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Energy transport in glasses due to phonon hopping: Lifetime and ac behavior

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Anharmonic interactions between localized vibrational states and extended low-energy phonons can lead to thermally activated hopping of the localized states. Such a mechanism has been proposed to explain the thermal conductivity behavior of dielectric glasses and amorphous films above the so-called ''plateau temperature,'' i.e., in the high temperature regime. To investigate this transport scenario we derive rate equations for the occupation numbers of the localized states. Extending our previous model, we calculate the lifetimes of localized states and find them to increase with the energy of the state, in accordance with recent experiments as well as with the fracton hopping model (the functional form differs though). This is in contrast to another model for explaining the high temperature behavior of glasses, namely the model of diffusive transport by nonpropagating modes. Furthermore, the latter model predicts a decrease of the conductivity with increasing frequency of an ac temperature gradient. In our hopping model, on the other hand, the conductivity is frequency independent or might even increase. This could provide an additional approach in order to experimentally distinguish between these two models. Moreover, essential differences to electron hopping are discussed, including particle number and energy nonconservation, which would correspond to charge nonconservation in the electron case. These lead to some intricacies which have to be considered in deriving the current theory. [S0163-1829(99)01213-8]

I. INTRODUCTION

Recently, the existing theoretical frameworks to explain the high temperature behavior of heat conductivity in glasses have been reconsidered,[1,2] specifically the fracton hopping model by Orbach *et al.*[3–7] and the model of diffusive transport of nonpropagating modes by Allen and Feldman.[8,9] The debate between these two models centers around the lifetime of high-energy vibrational modes in dependence on the mode frequency. The diffusive transport model predicts a decrease of the lifetime with increasing mode frequency and the hopping model asserts an increasing lifetime. While the diffusive model is supported by simulations on structural *a*-Si models (of up to 4000 atoms to date[10]), as well as large 1D simulations, the hopping model behavior is supported by experimental evidence.[11–14]

To further elaborate on the differences between the hopping and the diffusive model we present calculations based on our hopping model,[15,16] which is — on the one hand — less specific than Orbach's model, in that it considers more or less unspecified localized modes, rather than fractons, but — on the other hand — goes beyond the fracton hopping model, in that it can explain the saturation tendency of the heat conductivity at high temperatures.[15]

We study a system of localized vibrational modes, which anharmonically interact with extended phonons and focus on the localized mode contribution to energy transport due to thermally excited hopping. This transport mechanism is assumed to determine the high temperature (i.e., above the plateau temperature) heat conductivity behavior. In Sec. II the model system is introduced, which differs from the former model of Refs. 15 and 16 in that it allows to incorporate a physically sound decay term, but, since multiphonon processes are neglected, the saturation tendency is absent. Section III briefly explains the nonequilibrium treatment of the extended modes. The rate equations for the occupation numbers of the localized modes are derived in Sec. IV. Section V shows the obtained results concerning the lifetime of the localized modes and the ac behavior of heat conductivity. The parameters are chosen with *a*-Si in mind. We find, as expected, an increase of the lifetime with the localized mode frequency. Another result is the increase of heat conductivity in an ac temperature gradient in the hopping system. This could provide a way to experimentally distinguish between hopping heat transport and the diffusive mechanism proposed by Allen and Feldman.[8,9] Finally, in Sec. VI the essential differences between electron and phonon hopping are discussed.

II. THE MODEL SYSTEM

A. Hamiltonian

We study the behavior of localized vibrational modes (which will be called ''optical phonons,'' irrespective of their origin), which interact anharmonically with extended phonons (which will here be called ''acoustic phonons'') and are subjected to a temperature gradient. The mechanism proper which leads to phonon localization is not explicitly considered. It is assumed that there is a mobility edge ω_c separating the spectrum of extended modes (satisfying $\omega_q < \omega_c$, characterized by the index q and the wave vector $\mathbf{q}$) from the localized modes ($\omega_m > \omega_c$, characterized by the ''site'' index m and the localization center $\mathbf{R}_m$). The highest frequency of the extended phonons is in the following denoted as Debye frequency $\omega_{D'}$. There may or may not be a gap between the frequencies of extended and localized phonons.

The model Hamiltonian

$$H=H_0+H_1+H_2+H_a, \tag{1}$$

is decomposed into the harmonic contribution

$$H_0=\sum_q \hbar\omega_q b_q^\dagger b_q+\sum_m \hbar\omega_m c_m^\dagger c_m \tag{2}$$

and the anharmonic terms of third order in the displacements

$$H_1=\sum_{mqq'} \phi_m^{qq'}(b_q^\dagger+b_{-q})(b_{q'}^\dagger+b_{-q'})(c_m^\dagger+c_m), \tag{3}$$

$$H_2=\sum_{mm'q} \phi_{mm'}^{q}(b_q^\dagger+b_{-q})(c_m^\dagger+c_m)(c_{m'}^\dagger+c_{m'}), \tag{4}$$

$$H_a=\sum_{qq'q''} \phi^{qq'q''}(b_q^\dagger+b_{-q})(b_{q'}^\dagger+b_{-q'})(b_{q''}^\dagger+b_{-q''}). \tag{5}$$

Here, $b_q^\dagger$ and b_q represent the creation and annihilation operators of extended phonons, whereas $c_m^\dagger$ and c_m denote those of localized phonons.

H_1 describes the interaction between two extended modes and one localized mode, H_2 the interaction between one extended mode and two localized modes, and H_a between three extended modes. The corresponding term with three localized phonons is omitted since the expected smallness of the interaction coefficients. The anharmonic coefficients $\phi^{qq'q''}$, $\phi_m^{qq'}$, and $\phi_{mm'}^{q}$ are assumed to be small and subsequently used as expansion parameters for a perturbation theoretical treatment.

The nonequilibrium situation is dealt with in accordance with our earlier study of phonon hopping,[15,16] i.e., the temperature gradient is treated as an external field. The obtained results are then correct up to first order in the temperature gradient. The external field yields the additional term H_β^t in the Hamiltonian satisfying the condition (see Appendix A)

$$\frac{i}{\hbar}[H_\beta^t,H]=\frac{\boldsymbol{\nabla}\beta(t)}{\beta}\cdot\mathbf{S}, \tag{6}$$

where $\mathbf{S}$ is the energy current operator and $\beta=1/k_BT$ the inverse temperature. The upper index t at H_β^t indicates the parametric time dependence, due to the time-dependent temperature gradient $\boldsymbol{\nabla}\beta(t)$. This time dependence has to be weaker (i.e., the external frequency ω has to be smaller) than the inverse of the time for the system to reach the stationary state, in order for the above approach (treatment of nonequilibrium by external field term) to be applicable.

The energy current operators for localized (index O for optical phonons) and extended (index A for acoustic phonons) modes and the corresponding external field terms read

$$\mathbf{S}^O=\sum_m \hbar\omega_m\mathbf{R}_m\frac{d}{dt}(c_m^\dagger c_m), \tag{7}$$

$$H_\beta^O=-\frac{\boldsymbol{\nabla}\beta}{\beta}\sum_m \hbar\omega_m\mathbf{R}_m c_m^\dagger c_m, \tag{8}$$

$$\mathbf{S}^A=\sum_q \hbar\omega_q\frac{\partial\omega_q}{\partial\mathbf{q}}b_q^\dagger b_q, \tag{9}$$

$$H_\beta^A=-i\frac{\boldsymbol{\nabla}\beta}{\beta}\sum_q \frac{\partial}{\partial\boldsymbol{\kappa}}(b_{q-\kappa/2}^\dagger b_{q+\kappa/2})_{\boldsymbol{\kappa}=0}. \tag{10}$$

Possible anharmonic contributions have been omitted.

B. Anharmonic coefficients

Estimates of the anharmonic coefficients will be derived in this subsection, mainly in order to obtain their dependence on the parameters. Assuming a purely pairwise interaction potential between the atoms, i.e., a potential energy of the form

$$V=\frac{1}{2}\sum_{l\neq l'} \mathsf{V}(|\mathbf{r}_l-\mathbf{r}_{l'}|), \tag{11}$$

the expansion into third order in the atomic displacement $\mathbf{u}_l=\mathbf{r}_l-\mathbf{R}_l$ yields an interaction tensor of third order of the form

$$\mathsf{V}_{ll'l''}^{abc}=\sum_{l'''(\neq l)} A_{ll''}^{abc}(\delta_{ll'}-\delta_{l'''l'})(\delta_{ll''}-\delta_{l'''l''}). \tag{12}$$

Here, $\mathbf{r}_l$ is the position of atom l, $\mathbf{R}_l$ its rest position, and the third order potential energy term reads $(1/3!)\Sigma_{ll'l''}\Sigma_{abc}\mathsf{V}_{ll'l''}^{abc}u_l^a u_{l'}^b u_{l''}^c$. The tensor A is antisymmetric in the atomic site indices and fully symmetric under permutations of the Cartesian coordinates a, b, and c.

The displacements are now expressed by the normal mode coordinates

$$\mathbf{u}_l=\sum_j \mathbf{e}_{lj}U_j, \tag{13}$$

where j runs over both, q and m, the $\mathbf{e}_{lj}$ are the eigenvectors in site representation and

$$U_j=\begin{cases} b_q^\dagger+b_{-q} & \text{if } j=q\\ c_m^\dagger+c_m & \text{if } j=m.\end{cases} \tag{14}$$

The eigenvectors of the localized states are taken to be

$$\mathbf{e}_{lm}=\sqrt{\frac{\hbar}{2M\omega_m}}\delta_{lm}\mathbf{e}_m \tag{15}$$

and of the extended states

$$\mathbf{e}_{lq}=\sqrt{\frac{\hbar}{2M\omega_q N}}e^{i\mathbf{q}\cdot\mathbf{R}_l}\mathbf{e}_q, \tag{16}$$

where $\mathbf{e}_m$ and $\mathbf{e}_q$ are unit vectors. The atomic mass M has been assumed to be site independent. N denotes the number of atoms.

Using the fact, that the acoustic phonons have a very long wavelength, $|\mathbf{q}|\ll 1/a$ (with a a typical atomic distance), one obtains after some algebra

$$\phi_m^{qq'}=\frac{\gamma}{3!\sqrt{\mathcal{V}}}\left(\frac{\hbar}{2\rho}\right)^{3/2}\frac{\exp(i(\mathbf{q}+\mathbf{q}')\cdot\mathbf{R}_m)}{ac^2\sqrt{N}}\sqrt{\frac{\omega_q\omega_{q'}}{\omega_m}}. \tag{17}$$

Here, a is the mean atomic distance (the ‘‘lattice constant’’), $\mathcal{V}=Na^3$ the total volume of the system, ρ the mass density, c the sound velocity and γ an effective anharmonicity parameter (essentially the configurational average of the scalar product of the tensor A with the mode eigenvectors $\mathbf{e}_m$ and $\mathbf{e}_q$).

Analogously, one obtains

$$\phi^q_{mm'}=\frac{\gamma}{3!\sqrt{\mathcal{V}}}\left(\frac{\hbar}{2\rho}\right)^{3/2}\frac{\exp(i\,\mathbf{q}\cdot(\mathbf{R}_m+\mathbf{R}_{m'})/2)}{a^2c}\times\sqrt{\frac{\omega_q}{\omega_m\omega_{m'}}}\exp(-\alpha|\mathbf{R}_m-\mathbf{R}_{m'}|), \tag{18}$$

where it is assumed that the $m=m'$ term is determined by the same effective parameter γ. Furthermore, the $m\neq m'$ terms are assumed to fall off exponentially with a parameter α as an inverse localization length. The δ-function expression (15) for the localized modes would yield a strong dependence of $\phi^q_{mm'}$ on the mode indices m and m', which it would be questionable to average over to get rid of this dependence [as has been done to obtain Eq. (18)]. However, the localized modes do not truly live on a single atom. The resulting summation over the atomic sites participating in a localized mode can be seen as an averaging, which makes the above assumptions reasonable.

Comparing the analogously obtained expression for the interaction coefficient of three extended phonons

$$\phi^{qq'q''}=\frac{\gamma}{3!\sqrt{\mathcal{V}}}\left(\frac{\hbar}{2\rho}\right)^{3/2}\frac{\sqrt{\omega_q\omega_{q'}\omega_{q''}}}{2c^3}\delta(\mathbf{q}+\mathbf{q}'+\mathbf{q}'') \tag{19}$$

with the corresponding expressions of other authors (for acoustic phonons in crystals) one obtains the estimates

$$\gamma\approx\rho c^2 \tag{20}$$

according to Gurevich[17] or

$$\gamma\approx 2|\gamma_G|\rho c^2 \tag{21}$$

according to Srivastava.[18] The first of these estimates is remarkable, since it is an order of magnitude estimation for an anharmonic parameter, which rests solely on harmonic quantities. The symbol γ_G denotes the mode averaged Grüneisen constant.

Since there are as yet no reliable data on anharmonic coefficients of amorphous solids, the relation (20) will be used throughout this work. Furthermore, the numerical parameters in this paper are chosen with a-Si in mind, and incidentally, γ_G of silicon is about 0.5 at room temperature.[18] [The Grüneisen constant is strongly temperature dependent, and even changes sign below 100 K for Si. However, the relation (21) is not intended to predict a temperature dependence of the effective anharmonic coupling constant γ, but merely to give an order of magnitude estimate of the energetic scale of third order interactions.]

III. THE EXTENDED MODES IN NONEQUILIBRIUM

In order to determine the nonequilibrium state of the extended phonons the expectation value (statistical mechanical average in the nonequilibrium situation)

$$n_{q\kappa}=\langle b^\dagger_{q-\kappa/2}b_{q+\kappa/2}\rangle \tag{22}$$

will be calculated. The nonequilibrium state of the acoustic phonons is taken into account by treating Eq. (10) as an external field term. This means we have to obtain

$$n_{q\kappa}(t)=\frac{1}{Z}\mathrm{Tr}(e^{-\beta(H_0+H_a)}U^\dagger(t)b^\dagger_{q-\kappa/2}b_{q+\kappa/2}U(t)) \tag{23}$$

in the limit $t\rightarrow\infty$. Here, Z is the partition function and the time evolution operator reads

$$U(t)=\exp(-i(H_0+H_a+H^A_\beta)t/\hbar). \tag{24}$$

Here, it has been assumed, that the acoustic phonon subsystem is unaffected by the state of the optical phonon subsystem.

Now, we obtain in Heisenberg representation

$$\frac{d}{dt}(b^\dagger_{q-\kappa/2}b_{q+\kappa/2})=\frac{i}{\hbar}[H_0+H_a+H^A_\beta,b^\dagger_{q-\kappa/2}b_{q+\kappa/2}]. \tag{25}$$

This yields a differential equation for $n_{q\kappa}$. The calculation of this commutator yields two operator terms of the form $b^\dagger b$ as well as terms containing three operators, stemming from the commutator with H_a. The time derivative of these three operator terms is subsequently calculated too, leading to four operator terms in addition to the three operator terms. These four operator terms are already second order in the anharmonicity (through H_a) and their expectation value can be calculated with H_0, i.e., the Wick theorem can be applied and the four operator terms are reduced to the (sum of) products of two operator terms. The differential equations thus obtained are then expanded into zeroth and first order in the temperature gradient, all higher order terms being omitted. The equilibrium distribution $N_q\equiv[\exp(\beta\hbar\omega_q)-1]^{-1}$ is taken as initial condition at $t=0$ and the solution at $t\rightarrow\infty$ (the stationary state) is determined.

This approach finally yields after a lengthy calculation

$$n_{q\kappa}=N_q\delta(\boldsymbol{\kappa})+i(\partial N_q/\partial\beta)\boldsymbol{\nabla}\beta\cdot\delta'(\boldsymbol{\kappa})+n_q^{\mathrm{AS}}\delta(\boldsymbol{\kappa}). \tag{26}$$

Here, $\delta'(\boldsymbol{\kappa})$ is the derivative of the δ-function with respect to its argument. n_q^{AS} is antisymmetric in $\mathbf{q}$:$n_{-q}^{\mathrm{AS}}=-n_q^{\mathrm{AS}}$. The kinetic equations for n_q^{AS}, which we obtain, are equivalent to those given, e.g., by Ref. 19. The first term on the right hand side corresponds to the equilibrium distribution and the second term to the deviation from equilibrium in the sense of local equilibrium. Note that both of these terms are independent on the details of interaction (they do not contain a ϕ parameter, for instance), whereas the third term is determined by the actual scattering mechanisms present and, moreover, governs the energy transport within the extended phonon subsystem, as can be seen, if one considers the expression determining the heat conductivity within the extended phonon subsystem[18]

$$\kappa=\frac{1}{\mathcal{V}|\nabla T|^2}\sum_{\mathbf{q}}\hbar\omega_q n_q^{\mathrm{AS}}\frac{\partial\omega_q}{\partial\mathbf{q}}\cdot\nabla T. \tag{27}$$

In order to really exploit the term n_q^{AS}, scattering on inhomogeneities or the interaction with soft modes and two level systems should certainly have been taken into consideration apart from the three phonon scattering. But since all expressions describing hopping transport are symmetric sums in $\mathbf{q}$ (as will be seen below), the discussed term is irrelevant for the purposes of this work.

IV. THE RATE EQUATIONS FOR THE LOCALIZED MODES

The external field term (8) can easily be incorporated into H_0 through the substitution

$$\omega_m\rightarrow\omega_m(1-\mathbf{R}_m\cdot\nabla\beta/\beta). \tag{28}$$

This substitution will be applied immediately before the linearization in the temperature gradient. The formalism can therefore proceed as for a system in equilibrium (as far as the localized modes are concerned).

The nonequilibrium distribution of the extended phonons can also be taken into consideration by inserting certain substitutions in the final phases of the calculation only. The distribution function $n_{q\kappa}$ of the acoustic phonons is nondiagonal due to the δ' term in Eq. (26), which nevertheless only has support on a single point, namely $\kappa=0$. This δ' term leads finally to a derivative of the anharmonic constants ϕ with respect to their wave-vector arguments, which has to be taken at $\kappa=0$, i.e., the finally occurring expectation values $n_{q\kappa}$ are diagonal (and are simply denoted as n_q). A careful analysis yields the substitutions

$$|\phi_m^{qq'}|^2 n_q\rightarrow|\phi_m^{qq'}|^2 N_q(1-\hbar\omega_q(1+N_q)\mathbf{R}_m\cdot\nabla\beta) \tag{29}$$

$$|\phi_{mm'}^{q}|^2 n_q\rightarrow|\phi_{mm'}^{q}|^2 N_q(1-\hbar\omega_q(1+N_q)\times(\mathbf{R}_m+\mathbf{R}_{m'})\cdot\nabla\beta/2), \tag{30}$$

which are to be applied at the end of the calculations in order to introduce the temperature gradient. The acoustic phonon subsystem will therefore be considered to be in equilibrium for now.

Rate equations for the distribution function n_m of the optical phonons will be calculated using the Konstantinov-Perel diagram technique.[20,21] All diagrams up to second order in the interactions H_1 and H_2 are taken into consideration. Furthermore, the Markovian limit is already taken in the expressions below.

The diagrams which contain two interaction points corresponding to H_1 describe the decay of an optical phonon into two acoustic phonons and yield the expression

$$\left.\frac{d}{dt}n_m\right|_{\mathrm{decay}}=\frac{2\pi}{\hbar^2}\sum_{qq'}|\phi_m^{qq'}|^2\delta(\omega_m-\omega_q-\omega_{q'})\times[n_q n_{q'}(1+n_m)-(1+n_q)(1+n_{q'})n_m]. \tag{31}$$

The hopping contribution, arising from diagrams with two H_2 interaction points, reads

$$\begin{aligned}\left.\frac{d}{dt}n_m\right|_{\mathrm{hopping}}=\frac{4\pi}{\hbar^2}\sum_{qm'}|\phi_{mm'}^{q}|^2\{&\delta(\omega_m-\omega_{m'}-\omega_q)\\&\times[(1+n_m)n_{m'}n_q-n_m(1+n_{m'})(1+n_q)]\\&+\delta(\omega_m-\omega_{m'}+\omega_q)\\&\times[(1+n_m)n_{m'}(1+n_q)-n_m(1+n_{m'})n_q]\}.\end{aligned} \tag{32}$$

There are no diagrams with both a H_1 and a H_2 interaction point, since this would yield expectation values of odd numbers of creation and annihilation operators.

The nonequilibrium situation is now taken into consideration by the substitutions (28), (29), and (30). The resulting equations are subsequently linearized with respect to $\nabla\beta$. An upper index (0) or (1) will denote the corresponding quantities of zeroth or first order in $\nabla\beta$, respectively. The acoustic phonons obey

$$n_q^{(0)}=N_q\equiv\{\exp(\beta\hbar\omega_q)-1\}^{-1}. \tag{33}$$

The sum of Eqs. (31) and (32) yield the searched for rate equations and read in zeroth order

$$\frac{d}{dt}n_m^{(0)}=W_m^{(0)}(e^{-\beta\hbar\omega_m/2}(1+n_m^{(0)})-e^{\beta\hbar\omega_m/2}n_m^{(0)}) \tag{34}$$

$$+\sum_{m'}(W_{m'm}^{(0)}(1+n_m^{(0)})n_{m'}^{(0)}-W_{mm'}^{(0)}n_m^{(0)}(1+n_{m'}^{(0)})), \tag{35}$$

with

$$W_{m'm}^{(0)}=\frac{2\pi}{\hbar^2}\frac{e^{\beta\hbar(\omega_{m'}-\omega_m)/2}}{\sinh(\beta\hbar|\omega_m-\omega_{m'}|/2)}\times\sum_q|\phi_{mm'}^{q}|^2\delta(\omega_q-|\omega_m-\omega_{m'}|) \tag{36}$$

and

$$W_m^{(0)}=\frac{\pi}{2\hbar^2}\sum_{qq'}|\phi_m^{qq'}|^2\frac{\delta(\omega_m-\omega_q-\omega_{q'})}{\sinh(\beta\hbar\omega_q/2)\sinh(\beta\hbar\omega_{q'}/2)}. \tag{37}$$

Equation (35) is solved by

$$n_m^{(0)}=N_m\equiv\{\exp(\beta\hbar\omega_m)-1\}^{-1}. \tag{38}$$

To first order in $\nabla\beta$ the substitutions (29) and (30) (i.e., the nonequilibrium distribution of the acoustic phonons) give rise to the terms

$$-\frac{\hbar\omega_m\mathbf{R}_m\cdot\nabla\beta}{\tau_m}+\sum_{m'}\Gamma_{m'm}\hbar(\omega_{m'}-\omega_m)\frac{\mathbf{R}_m+\mathbf{R}_{m'}}{2}\cdot\nabla\beta \tag{39}$$

in the rate equations. The substitution (28) contributes the first order terms

$$+\frac{\hbar\omega_m\mathbf{R}_m\cdot\nabla\beta}{\tau_m}+\sum_{m'}\Gamma_{m'm}\hbar(\mathbf{R}_m\omega_m-\mathbf{R}_{m'}\omega_{m'})\cdot\nabla\beta. \tag{40}$$

Here, the inverse (direct decay) lifetime is

$$\frac{1}{\tau_m}=\frac{\pi}{4\hbar^2\sinh(\beta\hbar\omega_m/2)}\times\sum_{qq'}|\phi_m^{qq'}|^2\frac{\delta(\omega_m-\omega_q-\omega_{q'})}{\sinh(\beta\hbar\omega_q/2)\sinh(\beta\hbar\omega_{q'}/2)} \tag{41}$$

and the symmetrized hopping rate

$$\Gamma_{m'm}=\frac{\pi}{2\hbar^2\sinh(\beta\hbar\omega_m/2)\sinh(\beta\hbar\omega_{m'}/2)}\times\sum_q|\phi_{mm'}^q|^2\frac{\delta(\omega_q-|\omega_m-\omega_{m'}|)}{\sinh(\beta\hbar\omega_q/2)}. \tag{42}$$

The first order rate equations thus altogether read

$$\frac{d}{dt}n_m^{(1)}=-\frac{n_m^{(1)}}{\tau_m N_m(1+N_m)}+\sum_{m'}\Gamma_{m'm}\left(\frac{n_{m'}^{(1)}}{N_{m'}(1+N_{m'})}-\frac{n_m^{(1)}}{N_m(1+N_m)}\right)+\sum_{m'}\Gamma_{m'm}\hbar\frac{\omega_{m'}+\omega_m}{2}(\mathbf{R}_m-\mathbf{R}_{m'})\cdot\nabla\beta. \tag{43}$$

Note that this system of equations is translationally invariant, whereas the corresponding system without the nonequilibrium acoustic phonons would not be translation invariant. Somewhat surprisingly, for $\Gamma_{m'm}\equiv 0$ (without hopping) the asymptotic distribution is $n_m^{(1)}=0$ even with an applied temperature gradient. This is easily explained, though, since the external field treatment of the nonequilibrium state ignores the difference between local and total equilibrium, as is shown above. To account for this difference, one can either interpret $n_m^{(1)}$ as the deviation from local equilibrium, or, add the missing terms [i.e., $n_m^{(1)}\rightarrow n_m^{(1)}+N_m(1+N_m)\hbar\omega_m\mathbf{R}_m\cdot\nabla\beta$].

The thermal current (7) is unaffected by this difference and the quantities $n_m^{(1)}$ could be seen as artificially arising in the formalism without their having any specific physical meaning. However, in order to numerically simulate the system of rate equations for a (necessarily) finite system, boundary conditions have to be specified, which necessitates a more detailed knowledge.

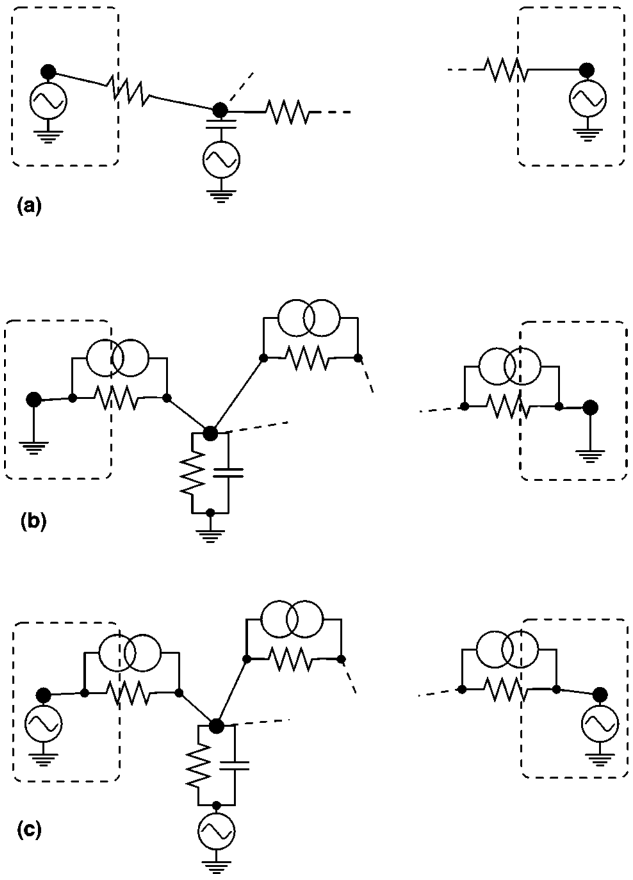

FIG. 1. The equivalent electrical scheme for (a) electron hopping and (b) and (c) phonon hopping. Note the occurrence of current sources and grounding resistances in the phonon case. For details see the text.

Introducing the generalized chemical potential $\delta\mu_m$

$$n_m^{(1)}=N_m(1+N_m)e^{i\omega t}\delta\mu_m \tag{44}$$

the rate equations (43) become

$$(i\omega N_m(1+N_m)+1/\tau_m)\delta\mu_m=\sum_{m'}\Gamma_{m'm}(\delta\mu_{m'}-\delta\mu_m)+\sum_{m'}\Gamma_{m'm}\hbar\frac{\omega_m+\omega_{m'}}{2}(\mathbf{R}_m-\mathbf{R}_{m'})\cdot\nabla\beta. \tag{45}$$

Here ω is the frequency of the externally applied temperature gradient. The energy current (7) can now be split into an "Ohmic" part

$$\mathbf{S}^{\mathrm{ohm}}=\frac{1}{2}\sum_{mm'}\Gamma_{m'm}\hbar\frac{\omega_m+\omega_{m'}}{2}(\mathbf{R}_m\omega_m-\mathbf{R}_{m'}\omega_{m'})\circ(\mathbf{R}_m-\mathbf{R}_{m'})\cdot\nabla\beta, \tag{46}$$

and a diffusive part

$$\mathbf{S}^{\mathrm{diff}}=\frac{1}{2}\sum_{mm'}\Gamma_{m'm}\hbar(\mathbf{R}_m\omega_m-\mathbf{R}_{m'}\omega_{m'})(\delta\mu_{m'}-\delta\mu_m), \tag{47}$$

where $\circ$ denotes the dyadic product.

We are now in a position to compare the obtained rate equations with the analogous expressions valid for electron hopping (see, e.g., Ref. 21). Figure 1(a) shows the usual Abrahams-Miller network used in the theory of electron hopping (see, e.g., Ref. 21 and references therein). The fat dots correspond to the localization sites. The rate equation (45) corresponds to Fig. 1(b). The resistances between the sites are $1/\Gamma_{m'm}$ and the capacitances are $N_m(1+N_m)$. These are fully analogous to the electron case (except for the now nonelectrical units, of course). The last term of Eq. (45) gives rise to the current sources between the sites, which cannot be transformed into resistances, since the resulting current is not proportional to the ''voltage'' difference $\delta\mu_{m'}-\delta\mu_m$. Finally, the decay term gives rise to the grounding resistances equal to τ_m. These differences are discussed in Sec. VI.

Figure 1(c) shows a transformed version of 1(b). It arises, if the $n_m^{(1)}$ (and thus the $\delta\mu_m$) are *not* interpreted as deviations from local equilibrium, but as the true occupation numbers. The local equilibrium expectation values give rise to the voltage sources. Note, that the current sources are transformed in this case. They now correspond to the last term of Eq. (39). Furthermore, the sites inside a heat bath are not all linked to the same voltage source (electrode) as is the case for electron hopping, because the equilibrium occupation number does depend on the individual site energies.

V. LIFETIME AND AC BEHAVIOR

All numerical values in this paper are chosen with *a*-Si in mind. This is because, even though *a*-Si is possibly somewhat exceptional, it is the only amorphous material for which there are lifetime measurements of high-energy vibrational modes available, of which the authors are aware.

The density of states of the extended phonons is taken to follow the three dimensional Debye model

$$g(\omega)=3\mathcal{N}\omega^2/\omega_{D'}^3. \tag{48}$$

Here, $\mathcal{N}$ is the number of extended modes.

The considered high temperature case corresponds to $\beta\hbar\omega_{D'}\ll 1$. The sinh functions containing acoustic phonon frequencies can therefore be approximated by their argument (the first term of their Taylor series). One finally obtains

$$\frac{1}{\tau_m}=\mathcal{A}\left(\frac{\mathcal{N}}{N}\right)^2\frac{1}{10}\times\frac{12-(\omega_m/\omega_{D'})^5+20(\omega_m/\omega_{D'})^2-30(\omega_m/\omega_{D'})}{\beta^2\hbar^2\omega_{D'}\omega_m\sinh(\beta\hbar\omega_m/2)} \tag{49}$$

for $\omega_m<2\omega_{D'}$ ($1/\tau_m=0$ otherwise) and

$$\Gamma_{m'm}=\mathcal{A}\left(\frac{c}{a\,\omega_{D'}}\right)^2\left(\frac{\mathcal{N}}{N}\right)\times\frac{(\omega_m-\omega_{m'})^2e^{-2\alpha|\mathbf{R}_m-\mathbf{R}_{m'}|}}{\beta\hbar\omega_{D'}\omega_m\omega_{m'}\sinh(\beta\hbar\omega_m/2)\sinh(\beta\hbar\omega_{m'}/2)} \tag{50}$$

for $|\omega_m-\omega_{m'}|<\omega_{D'}$ ($\Gamma_{m'm}=0$ otherwise), where the quantity

$$\mathcal{A}=\frac{\pi\hbar\gamma^2}{96\rho^3a^5c^4} \tag{51}$$

has been introduced.

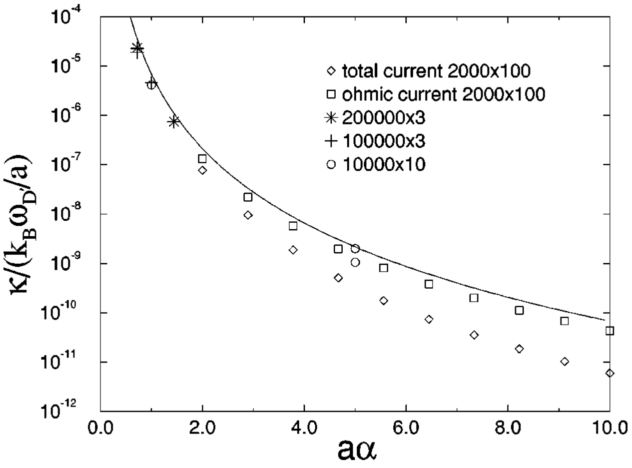

FIG. 2. The heat conductivity for different localization parameters $a\alpha$. The temperature is chosen as $4\hbar\omega_{D'}/k_B$; all other parameters are as given in the text. The solid line shows the approximation (B7). The first data set is the total conductivity; all others only show the Ohmic conductivity. The numbers given in the legend mean [number of optical oscillators]× [number of systems in the configuration average].

Assuming that $(2\pi)^3/\mathcal{V}$ is the volume per extended mode in wave vector space, the maximal wave vector is $q_D=\sqrt[3]{2\pi^2\mathcal{N}/\mathcal{V}}$. Using $\omega_{D'}=cq_D$ one obtains

$$\frac{\mathcal{N}}{N}=\frac{1}{2\pi^2}\left(\frac{a\,\omega_{D'}}{c}\right)^3 \tag{52}$$

as an approximation for the relation $\mathcal{N}/N$.

The numerical values will now be estimated for amorphous silicon (a-Si). Scholten and Dijkhuis[14] use $c=5000$ m/s and a localization frequency of $2\pi\times1.95$ THz (corresponding to 65 cm^{-1}). The spectrum of states in *a*-Si reaches up to 70 meV (570 cm^{-1}, cf. Ref. 8). We choose $\omega_{D'}<\omega_m<8\omega_{D'}$. The atomic mass is $\rho a^3=M=28$ u (u denotes the atomic mass unit). The anharmonicity constant γ is estimated as ρc^2. The atomic distance is $a=2.75$ Å.[22]

These values yield $\mathcal{A}=9.3\times10^8$ Hz$=7.7\times10^{-5}\,\omega_{D'}$, $c/(a\omega_{D'})=1.5$, $\mathcal{N}/N=0.015$, and $k_B\omega_{D'}/a=0.6$ W/(m K) (the unit of heat conductivity in the numerical calculations).

The total number of localized modes is three times as large as the number of atoms in the considered case (only a few percent of the modes are extended). Since the localized modes will have significant amplitude even several atomic distances from the localization center, the localization exponent α can be assumed to be small in relation to the inverse atomic distance $1/a$. Appendix B elaborates upon expressions for the lifetime of localized modes and the thermal conductivity in systems with $\alpha a\ll 1$.

To assess the quality of the estimates obtained in Appendix B, Fig. 2 shows some calculations of κ using the parameters for *a*-Si as cited above. The relation (B7) yields a rea-

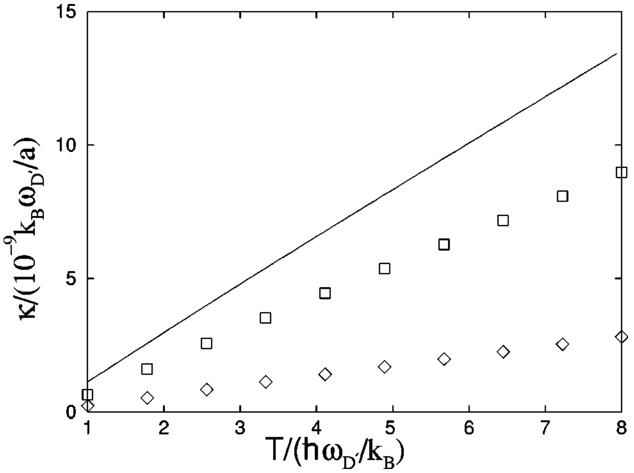

FIG. 3. The heat conductivity in dependence on temperature. The parameter $a\alpha$ is chosen as 4, all other parameters are as given in the text. The solid line shows the approximation (B7). The diamonds show the total conductivity, numerically obtained by averaging over 100 systems of 2000 oscillators each. The squares show the corresponding Ohmic conductivity.

sonable estimate of the Ohmic current even for large $a\alpha$. But, the magnitude of the diffusive current increases with $a\alpha$ and renders the estimate invalid for large values of $a\alpha$. For sufficiently large $a\alpha$ the total current should decrease exponentially as in percolation theory.

The numerical data points, here and in the following, are obtained as follows. A three dimensional box is filled with localization sites of random energy and location. The sites within a 10% slice on two opposing faces of the box are taken to constitute the heat baths, i.e., their $\delta\mu_m$ are fixed. The system of rate equations (45) is then solved and the energy current (7) (denoted as total current) is calculated, along with its components [Eqs. (46) and (47)]. Actually, there is a third component to the total current, arising due to the decay terms. This is discussed in Sec. VI. The numerical calculations showed, however, that it is negligible ($<10\%$ of $\mathbf{S}^{O}$) for the parameter values used here. The next step is to carry out a configurational average.

As expected, the temperature dependence of κ is practically linear as shown in Fig. 3. There is no saturation behavior in this model, since multiphonon processes are neglected in contrast to our former model.[15,16]

Very small $a\alpha$ would imply the numerical solution of very large systems to obtain meaningful results, because the interaction range between the oscillators is large. The following calculations rest therefore on the approximate solutions derived in Appendix B.

Exploiting Eqs. (B5) and (B8), the parameter $(a\alpha)$ is calculated for a-Si. The value[13] $\kappa/T = 6\times10^{-3}$ W/m K^2 leads to $(a\alpha)\approx 1/13$. The measurements of Scholten[14] yield lifetimes between 1 and >70 ns for the states between 150 cm^{-1} and 480 cm^{-1}. The values lead to $(a\alpha)\approx 1/3$ (cf. Table I), where this quantity somewhat increases with increasing energy of the state (except for the value at 300 cm^{-1}).

These two values are of the same order of magnitude, but show a significant difference nevertheless. Above all, we note, that localization lengths of the order of 3 to 13 atomic distances appear realistic. It is furthermore noteworthy, that all parameters have been used as given, without choosing special values (fitting). Especially, only rough estimates have been used for the anharmonicity parameter γ, the localization edge $\omega_{D'}$, and the fraction of extended modes $\mathcal{N}/3N$. Varying these parameters, the lifetime and heat conductivity results can be brought into better agreement. For instance, the (probably unrealistic) decrease of γ by three orders of magnitude yields coinciding values for $(a\alpha)$ (then about 1/130). However, a systematic adaptation of the parameters to the experimental values is certainly premature, since only few measurements of the lifetime are available, and with uncertain error bars at that. The lifetime of the localized states in a-Si has been measured by Scholten at five frequencies, where there are given very large error bars for the highest frequency states, essentially indicating, that the values give only the order of magnitude. We are not aware of further such measurements.

TABLE I. The values for the localization parameter $a\alpha$ of a-Si as obtained by Eq. (B5) using the lifetime values of Scholten. The values of τ are obtained from Fig. 2 of Ref. 14.

ω cm^{-1}	τ ns	$1/(a\alpha)$
150	2	4.0
200	5	3.6
300	5	4.7
400	40	2.8
480	70	2.6

The density of states $g(\omega)$ usually depends on energy ω. The inverse localization length α will similarly be a function of ω. Both these dependencies have been neglected here, since the amount of available data is insufficient to make the sophistication reasonable. This is especially clear, if one considers the uncertainty in the ''basic'' model parameters γ, $\omega_{D'}$ and $\mathcal{N}/N$.

The above stated increase of α for increasing energy of the state, as obtained from the lifetime measurements, indicates a stronger localization for higher energy states, which would be expected. The small value of α, as obtained from the heat conductivity, can be seen as an indication that the main contribution to energy transport stems from energetically low lying localized modes. This behavior would correspond to the fracton model results.

To determine the ac behavior of the heat conductivity, the system of rate equations was solved for the above given parameters together with $a\alpha = 4$. Figure 4 shows the obtained frequency dependence of the real part of κ. As can be seen, the heat conductivity increases with the external frequency, as is the case for the electrical conductivity in the case of electron hopping. However, in calculating the frequency dependence of heat conductivity one has to note the fundamental difference of it from the frequency dependence of the electrical conductivity of a system of charged particles. There is a problem in that the temperature gradient inside the probe is delayed relative to a changing temperature at the contacts. To describe such a (time-dependent) process by a quantity $\kappa(\omega)$ only makes sense if the retardation is small, or if the temperature change somehow directly effects the inte-

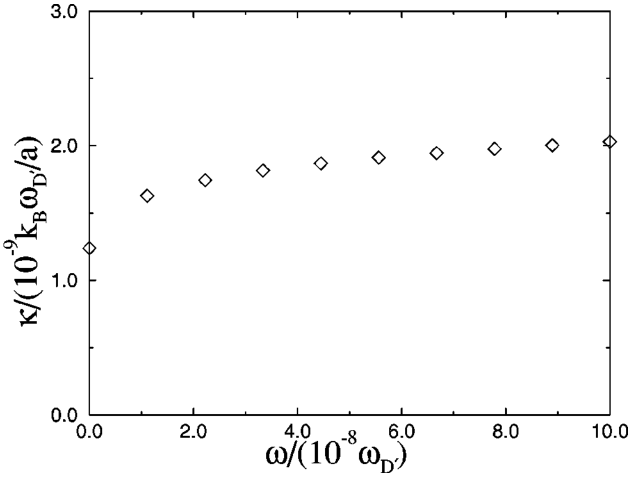

FIG. 4. The heat conductivity in dependence on external frequency of the temperature gradient. The mean temperature is chosen as $4\hbar\omega_{D'}/k_B$ and the localization parameter as $a\alpha=4$. All other parameters are as given in the text. The calculation used systems of 1000 optical oscillators and averaged over 100 disorder configurations.

rior of the sample, and not only the surface. Thus, the relation $\kappa(\omega)$ makes sense only for sufficiently small frequencies.

The calculations are therefore only valid for thin samples. As a first approximation one can assume, that the energy travels 3 atomic distances — according to the above given extension of the states — within the lifetime of order 70 ns, this gives a lower limit for the velocity of energy transport. Assuming that this velocity (about 0.1 Å/ns) controls the ''propagation'' of the temperature gradient, the maximal external frequency would be 10^5 Hz for a sample of 1000 Å thickness.

However, the proposed smallness of $a\alpha$ for *a*-Si and other dense glasses leads to a very small diffusive current. The ohmic current is frequency independent and the increase with frequency can therefore probably not be seen in these glasses. But the current should at least stay constant with increasing frequency, in contrast to the diffusive model of Allen and Feldman. This could provide an additional way to experimentally distinguish between these models — apart from the lifetime behavior.

VI. COMPARISON BETWEEN ELECTRON AND PHONON HOPPING

There are three basic problems relating to the derived rate equations and the considered hopping current: particle number nonconservation, energy nonconservation, and noninvariance of the hopping current with respect to coordinate translations. These are discussed in the following paragraphs.

(i) In contrast to electron transport (which conserves the electron number), Eq. (43) does not conserve the total number of optical phonons

$$\frac{d}{dt}\sum_m n_m^{(1)}(t)=-\sum_m \frac{n_m^{(1)}(t)}{\tau_m N_m(1+N_m)}. \tag{53}$$

The particle number nonconservation is due to the decay of optical phonons into acoustic ones. In a disordered system the effective relaxation time $\tau_m N_m(1+N_m)$ is a random quantity and depends on m. Thus, the decay of optical phonons does not have an exponential character. However, for weak disorder, when the inverse relaxation time may be replaced by an average quantity $\overline{\tau^{-1}}$, the decay becomes exponential

$$N(t)=N_0\exp(-t/\bar{\tau}), \tag{54}$$

$$\frac{1}{\bar{\tau}}=\left\langle\frac{1}{\tau_m N_m(1+N_m)}\right\rangle, \tag{55}$$

$$N(t)=\sum_m n_m^{(1)}(t). \tag{56}$$

The angle brackets indicate the configuration average. The concrete expression (41) for τ_m describes the decay process of an optical phonon into two acoustic phonons and is applicable only in the case of a sufficiently small gap between the frequencies of optical and acoustic modes $\omega_m<2\omega_{D'}$. For a large gap $\omega_m\gg\omega_{D'}$ an optical phonon has to decay into several acoustic phonons. In this case for weak anharmonicity the lifetime τ_m will be sharply increased and one can expect that $\tau_m\propto\exp(\omega_m^2/\omega_0^2)$, where the characteristic frequency ω_0 is proportional to the anharmonic constant $\phi_m^{qq'}$, which governs the interaction between optical and acoustic vibrations.

The presence of optical phonon decay strongly influences the hopping transport, especially in large systems and for large times. The problem is that the subsystem of optical phonons is not closed, but loses particles to the acoustic subsystem. Therefore, equations of the form (43) or (45) do not describe the stationary state at large times and for large systems, and $n_m^{(1)}(t)\rightarrow 0$ for $t\rightarrow\infty$. The stationary state can only be obtained by taking the transitions from the acoustic into the optical subsystem into account. The characteristic time of these reverse transitions τ_m' is large and satisfies $\tau_m N_m(1+N_m)=\tau_m'(1+N_m)^2$. Thus, the transport equation in the form (43) describes the heat conduction of a system, if the traveling time of the particle (optical phonon) through the sample Δt is smaller than τ_m'. If $\tau_m<\Delta t<\tau_m'$, the heat conductivity calculated by Eq. (43) starts to decrease with increasing dimension of the sample.

The term with τ_m^{-1} in Eq. (43) actually has an analog in electron transport in disordered systems. The corresponding contribution to the electronic transport equation occurs for hopping transport in the presence of trapping. In this case the electrons are gradually captured in trapping centers and cease to contribute to the current. The stationary current in such systems with large sample dimensions (sample thickness is larger than the distance covered until trapped) is controlled by thermal ionization of the trapping centers.

Equation (43) also describes the process of transition to equilibrium of the subsystem of optical phonons, excited, e.g., by infrared irradiation (then the term $\nabla\beta$ has to be omitted, of course). Strictly speaking, Eq. (43) is applicable to those cases of optical excitation only, where the phonon system affected by irradiation only slightly deviates from thermodynamic equilibrium. For large deviation nonlinearized equations had to be used. There are two energy dissipation channels driving the system to thermodynamic equilibrium. The first is connected with the direct decay of optical phonons into acoustic ones (i.e., the term τ_m^{-1}). The second channel is caused by hopping of optical phonons between sites with a gradual loss of energy up to the minimal value $\omega_{\min}$, followed by the direct decay of optical phonons with $\omega_{\min}$ into acoustic phonons. The relation between these two channels is governed by the ratio $\tau_m/\Gamma^{-1}_{m'm}$, i.e., the ratio between the time of direct recombination and the time of hopping events. If this ratio is small, then direct transitions prevail. Then, if the sample has been excited by monochromatic light with the frequency ω, the relaxation has exponential character $\exp(-t/\tau)$, and the relaxation time equals $\tau_m(\omega_m=\omega)$, i.e., is proportional to $\exp(\omega^2/\omega_0^2)$. If, on the other hand, $\tau_m/\Gamma^{-1}_{m'm}$ is large, the relaxation proceeds in two stages. At first, the energy relaxation takes place by hopping inside the subsystem of optical phonons from sites with phonon energy $\hbar\omega$ to finally sites with $\hbar\omega_{\min}$. In this stage the relaxation in a strongly disordered system has a marked nonexponential character due to the large spread of hopping times (continuous-time random-walk theory). The duration and character of the relaxation in this stage depends on the exciting light frequency ω. The second stage of the relaxation consists of direct transitions from $\omega_{\min}$ in the optical subsystem into acoustic phonons. It has exponential character and does not depend on the light frequency.

(ii) The second fundamental difference of phonon transport as compared to electron transport consists in the fact, that in studying heat conductivity the relevant quantity is the energy current, whereas for electron transport it is the particle current. However, Eq. (43) does not conserve the total energy of the optical phonon subsystem $[(d/dt)\Sigma_m\hbar\omega_m n_m^{(1)}(t)\neq 0]$ even if the direct decay of optical phonons is neglected $(\tau_m\rightarrow\infty)$. The cause of this nonconservation is the inelastic nature of the elementary hopping processes, which are accompanied by absorption or emission of acoustic phonons [cf. Eq. (42)]. The processes with emission of an acoustic phonon are more probable, than those with absorption. Therefore, successive hops of an optical phonon lead to a decrease of its energy, the loss being transferred to the thermostat (the subsystem of acoustic phonons). This dissipation lasts until the energy of the optical phonon reaches the lower limit of the spectrum $\omega_{\min}$. Here, a balance between hops with absorption and emission of acoustic phonons is attained and no energy is dissipated, provided, of course, that there are no decay processes of optical into acoustic phonons $(\tau_m\rightarrow\infty)$. In this sense, the lower spectral limit of optical phonons plays a role similar to the value of the chemical potential in electron transport. In this final regime all hopping events take place between sites, which have an energy in the interval between $\omega_{\min}$ and $\omega_{\min}+\Delta\omega$. For large temperatures the Debye frequency $\omega_{D'}$ characterizes the inelastic energy of a hop in which one acoustic phonon takes part and accordingly $\Delta\omega\approx\omega_{D'}$. For low temperatures $kT<\hbar\omega_{D'}$ the width of the energy band $\Delta\omega$ carrying the current depends on the temperature and, especially, $\Delta\omega\rightarrow 0$ for $T\rightarrow 0$, because the characteristic energy for the hopping transitions is of the order kT.

To describe the dependence of the heat conductivity on the concentration of localization centers n one may make use of percolation theory. The corresponding basic relation for the heat conductivity is $\kappa\propto\exp(-2\alpha R_c)$, where α^{-1} denotes the radius of the localized state and R_c is the typical hopping distance. This distance is — apart from a numerical factor η — equal to the mean distance between sites lying in the energy interval between $\omega_{\min}$ and $\omega_{\min}+\Delta\omega$. If the density of states of optical phonons is a constant in the interval from $\omega_{\min}$ to $\omega_{\min}+\Omega_{\max}$, then $R_c=\eta(n\Omega_{\max}/\Delta\omega)^{1/d}$, where d denotes the spatial dimension. At low temperatures $kT<\hbar\omega_{D'}$, the characteristic hopping distance depends on temperature (cf. the Mott law for low-temperature electronic hopping conductivity).

(iii) The presence of energy dissipation $[\Sigma_m\hbar\omega_m(dn_m^{(1)}/dt)\neq 0]$ for hopping transitions of optical phonons leads to the third serious difference for the calculation of heat conductivity in contrast to the electronic electrical conductivity. The problem is that the expression (7) for the heat current density

$$\mathbf{s}=\frac{1}{\mathcal{V}}\sum_m \mathbf{R}_m\hbar\omega_m\frac{dn_m^{(1)}(t)}{dt} \tag{57}$$

is not invariant with respect to a change of the origin of the coordinate system $\mathbf{R}_m\rightarrow\mathbf{R}_m+\mathbf{R}_0$, where $\mathbf{R}_0$ denotes an arbitrary radius vector. Under these circumstances the relation (57) requires to be stated differently:

$$\mathbf{s}=\frac{1}{\mathcal{V}}\sum_m \mathbf{R}_m\hbar\left\{\omega_m\frac{dn_m^{(1)}(t)}{dt}-\frac{1}{N}\sum_{m'}\omega_{m'}\frac{dn_{m'}^{(1)}(t)}{dt}\right\}, \tag{58}$$

where N now denotes the number of localization centers. The relation (58) is invariant with respect to translations $\mathbf{R}_m\rightarrow\mathbf{R}_m+\mathbf{R}_0$. We note that we already had to establish the invariance of the transport equations (43) with respect to translations. However, in the static limit, it does not describe the transport in terms of the combination $\delta\mu_m-\hbar\omega_m\mathbf{R}_m\nabla\beta$, the analogous notion in electron transport being the electrochemical potential in the case of a small deviation from the thermodynamic equilibrium. Accordingly, even if $\tau_m\rightarrow\infty$, Eq. (43) does not fulfill Kirchhoff's law in the random network of resistors $\Gamma^{-1}_{m'm}$, as it is the case for electron hopping. One has to additionally include electromotive forces between all pairs of sites in the equivalent electrical scheme [see Fig. 1(b)].

These difficulties with the invariance relative to a translation of the coordinate system for the calculation of heat conductivity in a system of localized phonons are a matter of principle. The nature of the problem lies in the choice of the interaction Hamiltonian with the ''external field'' $\nabla\beta, H^O_\beta$. For a translation of the origin of the coordinate system this Hamiltonian term changes according to

$$H^O_\beta\rightarrow H^O_\beta+\frac{\mathbf{R}_0\nabla\beta}{\beta}\sum_m \hbar\omega_m c_m^\dagger c_m. \tag{59}$$

This noninvariance is closely connected with the circumstance, that it is very difficult to separate the notion of the ''force'' $\nabla\beta$ — the temperature gradient — from the coordinate dependence of the temperature itself. As a result, for a translation $\mathbf{R}_m \rightarrow \mathbf{R}_m + \mathbf{R}_0$ the energy of the phonons $\Sigma_m \hbar \omega_m c_m^\dagger c_m$ obtains the additional factor $(1 + \mathbf{R}_0 \boldsymbol{\nabla} \beta / \beta)$. This change describes the displacement of the sample as a whole by the vector $\mathbf{R}_0$ in an inhomogeneous temperature field. For a position dependent temperature by-effects occur, such as, e.g., a spatial variation of the heat capacity (through the temperature variation). In a phenomenological derivation of the equations for the heat conductivity, these effects are neglected.[24] In the kinetics of electrons the right limiting procedure is to first let the volume of the system go to infinity, and only thereafter the time (measured relative to the moment the electric field is turned on). If, on the other hand, a thermal deviation from the state of thermal equilibrium is considered, one has to be very cautious in the transition to an infinitely large system, because the linear approximation in the ''force'' $\boldsymbol{\nabla} \beta$ has to assume, that the dimensionless parameter $L \boldsymbol{\nabla} \beta / \beta$ remains small (L denotes the linear dimension of the system).

VII. CONCLUSIONS

We investigated the behavior of localized vibrational states which anharmonically interact with extended states (acoustic phonons) under the assumption, that the anharmonicity is weak and can be treated perturbatively. Furthermore, we assume, that system is exposed to a temperature gradient and derive rate equations for the occupation numbers of the localized states in the Markov limit and in linear order in $\boldsymbol{\nabla} \beta$. Our model is rather generic, in that it can accommodate quite arbitrary dependencies of the anharmonic ''constants'' ϕ on their indices (except for some requirements having to do with the assumed translation invariance of certain terms). They can be arbitrary functions of the frequencies of the interacting modes. A restriction of the model is its applicability to the high temperature regime only, i.e., temperatures above the plateau region, since two-level systems have been neglected.

For a certain — rather simple — choice of the anharmonic coefficients, we try to catch the generic behavior of glassy systems. We solved the rate equations numerically and obtained analytic expressions for a limiting case (''dense'' systems), which compare very good with the numerical results. The lifetime of localized modes increases with the mode frequency in accordance with the fracton hopping model (but following a different functional dependence) but in contrast to the diffusive model of Allen and Feldman. The increase of the heat conductivity with temperature is reproduced as well.

Another result is the ac behavior of heat conductivity. It is shown that κ slightly increases with the external frequency, and in practice will probably be seen as constant. This is in contrast to the model of Allen and Feldman, which predict a decrease of κ with frequency. However, the situation here is not fully clear yet. It is not certain how the calculated $\kappa(\omega)$ of Refs. 8 and 22 are to be interpreted, since the authors have omitted some terms, which do not contribute in the limit $\omega = 0$. But, a molecular dynamics simulation[23] of a similar a-Si model also shows a decrease of κ with frequency. This decrease is therefore perhaps an artifact of the specific model structure and not a generic property of the model of diffusive transport of nonpropagating modes. The hopping behavior predicted in this paper is possibly not seen in the simulation, because a localization radius of 3 atomic distances (see Sec. V) would be of the order of the sample size. These problems need further attention and careful scrutinization.

Finally, the phonon hopping is formally compared to the known electron hopping and the essential differences are discussed. These are mainly particle number nonconservation, energy nonconservation, and difficulties regarding the external field treatment of nonequilibrium.

The particle number nonconservation would require one to consider a production term in addition to the decay term of optical phonons in order to describe the hopping heat conductivity of very thick samples. The thickness here is determined by the ratio of the travelling time of an optical phonon through the sample to the decay or production rate. To follow this program, one had to take into consideration the energy transport within the extended phonon subsystem. Moreover, the relaxation behavior differs strongly depending on the ratio between decay and hopping rate.

Due to the energy nonconservation of hopping events (from the perspective of the localized phonon subsystem) the energy transport through hopping takes place within an energy band near the lowest localized mode frequency in a sufficiently large system. The width of this band becomes temperature dependent for sufficiently low temperatures.

The difficulty to separate the temperature gradient, which acts as an external ''force'' driving the current, from the coordinate dependence of the temperature itself leads to the noninvariance under translations of the expressions for the hopping current.

APPENDIX A: NONEQUILIBRIUM AS AN EXTERNAL FIELD

The studied nonequilibrium system is considered to be thermodynamically described by a (given) temperature field

$$\beta(\mathbf{x}, t) = \beta + e^{i\omega t} \boldsymbol{\nabla} \beta \cdot \mathbf{x}. \tag{A1}$$

Note that the same symbol β is used for several quantities (e.g., mean inverse temperature, time- and position-dependent inverse temperature). The correct meaning in each case is indicated by the arguments and is as well clear from context.

The statistical operator of such a system only contains the energy density $h(\mathbf{x})$ and the energy current density $\mathbf{s}(\mathbf{x})$. These quantities satisfy the local energy conservation relation

$$\frac{\partial h(\mathbf{x})}{\partial t} + \mathrm{div} \;\; \mathbf{s}(\mathbf{x}) = 0. \tag{A2}$$

The Hamiltonian and the operator of the total energy current are the volume integrals of these operator densities.

According to Zubarev,[25] such a system can be described by the nonequilibrium statistical operator

$$\hat{\rho}(t) = \frac{1}{Q} \exp\left\{ -\epsilon \int_{-\infty}^{0} dt' \, e^{\epsilon t'} \int d^3\mathbf{x} \beta(\mathbf{x}, t+t') h(\mathbf{x}, t') \right\}. \tag{A3}$$

Time arguments of operators in round brackets denote here (at h) and in the following the Heisenberg representation. The limit of $\epsilon \to +0$ has to be taken after the thermodynamic limit and will not be explicitly stated in the following. Q is the normalization factor, i.e., a (generalized) partition function.

Integration by parts and making use of Eq. (A2) yields

$$\hat{\rho}(t) = Q^{-1}\exp\left\{ -\int d^3\mathbf{x}\beta(\mathbf{x},t)h(\mathbf{x}) + \int_{-\infty}^{0} dt'\, e^{\epsilon t'} \int d^3\mathbf{x}\boldsymbol{\nabla}\beta(\mathbf{x},t+t')\cdot\mathbf{s}(\mathbf{x},t') \right\}, \tag{A4}$$

where the time derivative of the temperature has been neglected, as well as any boundary terms.

Insertion of Eq. (A1) leads to the expression

$$\hat{\rho}(t) = Q^{-1}\exp\left\{ -\beta H + \int_{-\infty}^{0} dt'\, e^{\epsilon t'}\hat{\mathbf{S}}(t')\cdot\boldsymbol{\nabla}\beta(t+t') - \int d^3\mathbf{x}h(\mathbf{x})\,\mathbf{x}\cdot\boldsymbol{\nabla}\beta(t) \right\}. \tag{A5}$$

Up to linear order in the temperature gradient, this yields

$$\hat{\rho}(t) \approx \frac{\exp(-\beta H)}{Q} \times \left\{ 1 + \frac{1}{\beta}\int_{-\infty}^{0} dt' \int_0^{\beta} d\lambda\, e^{\epsilon t'}\hat{\mathbf{S}}(t'-i\hbar\lambda)\cdot\boldsymbol{\nabla}\beta(t+t') - \frac{1}{\beta}\int_0^{\beta} d\lambda \int d^3\mathbf{x}h(\mathbf{x},-i\hbar\lambda)\,\mathbf{x}\cdot\boldsymbol{\nabla}\beta(t) \right\}. \tag{A6}$$

The expectation value of an (arbitrary) operator $\hat{A}$ with the statistical operator (A6)

$$\langle \hat{A}\rangle_t = \mathrm{Tr}\{\hat{\rho}(t)\hat{A}\} \tag{A7}$$

is (omitting the last term)

$$\langle \hat{A}\rangle_t = \langle \hat{A}\rangle^{\mathrm{eq}} + \int_{-\infty}^{0} dt' \int_0^{\beta} d\lambda\, e^{\epsilon t'} \frac{\boldsymbol{\nabla}\beta(t+t')}{\beta}\cdot\langle \hat{\mathbf{S}}(t'-i\hbar\lambda)\hat{A}\rangle^{\mathrm{eq}}. \tag{A8}$$

The symbol $\langle \cdots \rangle^{\mathrm{eq}}$ denotes the expectation value with the equilibrium statistical operator

$$\hat{\rho}^{\mathrm{eq}} = \frac{1}{Q^{\mathrm{eq}}} e^{-\beta H}. \tag{A9}$$

The term omitted in Eq. (A8) corresponds to the difference between the statistical operator of local equilibrium and those of equilibrium (in linear approximation in the temperature gradient, of course)

$$\langle \hat{A}\rangle^{\mathrm{loc}} - \langle \hat{A}\rangle^{\mathrm{eq}}, \tag{A10}$$

where

$$\rho^{\mathrm{loc}} = \frac{1}{Q^{\mathrm{loc}}} e^{-\int d^3\mathbf{x}\beta(\mathbf{x})h(\mathbf{x})}. \tag{A11}$$

The equilibrium expectation value of the current operator is zero as well as the expectation value in local equilibrium. This term is therefore neglected in this work and only briefly considered in the paragraph after Eq. (43).

Applying Eq. (A8) on $\mathbf{S}$ one obtains the known thermal Kubo formula

$$\kappa = \frac{1}{T\mathcal{V}}\int_{-\infty}^{0} dt \int_0^{\beta} d\lambda\, e^{(\epsilon+i\omega)t}\langle \hat{\mathbf{S}}(t-i\hbar\lambda)\hat{\mathbf{S}}\rangle^{\mathrm{eq}}. \tag{A12}$$

The nonequilibrium state of the system will now be taken into consideration in the dynamics of the system instead of in the statistical operator. To this end, the system Hamiltonian H is supplemented by a fictitious external field term H_β^t. The upper index t denotes a possibly explicit time dependence (in this case of the temperature gradient). Now, the sum $H + H_\beta^t$ determines the dynamics, i.e., the time evolution operator U reads

$$U(t,t_0) = \mathcal{T}\exp\left\{ -\frac{i}{\hbar}\int_{t_0}^{t} dt'\,(H + H_\beta^{t'}) \right\}, \tag{A13}$$

($\mathcal{T}$ denotes the time ordering super operator), whereas the statistical operator only contains H (and is those of equilibrium).

The expectation values obtained in this way will (for now) be written with an overbar, to distinguish them from Eq. (A8)

$$\overline{A}_t = \langle U^\dagger(t,t_0)\hat{A}U(t,t_0)\rangle^{\mathrm{eq}}. \tag{A14}$$

The first terms of the Dyson expansion of U with respect to H_β are

$$U(t,t_0) \approx e^{-(i/\hbar)H(t-t_0)}\left(1 - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, H_\beta^{t'}(t'-t_0) \right). \tag{A15}$$

The time argument in round brackets again denotes the Heisenberg representation (with respect to H)

$$H_\beta^{t'}(t) = e^{(i/\hbar)Ht}H_\beta^{t'}e^{-(i/\hbar)Ht}. \tag{A16}$$

The expectation value (A14) up to first order in H_β reads

$$\overline{A}_t = \langle \hat{A}\rangle^{\mathrm{eq}} + \frac{i}{\hbar}\int_{t_0}^{t} dt'\, \langle [H_\beta^{t'}(t'-t_0), \hat{A}(t-t_0)]\rangle^{\mathrm{eq}} \tag{A17}$$

and using the Kubo identity becomes

$$\overline{A}_t = \langle \hat{A}\rangle^{\mathrm{eq}} + \frac{i}{\hbar}\int_{t_0-t}^{0} dt' \int_0^{\beta} d\lambda\, \langle [H_\beta^{t'+t}(t'-i\hbar\lambda), H]\hat{A}\rangle^{\mathrm{eq}}. \tag{A18}$$

The artificial dynamics due to H_β is only relevant in the limit $t - t_0 \to \infty$. It holds (if any of the limits exist)

$$\lim_{t-t_0\to\infty}\overline{A_t}=\lim_{s\to 0}s\int_0^{\infty}d(t-t_0)\,e^{-s(t-t_0)}\overline{A_t}. \tag{A19}$$

Inserting Eq. (A18) and integration by parts yields

$$\lim_{t-t_0\to\infty}\overline{A_t}=\langle\hat{A}\rangle^{\mathrm{eq}}+\lim_{s\to 0}\frac{i}{\hbar}\int_{-\infty}^{0}dt'\,e^{st'}\times\int_0^{\beta}d\lambda\langle[H_{\beta}^{t+t'}(t'-i\hbar\lambda),H]\hat{A}\rangle^{\mathrm{eq}}. \tag{A20}$$

The comparison with Eq. (A8) shows that the nonequilibrium state can be represented by an external field term (in linear order in the temperature gradient), if it satisfies the condition (6).

The time dependence of the temperature gradient (e.g., the frequency ω) has to be weaker (smaller) than the inverse relaxation time in order for the above equivalence to hold.

APPENDIX B: DENSE SYSTEMS

A system of localized states where not only the next nearest neighbors interact but a large quantity of them is a ‘‘dense system’’ in the sense of this work. Specifically, the following shall be the conditions satisfied by a dense system.

(i) There are only a few extended modes: $\mathcal{N}/N\ll 1$.

(ii) The extended modes lie very low energetically: $\omega_{D'}\ll\omega_{\max}$.

(iii) The interaction range of the localized modes spans many atomic distances: $\alpha a\ll 1$.

Because of condition (i), there are about three localized modes per atom. According to condition (ii) the decay into two extended phonons is for most of the localized modes energetically forbidden and the decay current will be omitted. Condition (iii) implies, that very many states interact with any single given state. The diffusive current Eq. (47) is therefore small and can be neglected. This fully corresponds to the equivalent finding in the electron hopping theory (see, e.g., Ref. 21) and can be qualitatively understood as follows. The large number of interacting sites leads to an averaging of their mutual influence, such that the $\delta\mu_m$ become small. The data shown in Fig. 2 verifies this argument. Furthermore, the averages over the energetic and the spatial disorder will be taken independently.

Let us first consider the case of low temperatures ($k_BT\ll\hbar\omega_{D'}$) without a temperature gradient. We assume that only one mode is excited beyond its equilibrium occupation. The relevant rate equation now reads

$$\frac{d}{dt}n_m^{(1)}=-\frac{n_m^{(1)}}{N_m(1+N_m)}\sum_{m'}\Gamma_{m'm} \tag{B1}$$

and the inverse lifetime of mode m equals

$$(\tau_m^h)^{-1}=4\sinh^2(\beta\hbar\omega_m/2)\sum_m\Gamma_{m'm}. \tag{B2}$$

The upper index h indicates, that this lifetime is solely based on hopping processes (i.e., decay processes have been neglected).

Using

$$\Gamma_{m'm}=\mathcal{A}\left(\frac{c}{a\omega_{D'}}\right)^2\left(\frac{\mathcal{N}}{N}\right)\frac{|\omega_m-\omega_{m'}|^3}{2\omega_{D'}\omega_m\omega_{m'}}\frac{\exp(-2\alpha|\mathbf{R}_m-\mathbf{R}_{m'}|)}{\sinh(\beta\hbar\omega_m/2)\sinh(\beta\hbar\omega_{m'}/2)\sinh(\beta\hbar|\omega_m-\omega_{m'}|/2)} \tag{B3}$$

and substituting the sum over m' by an independent average over spatial and energetic disorder

$$\sum_{m'}\to\frac{3N}{\mathcal{V}(\omega_{\max}-\omega_{D'})}\int d^3\mathbf{R}_{m'}\int_{\omega_{D'}}^{\omega_{\max}}d\omega_{m'} \tag{B4}$$

we obtain in the low temperature approximation

$$\tau^h(\omega)=\left(\frac{\omega}{\omega_{D'}}\right)^2\left[\mathcal{A}\left(\frac{c}{a\omega_{D'}}\right)^2\left(\frac{\mathcal{N}}{N}\right)\right]^{-1}\frac{(\alpha a)^3}{3\pi}\,\frac{\omega_{\max}-\omega_{D'}}{\omega_{D'}}, \tag{B5}$$

where ω_m has been replaced by the generic argument ω.

The heat conductivity can be analogously derived for a dense system. The current density reduces to

$$\mathbf{s}=\frac{1}{2\mathcal{V}}\sum_{mm'}\Gamma_{mm'}\hbar(\omega_m\mathbf{R}_m-\omega_{m'}\mathbf{R}_{m'})\hbar\,\frac{\omega_m+\omega_{m'}}{2}\times(\mathbf{R}_m-\mathbf{R}_{m'})\cdot\boldsymbol{\nabla}\beta. \tag{B6}$$

In the limit of high temperatures ($\beta\hbar\omega_{D'}\ll 1$) we obtain (if there is no gap between acoustic and optical phonons, such that $\omega_{D'}=\omega_{\min}$)

$$\kappa=\frac{k_B}{a}\mathcal{A}\left(\frac{c}{a\omega_{D'}}\right)^2\left(\frac{\mathcal{N}}{N}\right)\frac{6\pi}{(\alpha a)^5}\left(\frac{\omega_{D'}}{\omega_{\max}-\omega_{D'}}\right)^2\times\left[\coth\left(\frac{\hbar\omega_{D'}}{2k_BT}\right)-\coth\left(\frac{\hbar\omega_{\max}}{2k_BT}\right)\right], \tag{B7}$$

which is approximately

$$\kappa\approx\mathcal{A}\left(\frac{c}{a\omega_{D'}}\right)^2\left(\frac{\mathcal{N}}{N}\right)\frac{6\pi}{(\alpha a)^5}\left(\frac{\omega_{D'}}{\omega_{\max}-\omega_{D'}}\right)^2\frac{2k_B^2T}{\hbar\omega_{D'}a}. \tag{B8}$$

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