

Heat flow through an insulating nanocrystal

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(Received 29 September 1999)

We calculate the low temperature, quantum mechanical rate of heat flow through a nanocrystal due to phonon transport by solving a many-body Schrödinger equation for oscillators in Fermi resonance. By analogy to Raman scattering through molecules, we find that normal processes due to anharmonicity of the nanocrystal give rise, over an intermediate range of lengths, to a largely length-independent thermal conductivity that resembles Fourier's law, but is in fact of a different origin. For longer crystals conductivity rises with length, as predicted for a harmonic solid. For shorter nanocrystals thermal conductivity also rises with length, followed by a turnover regime in which thermal conductivity is size specific.

PACS number(s): 63.22.+m, 44.10.+i, 61.46.+w, 85.30.Vw

I. INTRODUCTION

Recent progress in the direct measurement of heat conduction by phonons through suspended nanostructures [1], which may permit calorimetry at the level of individual phonons ("yoctocalorimetry") [2], has generated renewed interest and activity in the quantum mechanical theory of the thermal conductivity of electrical insulators [3–5]. Theory has focused on calculation of the thermal conductance by drawing on analogies to electrical transmission through confined geometries pioneered by Landauer [6]. Both adiabatic and nonadiabatic regimes have been addressed, where the latter treats reflection of phonons related to the specific geometry of the bridge-reservoir interface. Theoretical work on the quantum mechanical thermal conductance through a narrow bridge has hereto treated the modes of the bridge as harmonic. As a result, the thermal conductivity diverges as the length of the bridge increases. In this article, we show that anharmonicity modifies heat flow in a nanocrystal and, over a range of lengths, leads to a nearly length-independent low temperature thermal conductivity that is apparently consistent with the Fourier heat law.

The system through which heat is conducted is depicted in Fig. 1. A nanocrystal bridging two reservoirs at slightly different temperatures transmits heat between the reservoirs as phonons enter or leave. As in the nonadiabatic models considered earlier [3,4], phonons are reflected at the interface of the reservoir and nanocrystal. The nanocrystal thus acts effectively as a "quantum dot" or cluster through which phonons pass. We can expect the thermal conductivity of the nanocrystal to depend sensitively on its size, as do thermodynamic [7] and electrical transport [8] properties of clusters, and indeed we observe regimes of strong size dependence in the calculations we present below. As in earlier models [3–5], we take the reservoirs to be effectively two-dimensional objects and assume, as in earlier work [3–5], an effectively one-dimensional nanocrystal, consistent with the experimental device described in Ref. [1]. Since our focus is on phonon-phonon scattering due to anharmonicity and its effect on thermal conductivity through the nanocrystal, we assume a perfect nanocrystal, with no diffuse scattering from

asperities along its edges or impurities within it.

The role of anharmonicity in thermal conductivity of a macroscopic object was clarified by Peierls long ago [9]. Phonon scattering through umklapp processes thermalizes the phonons locally along the macroscopic conductor, thus providing a mechanism for resistance that is otherwise absent in the harmonic approximation. At low temperatures, however, umklapp collisions become exponentially rare, and scattering from imperfections on the surface or in the conductor become the predominant means of thermal resistance [10]. In the model we consider, depicted in Fig. 1, phonons conduct heat through a finite-size object at low temperature. Phonon scattering occurs through the so-called normal processes rather than umklapp processes, but these, as we show below, can still affect thermal conduction in a finite system. At the interface of the nanocrystal and reservoir some phonons are reflected, and, as seen below, the degree of reflection or transmission, i.e., the tunneling probability, depends on the mode frequencies of the nanocrystal; if a high-frequency phonon scatters normally into two low frequency phonons via cubic anharmonic coupling, the rate of heat transmitted to the lower temperature reservoir is not the same as had no scattering occurred.

We address the nature of heat transfer through a quantum mechanical nanocrystal by solving a many-body Schrödinger equation for many oscillators, each representing a normal mode of the nanocrystal, in Fermi resonance. We restrict

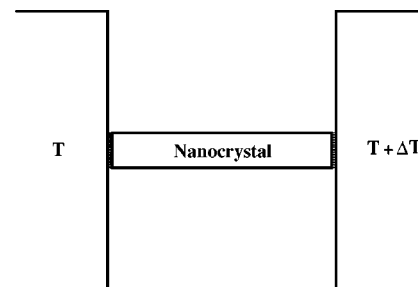


FIG. 1. Schematic illustration of a nanocrystal bridging two 2D thermal reservoirs. The length of the nanocrystal is assumed much greater than its width. The reservoir on the right is at a temperature higher by ΔT .

ourselves to low temperatures, of order 1 K. At low temperature normal processes are the predominant means for phonon-phonon scattering in a perfect crystal. This both simplifies our quantum mechanical calculations and allows us to examine if normal processes, which in macroscopic crystals have at most a very small effect on thermal conduction owing to momentum conservation [11,12], might have a greater influence on heat flow through finite systems. Detailed experimental study of these effects at low temperatures is now beginning to become possible [1,2]. Classical heat transfer through finite systems at low temperatures [13–20], including investigation of the specific role of anharmonicity on thermal conduction, has already received a great deal of attention, but corresponding quantum mechanical studies of heat flow in mesoscopic systems have not been extensive. The classical studies aimed at elucidating the necessary and sufficient conditions for heat transfer to follow Fourier's law. In fact such studies have shown anomalous transport connected to boundary effects. We shall comment briefly on some of these studies at the end of this article.

We make use of a correspondence between quantum mechanical heat flow through a nanocrystal and the calculation of Raman scattering of photons by a molecule. In a Raman process [21,22], a molecule absorbs and then emits photons, while thermal conduction arises from phonons absorbed and emitted by the nanocrystal. The rate of scattering through a molecule depends sensitively on the rate of energy redistribution within the molecule on the time scale of the Raman process, which results from anharmonic coupling among molecular vibrations. Likewise, anharmonicity may redistribute phononic energy absorbed by the nanocrystal among its modes. The rate of energy redistribution arising from phonon scattering within the nanocrystal ultimately affects the thermal conductivity, just as the rate of vibrational energy redistribution affects the Raman scattering of a molecule. We therefore compute the rate of energy redistribution in the nanocrystal due to anharmonicity as part of calculating its thermal conductivity. We find that, due to both normal scattering and the nanocrystal-reservoir interactions, there is a range of nanocrystal lengths over which compliance with Fourier's law is apparent.

II. THERMAL CONDUCTIVITY OF NANOCRYSTAL

We define the system of a nanocrystal coupled to reservoirs illustrated in Fig. 1 by the Hamiltonian $H = H_0 + H_1$. The zero-order Hamiltonian is taken to be harmonic,

$$H_0 = \sum_r \hbar \omega_r a_r^\dagger a_r + \sum_l \hbar \omega_l a_l^\dagger a_l + \sum_q \hbar \omega_q a_q^\dagger a_q, \quad (1)$$

where ω is a mode frequency and a the number operator of modes r , l and q , which label modes of the right and left reservoirs, and the nanocrystal, respectively. The interaction Hamiltonian is

$$H_1 = H_{RQ} + H_{LQ} + H_{NC}, \quad (2)$$

where these terms describe the interaction between the right reservoir and nanocrystal, the left reservoir and nanocrystal, and the anharmonic couplings within the nanocrystal, respectively. We define

$$H_{RQ} = \sum_{r,q} t_{rq} a_r^\dagger a_q + \text{H.c.}, \quad (3a)$$

$$H_{LQ} = \sum_{l,q} t_{lq} a_l^\dagger a_q + \text{H.c.}, \quad (3b)$$

$$H_{NC} = \sum_{q,q',q''} u_{q,q',q''} (a_q^\dagger + a_q)(a_{q'}^\dagger + a_{q'})(a_{q''}^\dagger + a_{q''}). \quad (3c)$$

We assume the contribution of higher order anharmonic coupling terms to the rate of energy redistribution within the nanocrystal is relatively small at low temperature, as is the case for large molecules [23].

We first evaluate the rate of energy transfer from the higher temperature to the lower temperature reservoir through the nanocrystal, which we write as

$$H^+ = \int d\omega_r \rho(\omega_r) \hbar \omega_r \Gamma_r. \quad (4)$$

The energy transfer rate through the nanocrystal in the other direction is H^- , expressed by replacing r by l . From the energy transfer rate through the nanocrystal we obtain the thermal conductivity as

$$\kappa = L(H^+ - H^-)/\Delta T, \quad (5)$$

where ΔT is the difference in the temperatures of the reservoirs, and L is the length of the nanocrystal. We calculate the rate of heat transfer using the golden rule since we assume that, due to constrictions or physical separation at the reservoir-nanocrystal interface, states of the reservoir and nanocrystal are weakly coupled. The rate of decay from the right reservoir to the left one is then

$$\Gamma_r = \sum_l \frac{2\pi}{\hbar^2} |V_{lr}|^2 \rho(\omega_l), \quad (6)$$

where V_{lr} , defined below, are matrix elements coupling the two reservoirs via the nanocrystal. In the following we assume for simplicity that the properties of the left and right reservoirs other than the temperature are identical, so that the mode densities, $\rho(\omega)$, of both reservoirs at the same mode frequency are the same. We use the Debye approximation for the mode density of the two-dimensional reservoirs,

$$\rho(\omega) = \beta \omega, \quad (7)$$

where β depends on the volume of and speed of sound through the reservoirs.

We calculate the coupling matrix elements in Eq. (6) by analogy to the theory of Raman scattering. For the system defined above

$$|V_{lr}|^2 = \hbar^{-2} \left| \sum_q \sum_{n_q} \frac{(\bar{n}_l + 1)^{1/2} (n_q + 1) \bar{n}_r^{1/2} t_{lq} t_{qr}}{\omega - \omega_q + i\gamma_q} \right|^2. \quad (8)$$

In Eq. (8), n_l , n_r and n_q are the occupation numbers of modes, l , r , and q , respectively, belonging respectively to the left and right reservoirs, and the nanocrystal; \bar{n} denotes most

probable value, calculated with the Planck distribution. The coefficients t_{rq} and t_{lq} account for the linear coupling between the atoms at the ends of the reservoirs and nanocrystal. If the mass-weighted normal coordinates contain contributions from each internal coordinate of the system [24], t_{rq} and t_{lq} scale as the square root of the product of the frequencies of the coupled modes,

$$t_{lq} = \alpha N^{-1/2} \hbar (\omega_l \omega_q)^{1/2}, \quad (9)$$

where N is the number of atoms along the length of the nanocrystal. We assume the dimensionless coefficient α has been calculated for a particular system.

The imaginary part γ_q in Eq. (8) corresponds to the decay rate from states containing n_q phonons in mode q . There are two contributions to this decay. There is decay due to coupling of the nanocrystal modes to the reservoirs $\gamma_q^{(h)}$ and there is decay $\gamma_q^{(\text{anh})}$, due to phonon scattering in the nanocrystal caused by the anharmonic terms of H_1 . We assume for simplicity that the line widths of the nanocrystal levels are sufficiently narrow so that $\gamma_q + \gamma_{q'} \ll \omega_q - \omega_{q'}$, $q \neq q'$, which can always be realized by making α sufficiently small. In the absence of anharmonicity, we note that if this condition holds for one N it holds for any other, since $\gamma_q^{(h)}$ varies as N^{-1} (see below). We discuss the limit of overlapping resonances at the end of Sec. III. We are then left with integrating Eq. (4) to calculate the energy transfer rate from the higher temperature reservoir to the lower temperature reservoir through the nanocrystal.

Let us consider first the harmonic case, i.e., $H_1 = H_{RQ} + H_{LQ}$. Upon integration of Eq. (4) and thermally averaging n_q , we find

$$H_h^+ = \frac{\pi}{\hbar^3} \frac{\alpha^2 \beta}{N} \sum_q \bar{n}_r(\omega_q) [\bar{n}_l(\omega_q) + 1] (\hbar \omega_q)^4, \quad (10)$$

where h denotes harmonic. In the limit $\Delta T \rightarrow 0$, the thermal conductivity is $\kappa_h = L dH^+ / dT$. Writing $x_q = \hbar \omega_q / k_B T$ and $L = aN$, where a is the interatomic spacing,

$$\kappa_h = \frac{\pi \alpha^2 \beta a}{\hbar^3} k_B^4 T^3 \sum_q \frac{x_q^5 e^{x_q} (e^{x_q} + 1)}{(e^{x_q} - 1)^3}, \quad (11)$$

where k_B is the Boltzmann constant. The mode frequencies of the nanocrystal at low temperature can be assumed to vary as $\omega_q = \sqrt{c^2 k_q^2 + \omega_m^2}$, where c is the speed of sound, k_q is the wave vector of mode q , and m labels a waveguide mode of the narrow nanocrystal. At sufficiently low temperatures, only the lowest waveguide mode, $m=0$, contributes significantly to the thermal conductivity of a narrow structure [3–5] like the nanocrystal in Fig. 1; since $\omega_0 = 0$, $\omega_q = ck_q$. The dispersion could also be nonlinear (see below). By approximating the sum as an integral, $\sum_x \rightarrow \int dx \rho_x(x)$, where $\rho_x(x_q) \approx NT / \pi \Theta_D$ in the Debye approximation and Θ_D is the Debye temperature, we have

$$\kappa_h \approx \frac{5! \alpha^2 \beta a}{\hbar^3 \Theta_D} N k_B^4 T^4. \quad (12)$$

The numerical constant $5!$ is obtained by taking $\int dx [x^5 e^x (e^x + 1) / (e^x - 1)^3] \approx \int dx x^5 e^{-x}$ with limits from 0

to ∞ , which is justified at low temperature. We thus find that the thermal conductivity in the harmonic limit varies as $\kappa_h \sim NT^4$, in agreement with the temperature scaling for the low temperature, nonadiabatic thermal conductance derived by Angelescu, Cross, and Roukes [3]. As expected the thermal conductivity diverges in the harmonic limit.

We now include in the imaginary part, γ_q , of Eq. (8) the contribution due to energy redistribution within the nanocrystal, so that $\gamma_q = \gamma_q^{(h)} + \gamma_q^{(\text{anh})}$, where the latter term accounts for anharmonicity in the nanocrystal. In this case, upon integration of Eq. (4),

$$H^+ = \frac{2\pi^2}{\hbar^4} \frac{\alpha^4}{N^2} \times \sum_{q, n_q} \frac{\bar{n}_r(\omega_q) [\bar{n}_l(\omega_q) + 1] (n_q + 1)^2 (\hbar \omega_q)^5 \rho^2(\omega_q)}{\gamma_q^{(h)} + \gamma_q^{(\text{anh})}}. \quad (13)$$

Each term in the sum is given a Boltzmann weight in calculating the thermally averaged rate of energy transfer. $\gamma_q = (2\pi / \hbar^2) \sum_l |V_{lq}|^2 \rho(\omega_q)$, where V_{lq} are the matrix elements connecting states of the nanocrystal with n_q phonons in mode q with states of the (equivalent) reservoirs. Upon evaluation of the matrix elements, we find

$$\gamma_q^{(h)} = \frac{2\pi}{\hbar^3} \frac{\alpha^2 \beta}{N} (\hbar \omega_q)^3 (n_q + 1) [\bar{n}_l(\omega_q) + 1]. \quad (14)$$

To calculate the rate of energy transfer, we still need to compute the energy redistribution rate $\gamma_q^{(\text{anh})}$, due to anharmonic coupling, for states with n_q phonons in mode q . We thus need to estimate the size of the cubic coupling constants $u_{q,q',q''}$, that appear in the definition of H_1 , which vary as [24,25]

$$u_{q,q',q''} = RN^{-1/2} (\omega_q \omega_{q'} \omega_{q''})^{1/2} \delta(k_q + k_{q'} + k_{q''}). \quad (15)$$

Since we focus on low temperatures umklapp processes, which are exponentially rare, have been neglected. In molecules R is of the order 10^{-3} when the coupling matrix elements are expressed in units of K; we used $R = 2 \times 10^{-3}$ in our calculations.

In principle, a very large network of harmonic states of the nanocrystal are coupled together, even if we only consider cubic anharmonic terms. In practice, only relatively few of these states mix strongly, and we need only consider the subset of states that participate significantly in energy redistribution. The search for such states is a common problem faced in the computational study of vibrational energy redistribution in molecules, and is routinely performed by Artificial Intelligence algorithms, which are extensively discussed in Ref. [26]. We adopt this approach to calculate the effective subset of states that participate in energy redistribution in the nanocrystal. Briefly, starting with a state with n_q phonons in mode q , we search for the subset of states coupled by the anharmonic terms strongly enough and sufficiently close in energy, as determined by a cutoff criterion, then repeat this process iteratively to identify the network of states that form the basis of the reduced nanocrystal Hamil-

tonian. We also require that the average coupling times the average density of resonantly coupled states is of order 1, a necessary criterion for quantum mechanical energy flow in a finite coupled nonlinear oscillator system [23,27]. We then diagonalize the reduced Hamiltonian and determine $\gamma_q^{(\text{anh})}$ from the line width of the resulting spectrum. We compute $\gamma_q^{(\text{anh})}$ for each q and n_q , averaging over the phonons in all other modes, giving each combination a Boltzmann weight. Values of $\gamma_q^{(\text{anh})}$ are then introduced into Eq. (13), and the average rates of energy transfer are calculated. Finally, the thermal conductivity is obtained as $L(H^+ - H^-)/\Delta T$.

III. RESULTS AND DISCUSSION

We turn now to calculation of the quantum mechanical thermal conductivity through a nanocrystal bridging two reservoirs. Since we focus on low temperatures we assume, as discussed above, that only the lowest waveguide mode contributes to the thermal conductivity. We take the harmonic frequencies of the nanocrystal to follow the dispersion relation, $\omega_q = c'|\sin(ak_q/2)|$. We use $k_B c'/\hbar = 625$ K in our calculations, which is representative of Si. Values of k_q are discrete and spaced by $2\pi/Na$, where N is the number of atoms along the length of the crystal, and a the atomic spacing. We set the dimensionless coupling parameter in Eq. (9) to $\alpha = 1.4 \times 10^{-3}$ and set $\beta = 1$ in our definition of the reservoir mode density given by Eq. (7). We then calculate the thermal conductivity, κ , using both the harmonic and anharmonic Hamiltonians for nanocrystals ranging in length from 100 to 1200 atoms. The result for κ in the harmonic limit is given by Eq. (11), and the complete result including nanocrystal anharmonicity is computed as described at the end of the previous section. The thermal conductivity is plotted in Fig. 2, where we express κ in units of $\pi\alpha^2\beta ak_B^4/\hbar^3$; in these units the harmonic limit, κ_h , is independent of system specific parameters α , β , and a .

In Fig. 2(a) we plot the thermal conductivity κ at temperatures $T=1.0, 1.5, 1.7,$ and 2.0 K. Size specific effects leading to fluctuations in κ are apparent, particularly at 2.0 K. At each temperature the thermal conductivity follows predictions of the harmonic limit at smaller N , then, with the onset of energy redistribution and its increasing rate with larger N , κ turns over and is approximately constant by $N \approx 1000$ or roughly the 100 nm scale for these parameters. The turnover regime is clearly broader at smaller T . In Fig. 2(b) we compare κ with κ_h at $T=2.5$ K. Again, size dependence resulting in fluctuation of κ with N is apparent, while on average κ becomes independent of N with larger N , apparently consistent with Fourier's law, despite the absence of umklapp processes or diffuse scattering at the boundaries.

Normal scattering due to anharmonicity of the nanocrystal apparently affects thermal conductivity, giving rise to a regime where κ appears to be length-independent. Normal processes can affect κ because the rate of emission of phonons from the nanocrystal $\gamma^{(h)}$ depends on the frequencies and occupation numbers of the nanocrystal modes, as seen from Eq. (14). When the redistribution rate $\gamma^{(\text{anh})}$ of phonons within the nanocrystal is faster than the emission rate, the energy transfer rate from one reservoir to the other is affected. The energy transfer rate apparently varies as $1/N$ in

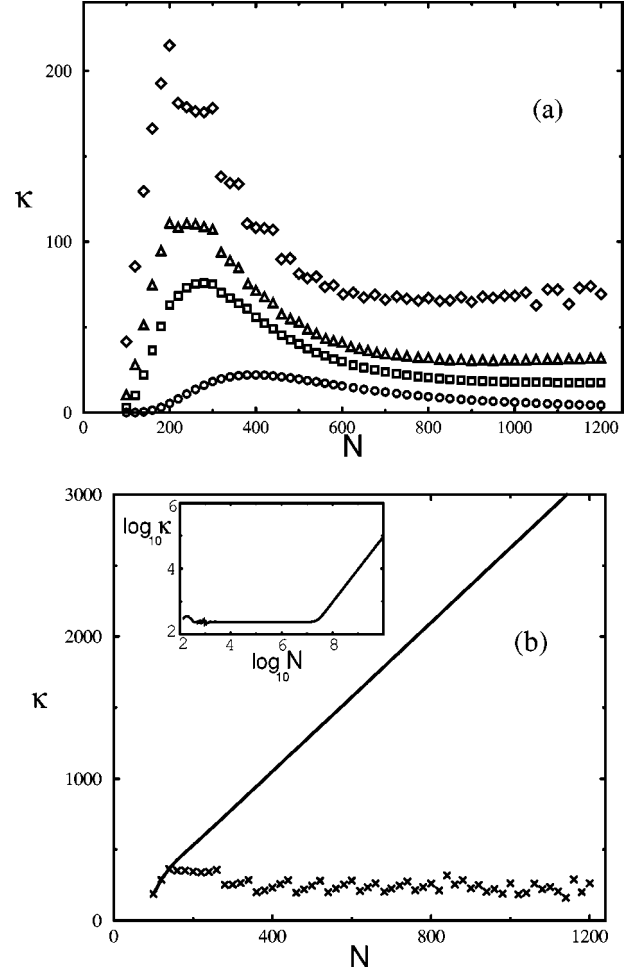


FIG. 2. (a) Thermal conductivity κ in units of $\pi\alpha^2\beta ak_B^4/\hbar^3$, as a function of length N at $T=1.0$ K (circles), 1.5 K (triangles), 1.7 K (squares), and 2.0 K (diamonds); (b) comparison of κ including anharmonicity (X) at $T=2.5$ K with the harmonic result (curve). The insert in (b) shows κ calculated for the anharmonic nanocrystal ultimately rising with N at large N .

this regime, giving rise to a thermal conductivity that does not vary with N .

The apparent independence of the thermal conductivity on the length of the nanocrystal would seem to indicate conformity to Fourier's law. However, the argument that normal scattering affects thermal conduction by redistributing phonons in the nanocrystal cannot be stretched to arbitrarily long crystals. For much longer crystals, redistribution of phonons by normal scattering is essentially complete following absorption; additional phonon-phonon scattering occurring within a longer crystal no longer affects the distribution of phonons that it emits. We show in the Appendix that this limit occurs when the resonances of the nanocrystal overlap. We note that in the harmonic limit, as discussed above, if the energy levels of the nanocrystal are resolvable at any given length of the nanocrystal, due to sufficiently weak coupling to the reservoirs, then they remain resolvable for any nanocrystal length. This is no longer the case for the anharmonic nanocrystal. Resonances will ultimately overlap as the nanocrystal grows. In the resonance-overlap limit, in the absence of umklapp processes, we find that κ rises with N , as shown in the Appendix. In this limit, we find

$$\kappa = \frac{\alpha^4 \beta^2 a k_B^6}{\hbar^5 \Theta_D^2} C N T^7, \quad (16)$$

where Θ_D is the Debye temperature and $C \approx 315\pi^2$. Using the limiting value for κ at sufficiently large N given by Eq. (16), we plot κ at $T = 2.5$ K in Fig. 2(b) over a wide range of N .

Normal scattering of phonons due to anharmonicity no longer significantly affects the energy transport rate through the nanocrystal when its length is sufficient for phonons entering from one reservoir to redistribute before reaching the other side. When the nanocrystal is this long, redistribution will have occurred before any phonon can be emitted. The traversal time across the nanocrystal is L/c , where L is the nanocrystal length and c is the speed of sound. The redistribution time is of order $1/\gamma^{(\text{anh})}$. Since c/L is of the order of the spacing of nanocrystal levels, resonance overlap occurs when $\gamma^{(\text{anh})} > c/L$. We thus indeed expect, as found in the Appendix, that the effect of normal scattering on heat transfer between the reservoirs, or thermal conductivity of the nanocrystal, is dramatically reduced upon increasing the length of the nanocrystal beyond that where the nanocrystal resonances begin to overlap. Ultimately, in the macroscopic limit and with only normal scattering, the thermal conductivity diverges with N , as it must [9,11,12].

IV. CONCLUDING REMARKS

We find the thermal conductivity of a low temperature nanocrystal coupled weakly to two thermal reservoirs apparently conforms to Fourier's heat law over a range of lengths due only to normal phonon-phonon scattering arising from anharmonicity. Redistribution of phonons within the nanocrystal by normal scattering following absorption affects the emission rate, reducing the rate of energy flow from the higher temperature reservoir to the lower as the length of the nanocrystal increases.

When the nanocrystal is so small that anharmonic effects at low temperature have no effect on heat flow, the thermal conductivity rises with the length of the nanocrystal, as expected for a harmonic system. The onset of the apparent Fourier heat law regime occurs about where the redistribution rate of phonons due to normal scattering is the same as the emission rate for phonons to tunnel out of the nanocrystal to the reservoirs. As the onset is approached, the thermal conductivity appears to fluctuate with nanocrystal size, then turns over to a regime in length where it appears length independent. Phonon redistribution by normal scattering ceases to affect the energy transfer rate from the high temperature reservoir to the low temperature reservoir when the scattering rate is so high that any phonon absorbed by the nanocrystal has sufficient time to scatter before reaching the other end. In this case, roughly where the resonances of the nanocrystal begin to overlap, the rate of heat transfer through the nanocrystal no longer varies with increasing crystal length, and the thermal conductivity diverges with length. This picture could change if, even assuming no asperities or other imperfections, we account for umklapp processes [9,12], which we have neglected in the low-temperature calculations presented in this article.

There have been numerous calculations of heat transfer by

phonons through classical one-dimensional objects [13–19]. These include calculations on harmonic chains with random impurities [13,14], anharmonic chains [13,15,16,19], and special quasi-one-dimensional models that have no obvious physical basis [17,18]. One long-standing puzzle since the early theoretical and computational studies of such a wide range of models has been the difficulty of extracting Fourier's heat law from the classical analysis of relatively simple systems. Though certain special models that exhibit strong chaos do, through numerical analysis [16–18], appear to exhibit Fourier's heat law, the study of models of chains of nonlinear oscillators coupled to thermal baths, even if chaotic, fail to yield a convergent thermal conductivity [15]. A recent numerical study [19] of heat flow through a classical nonlinear chain of order 10^2 atoms bridging two lattice reservoirs found that some forms for the chain-lattice interactions might give rise to a convergent thermal conductivity. Our analysis of quantum mechanical thermal conduction through an anharmonic nanocrystal highlights the difficulty of drawing conclusions about convergence of thermal conductivity from a numerical study with chains of 10^2 or 10^3 atoms.

A complete understanding of how Fourier's law of heat transfer through a macroscopic system evolves from a microscopic model still eludes us. We have addressed this problem here with a quantum mechanical study of heat transfer through a finite anharmonic crystal at low temperature. We have, however, restricted our analysis to include only some scattering processes, normal processes, that arise from anharmonicity. These, while very much more probable than umklapp processes at sufficiently low temperatures, ultimately cannot give rise to Fourier's law. We have found, however, an interesting regime of nanocrystal lengths over which the thermal conduction of a small crystal bridging two reservoirs appears to conform to Fourier's law.

ACKNOWLEDGMENTS

D.M.L. thanks A. Buldum and S. Ciraci of Bilkent University, Ankara, Turkey for helpful discussions. This work was supported in part by NSF Grant No. CHE-9530680.

APPENDIX

We provide here details of our calculation of the thermal conductance through a nanocrystal for the case where the energy level line-widths of the nanocrystal overlap. In this limit the line widths of the nanocrystal levels are sufficiently large so that $\gamma_q + \gamma_{q'} > \omega_q - \omega_{q'}$, $q \neq q'$, in which case Eq. (13) no longer gives the rate of heat transfer by phonons. The rate of heat transfer from the right, high temperature reservoir to the left, low temperature reservoir, assuming the reservoirs are otherwise identical, is given by

$$H^+ = \frac{2\pi}{\hbar^2} \int \int d\omega_r d\omega_l \rho(\omega_r) \hbar \omega_r |V_{lr}|^2 \rho^2(\omega_l), \quad (A1)$$

where $\rho(\omega)$ is the mode density of either reservoir at mode frequency ω . In Eq. (A1) we have replaced the sum in Eq. (6) with an integral and inserted this into Eq. (4). We calculate the coupling matrix elements in Eq. (A1) by analogy to

the theory of Raman scattering and resonance fluorescence, the former describing coherent and the latter incoherent absorption and emission of phonons by the nanocrystal bridge. We distinguish the coupling matrix elements accounting for Raman scattering and resonance fluorescence with the subscripts R and F , respectively. Then, since cross terms are negligible [21,22],

$$|V_{lr}|^2 = |V_{lr;R}|^2 + |V_{lr;F}|^2. \quad (\text{A2})$$

The Raman terms are given by

$$|V_{lr;R}|^2 = \hbar^{-2} \left| \sum_q \sum_{n_q} \frac{(\bar{n}_l + 1)^{1/2} (n_q + 1) \bar{n}_r^{1/2} t_{lq} t_{qr}}{\omega - \omega_q + i\gamma_q} \right|^2. \quad (\text{A3})$$

The resonance fluorescence terms are given by

$$|V_{lr;F}|^2 = \hbar^{-4} \left| \sum_{q,n_q} \sum_{m,n_m} \frac{(\bar{n}_l + 1)^{1/2} (n_m + 1)^{1/2} (n_q + 1)^{1/2} \bar{n}_r^{1/2} t_{lm} V_{mq}^{(\text{anh})} t_{qr}}{(\omega - \omega_m + i\gamma_m)(\omega - \omega_q + i\gamma_q)} \right|^2. \quad (\text{A4})$$

As discussed in the text, the linear coupling coefficients t_{lq} are given by $t_{lq} = \alpha N^{-1/2} \hbar(\omega_l \omega_q)^{1/2}$, where N is the number of atoms along the length of the nanocrystal; n_l , n_r , and n_q are the occupation numbers of modes, l , r , and q , respectively, belonging respectively to the left and right reservoirs, and the nanocrystal; \bar{n} denotes most probable value, calculated with the Planck distribution; $V_{mq}^{(\text{anh})}$ is the anharmonic contribution to the coupling between states q and m . We turn first to the contribution of the Raman, and then to the contribution of resonance fluorescence terms to the rate of heat transfer.

Inserting Eq. (A3) into Eq. (A1), we find for the Raman contribution to the heat transfer rate

$$H_R^+ = \frac{2\pi^2}{\hbar^4} \frac{\alpha^4}{N^2} \sum_{q,n_q} \sum_{q',n_{q'}} \frac{\bar{n}_r(\omega_q) [\bar{n}_l(\omega_q) + 1] (n_q + 1) (n_{q'} + \delta_{qq'}) (\hbar\omega_q)^4 \hbar\omega_{q'} \rho^2(\omega_q) (\gamma_q + \gamma_{q'})}{(\omega_q - \omega_{q'})^2 + (\gamma_q + \gamma_{q'})^2}. \quad (\text{A5})$$

Since we assume the resonances of the nanocrystal overlap, we can approximate the sum over q' as an integral, $\sum_{q'} \rightarrow \int d\omega_{q'} \rho_{nc}(\omega_{q'})$. In the Debye approximation, the nanocrystal mode density is $\rho_{nc}(\omega_{q'}) \approx N/\omega_D$, where ω_D is the Debye frequency. For simplicity, and without affecting the scaling of H^+ with N and T , we assume that $n_{q'} \approx n_q$ and $\omega_{q'} \approx \omega_q$ in the integral. Then the Raman contribution to the heat transfer rate becomes

$$H_R^+ = \frac{2\pi^3}{\hbar^4} \frac{\alpha^4}{N\omega_D} \sum_{q,n_q} \bar{n}_r(\omega_q) [\bar{n}_l(\omega_q) + 1] \times (n_q + 1) n_q (\hbar\omega_q)^5 \rho^2(\omega_q), \quad (\text{A6})$$

where we have neglected any terms of order N^{-2} . We approximate the sums over q and n_q as integrals. Then $\sum_q \rightarrow \int dx \rho_x(x_q)$, where $x_q = \hbar\omega_q/k_B T$; and $\sum_{n_q} \rightarrow \int dn_q [e^{-n_q \hbar\omega_q/k_B T}/Z]$, where Z is the partition function. We assume that the mode density of the 2-dimensional reservoirs can be described by the Debye approximation, $\rho = \beta\omega$. For the quasi-one-dimensional nanocrystal, $\rho_x(x_q) \approx NT/\pi\Theta_D$ in the Debye approximation, where Θ_D is the Debye temperature.

The heat transfer rate is then

$$H_R^+ \approx \frac{2\pi^2}{\hbar^6} \frac{\alpha^4 \beta^2}{\omega_D} \frac{k_B^7 T^8}{\Theta_D} \int dx \frac{x^7 e^{2x}}{(e^x - 1)^4}. \quad (\text{A7})$$

Importantly, we see that H^+ is independent of N , as it should be in the absence of unklapp processes. The thermal conductivity from the Raman contribution, $\kappa_R = (Na) dH_R^+/dT$, where Na is the length of the nanocrystal, is then

$$\kappa_R \approx \frac{2\pi^2 \alpha^4 \beta^2 a}{\hbar^5} N \frac{k_B^6 T^7}{\Theta_D^2} \int dx x^8 e^{-2x}, \quad (\text{A8})$$

where we approximated the integral in Eq. (A7) by $\int dx x^7 e^{-2x}$. The integral in Eq. (A8) gives $8!/2^9$ taking the limits of x to be 0 and ∞ , which is justified at low temperature.

The resonance fluorescence contribution to the rate of heat transfer is found upon inserting Eq. (A4) into Eq. (A1),

$$H_F^+ = \frac{4\pi^2}{\hbar^6} \frac{\alpha^4}{N^2} \sum_{q,n_q} \sum_{q',n_{q'}} \sum_{m,n_m} \sum_{m',n_{m'}} \frac{\bar{n}_r(\omega_q) [\bar{n}_l(\omega_q) + 1] (\hbar\omega_q)^4 \hbar\omega_{q'} \rho^2(\omega_q) (\gamma_q + \gamma_{q'}) V_{q'm'}^{(\text{anh})} V_{mq}^{(\text{anh})}}{[(\omega_q - \omega_{q'})^2 + (\gamma_q + \gamma_{q'})^2] (\omega_q - \omega_{q'} + i\gamma_m) (\omega_{q'} - \omega_{m'} - i\gamma_{m'})} \times [(n_q + 1) (n_{q'} + \delta_{qq'}) (n_m + 1) (n_{m'} + \delta_{mm'})]^{1/2}. \quad (\text{A9})$$

The harmonic (natural) linewidth due to coupling of zero-order nanocrystal mode q to the reservoirs is γ_q , while the contribution due to dephasing by the nanocrystal is γ_m . The sums over m and m' can be approximated by integrals, i.e., $\sum_m \rightarrow \pi^{-1} \int d\omega_m [\omega_q - \omega_m + i\gamma_m]^{-1}$, and likewise for m' . We assume for simplicity that $n_q = n_m \approx n_{q'} = n_{m'}$. Then since $\gamma^{(\text{anh})} \approx (\pi/\hbar^2)(|V^{(\text{anh})}|^2/\gamma_m)$, we find that $H_F^+ \approx H_R^+$.

We thus find that the rate of heat transfer due to the coherent Raman process of absorbing and emitting a phonon is the same as the incoherent, resonance fluorescent process, where emission follows dephasing due to anharmonic cou-

pling in the nanocrystal. We can understand this result in the following way. The intensity due to resonant Raman scattering is approximately [22] $I_R \approx Y_{\text{emit}} \Omega_{\text{abs}}$, where Ω_{abs} is the absorption rate and Y_{emit} is the emission probability. The intensity due to resonance fluorescence is approximately [22] $I_F \approx Y_{\text{emit}} Y_{\text{trans}} \Omega_{\text{abs}}$, where Y_{trans} is the probability of pure dephasing before emission. When there is resonance overlap due to anharmonic coupling within the nanocrystal, $Y_{\text{trans}} \approx 1$, so that the coherent and incoherent contributions to the heat transfer rate are about the same. The thermal conductivity is then $\kappa \approx 2\kappa_R$, which is Eq. (16).

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