. In the former, the temperature dependence of the phonon occupation numbers results in a strong increase in the thermal conductivity with increasing temperature; whereas, in the latter calculation, the anharmonicity causes the thermal conductivity to decrease with increasing temperature.

We have also calculated the electrical conductivity vs T and N for this model. Our results are indistinguishable from those presented in Ref. 2.

We find that the high-temperature LD results agree reasonably well with low-temperature MD results. This is so because at high temperatures the phonon occupation numbers which enter into the expression for κ in the LD formalism are equivalent to those in the fully classical MD simulations, and the anharmonicity in the low-temperature MD results is small.

The order of magnitude of κ for this model is fairly low but still may be of significance for actual GS. The lattice phonon contribution is therefore expected to dominate the experimental situation. However, strong evidence of the order-disorder transition is found in κ. A one order of magnitude change in κ at T_{c1} encourages us that this may be observed experimentally if a dielectric with a small enough phonon contribution could be found. We believe the cause of this large increase to be the lack of a third-order anharmonic term in the potential. It is interesting to note that a scalar variable interacting in a material with cubic symmetry will result in a dispersion curve with only one acoustic branch. In this case, following Peierls,[23] no cubic anharmonic processes can take place. Therefore, although this system has very little entropy, there is also very little scattering, resulting in a large increase in κ below T_{c1}.

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[1] See, e.g., B. Abeles, R.W. Cohen, and G.W. Cullen, Phys. Rev. Lett. **17**, 632 (1966); A. Davidson and M. Tinkham, Phys. Rev. B **13**, 3261 (1976).

[2] Z.Q. Wang and D. Stroud, Phys. Rev. B **44**, 9643 (1991).

[3] L. Jacobs, J.V. José, M.A. Novotny, and A.M. Goldman, Phys. Rev. B **38**, 4562 (1988).

[4] U. Geigenmüller, C.J. Lobb, and C.B. Whan, Phys. Rev. B **47**, 348 (1993).

[5] P.W. Anderson, in *Lectures on the Many Body Problem*, edited by E.R. Caianello (Academic Press, New York, 1964), Vol. 2, p. 113.

[6] A. Giannelli and C. Giovannella, J. Less Common Met. **164-165**, 1488 (1990).

[7] H.v. Löhneysen, Mater. Sci. Eng. A **133**, 51 (1991).

[8] J.V. José, Phys. Rev. B **29**, 2836 (1984).

[9] R.M. Bradley and S. Doniach, Phys. Rev. B **30**, 1138 (1984).

[10] W.L. McLean and M.J. Stephen, Phys. Rev. B **19**, 5925 (1979).

[11] M. Ferer, M.A. Moore, and M. Wortis, Phys. Rev. B **8**, 5205 (1973).

[12] V. Ambegaokar and A. Baratoff, Phys. Rev. Lett. **10**, 486 (1963); **11**, 104 (1963).

[13] P.G. de Gennes, *Superconductivity of Metals and Alloys* (W.A. Benjamin, Inc., New York, 1966), p. 10.

[14] E. Šimánek, Phys. Rev. B **22**, 459 (1980).

[15] R.E. Peierls, Ann. Phys. (Leipzig) **3**, 1055 (1929).

[16] R.J. Hardy, Phys. Rev. **132**, 168 (1963).

[17] P.B. Allen and J.L. Feldman, Phys. Rev. Lett. **62**, 645 (1989).

[18] A.J.C. Ladd, B. Moran, and W.G. Hoover, Phys. Rev. B **34**, 5058 (1986).

[19] P.B. Allen and J.L. Feldman Phys. Rev. B **48**, 12 581 (1993); J.L. Feldman *et al.*, Phys. Rev. B **48**, 12 589 (1993).

[20] J.K. Flicker and P.L. Leath, Phys. Rev. B **7**, 2296 (1973).

[21] J.H. Irving and J.G. Kirkwood, J. Chem. Phys. **18**, 817 (1950).

[22] Y.H. Lee, R. Biswas, C.M. Soukoulis, C.W. Wang, C.T. Chan, and K.M. Ho, Phys. Rev. B **43**, 6573 (1991).

[23] R.E. Peierls, *Quantum Theory of Solids* (Clarendon, Oxford, 1956), p. 40.