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Hopping theory of heat transport in disordered systems

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Heat transport is studied in a simple model system of Anderson localized optical (carrier) phonons which perform thermally activated hopping due to anharmonic interaction with delocalized acoustic phonons. The corresponding kinetic equations (rate equations) are derived by using the density-matrix formalism. The calculated hopping contribution to the heat conductivity exhibits a linear increase with temperature at lower temperatures and (depending on the choice of parameters) eventually reaches a "saturated" value at higher temperatures. Thus, unlike other authors, we do not need a special mechanism, such as lifetime broadening of the optical phonon states, to explain the transition to the saturation region. Furthermore, we show that particle (carrier) number nonconservation leads to a quenching of the hopping mechanism.

I. INTRODUCTION

In recent years, transport of vibrational energy in disordered insulating solids has attracted great interest in both theoretical[1–20] and experimental[21–28] studies. This interest has been much stimulated by the observation that the temperature dependence of the heat conductivity, $\kappa(T)$, of amorphous solids distinctively differs from that of crystals. In insulating crystals, at low T, κ is a cubic function of T, and at high T it decreases with $1/T$. This behavior can be well described by means of the Peierls-Boltzmann theory of a weakly interacting phonon gas (e.g., Refs. 29, 30 and references therein). In amorphous solids, one can distinguish three characteristic temperature regimes: (i) low T ($T \leq 1\,\mathrm{K}$), where κ is approximately a quadratic function of T, (ii) medium T ($T \approx 10$–$30\,\mathrm{K}$), where κ is constant ("plateau" region), and (iii) high T ($T > 30\,\mathrm{K}$), where κ rises smoothly and (mostly) reaches a limiting or "saturated" value.

The behavior of κ in the regime (i) can be well explained by phonon scattering off two-level systems,[1,2] whereas that in the regimes (ii) and (iii) is less well understood. Regime (ii) has evoked a wide variety of explanations,[5–9,12,14,15] such as Rayleigh scattering, localization, and inelastic scattering of phonons.

Specific attention is at present paid to the regime (iii), where interesting physical phenomena, such as diffusive motion of nonpropagating modes[11,12,19,20,26] or hopping of vibrational excitations,[4,10,17,22,24,27] are emerging as possible transport mechanisms. The diffusive mechanism is based on the idea that disorder is sufficient to cause a phonon mean free path of the order of the interatomic spacing, which implies vibrational modes do not propagate, but disorder is insufficient to cause all the states to localize. This mechanism does not require anharmonicity. By contrast, the hopping mechanism assumes localized vibrational states and needs anharmonicity to allow energy transport between such states.

Both the mechanisms open new conduction channels, in addition to the conventional channel of heat transport, by propagating long-wavelength acoustic modes. Both mechanisms cannot be described within the framework of the Peierls-Boltzmann theory. Which mechanism is actually operative in a given real material is in general an open problem. The current experimental and theoretical situation is not yet quite satisfactory. More experimental data are needed and the transport mechanisms require further theoretical inspection.

It is the purpose of this paper to examine the vibrational hopping transport on the basis of a rate equation approach. Before describing this approach in more detail, let us throw some light on previous studies related to the subject of this paper.

In an early simulation[31] evidence was seen that in a disordered vibrational system anharmonicity can enhance the value of κ at higher T.

The vibrational hopping mechanism was first theoretically studied[4,10] in a fractal system by considering localized vibrational states (fractons) interacting with acoustic modes. The corresponding transition probabilities between localized states were calculated by means of the golden rule. The heat conductivity κ was found to increase at high T linearly with T. It was argued that κ saturates if T is high enough so that the lifetime of the localized modes becomes comparable with the period of their vibrations. The results were applied to regime (iii) mentioned above.

A linear increase of κ with T over a large temperature range, without saturation at high T, was recently observed in certain complex silica glasses and interpreted in terms of vibrational hopping.[27] Results of simulations of $\kappa(T)$ in quasicrystalline systems seem also to support a hopping model.[17] Thermal conductivity experiments on boron carbides suggest hopping of vibrational energy, too.[22,32] In experiments[33] with high-energy nonequilibrium phonons, produced by intense pulsed optical excitations, evidence was seen for localized vibrational states in amorphous silicon, the necessary prerequisite for the hopping mechanism.

It may be argued that vibrational hopping may also be

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an important mechanism of energy transport in complex molecular systems subjected to intense optical excitation for reconstructing chemical bonds.

Thus, vibrational hopping appears to be an interesting transport mechanism, which is possibly operative in various systems. In order to substantiate its physical relevance, it seems to be reasonable not only to perform further studies of material-related aspects of this mechanism, but also to study its general features in suitable model systems by starting from first principles.

A study of the latter kind is the subject of the present paper.

The model system employed must be simple enough to allow a first principles approach, but it must also be complex enough to be physically relevant.

The basic model we use is one wherein the heat carriers are high-frequency (optical) phonons, which are assumed to be localized due to disorder and which are coupled with lower-frequency delocalized (acoustic) phonons.

Ignoring heat-carrier particle-number-nonconserving terms, the corresponding Hamiltonian (see also Refs. 34, 35) reduces to that commonly used in the theory of electron hopping (e.g., Refs. 36, 37), except that in the vibrational model the carrier particles are bosons instead of fermions as in the electronic case. Adopting this Hamiltonian and making use of the density-matrix formalism employed in the theory of electron hopping (e.g., Refs. 36–38) we derive a rate equation (master equation) for vibrational hopping, which allows us to study aspects of changing the carrier-particle statistics from fermions to bosons.

To investigate effects of particle-number nonconservation occurring in vibrational systems, we introduce, *ad hoc*, a corresponding term in the Hamiltonian and show that this term leads to an additional term in the rate equations, which describes carrier-particle decay.

The paper is organized as follows: In Sec. II, the Hamiltonian is introduced. In Sec. III, the heat conductivity in terms of the one-particle density matrix is formulated. In Sec. IV, the rate equations are derived. Section V is devoted to particle number nonconservation. In Sec. VI, the heat conductivity is calculated on the basis of the rate equations. In Sec. VII, we discuss our approach and the results obtained.

II. MODEL HAMILTONIAN

We consider a simplified model system of coupled local high-frequency harmonic oscillators (optical phonons) which interact anharmonically with low-frequency delocalized (acoustic) phonons. Each oscillator can be thought of as corresponding to a given vibrational mode of a single molecule in a molecular crystal. Assuming only one optical phonon branch and, for the time of being, ignoring decay processes of optical phonons, our model may be described by the following Hamiltonian:

$$H=\sum_{m}\epsilon_m a_m^\dagger a_m+\sum_{m\neq m'}J_{m'm}a_{m'}^\dagger a_m+\sum_{m\mathbf{q}}a_m^\dagger a_m\hbar\omega_{\mathbf{q}}\{u_m(\mathbf{q})b_{\mathbf{q}}+u_m^*(\mathbf{q})b_{\mathbf{q}}^\dagger\}+\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}(b_{\mathbf{q}}^\dagger b_{\mathbf{q}}+1/2), \tag{1}$$

where

$$u_m(\mathbf{q})=\frac{1}{\sqrt{2N}}\gamma_m(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}_m}. \tag{2}$$

Here $a_m^\dagger$ (a_m) corresponds to a (Bose) creation (annihilation) operator of a local (optical) mode with frequency $\epsilon_m/\hbar$ at site m; $J_{m'm}$ ("hopping" matrix element) describes the coupling between the oscillators at sites m and m'; $b_{\mathbf{q}}^\dagger$ ($b_{\mathbf{q}}$) corresponds to a (Bose) creation (annihilation) operator of an acoustic phonon with wave vector $\mathbf{q}$ and frequency $\omega_{\mathbf{q}}$ ($\mathbf{q}$ is assumed to include also the index of the vibrational branch); the dimensionless constant $\gamma_m(\mathbf{q})$ describes the coupling between optical and acoustic phonons; $\mathbf{R}_m$ is the position vector of site m; and N denotes the number of molecules in the system.

In the Hamiltonian (1), the optical phonons are described by the first two terms, the acoustic phonons by the fourth term, and the third term represents the interaction between optical and acoustic phonons.

The only anharmonicity in the model is between the local optical oscillators and the acoustic phonons.

$J_{m'm}$ is assumed to be a small quantity and to depend on $|\mathbf{R}_m-\mathbf{R}_{m'}|$. In the presence of disorder, ϵ_m and/or $J_{m'm}$ are random quantities. Moreover, $\gamma_m(\mathbf{q})$ may depend on m in a disordered system, but we shall neglect such dependence.

On studying vibrational hopping, we assume the disorder to be strong enough to localize the optical modes. But we assume the acoustic phonons not to be affected by disorder.

The Hamiltonian (1) can be obtained from the classical Hamiltonian of a two-atomic molecular system by assuming suitable interactions, introducing difference and center of gravity coordinates for each molecule, and expressing the displacement coordinates and conjugated momenta through creation and annihilation operators.

The Hamiltonian (1) is the Bose version of the Hamiltonian commonly used in the theory of electron hopping (cf. Refs. 36, 37).

Applying the polaron canonical transformation[39] to the Hamiltonian (1), we can write it in the form

$$H=\sum_{m}\tilde{\epsilon}_m a_m^\dagger a_m+\sum_{m\neq m'}J_{mm'}a_m^\dagger a_{m'}\Phi_{mm'}+\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}(b_{\mathbf{q}}^\dagger b_{\mathbf{q}}+1/2), \tag{3}$$

where

$$\tilde{\epsilon}_m=\epsilon_m-E_{pm}, \tag{4}$$

with

$$E_{pm}=\frac{1}{2N}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}|\gamma_m(\mathbf{q})|^2 \tag{5}$$

and

$$\Phi_{mm'} = \exp\left\{\frac{1}{\sqrt{2N}}\sum_{\mathbf{q}}\left[\gamma_m(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{R}_m) - \gamma_{m'}(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{R}_{m'})\right]b_{\mathbf{q}} - \text{H.c.}\right\}. \tag{6}$$

Here E_{pm} is the polaron shift of the energy of the mth oscillator and $\Phi_{mm'}$ is the multiphonon operator describing the formation of a polaron cloud.

We omit in the Hamiltonian (6) contributions due to interaction of "polarons" via virtual exchange of acoustic phonons, since already in (1) we have ignored anharmonicity in the optical phonon subsystem.

III. KUBO FORMULA AND HEAT CURRENT OPERATOR

Analogous to the well-known Kubo formula for the electrical conductivity, the thermal Kubo formula[40] relates the thermal conductivity tensor $\kappa_{\mu\nu}$ to (heat) current-current correlation functions as (cf. Refs. 41, 18)

$$\kappa_{\mu\nu} = \frac{1}{kT^2\Omega}\int_0^1 d\lambda \int_{-\infty}^{0} dt\, e^{i(\omega - i\epsilon)t} \times \langle S_\mu(0)S_\nu(t + i\hbar\beta\lambda)\rangle, \quad \epsilon \to +0. \tag{7}$$

Here k is the Boltzmann constant, Ω is the volume of the system, ω represents the frequency of an ac applied temperature gradient (the experimental case corresponds to $\omega = 0$), the symbol $\langle\cdots\rangle$ indicates the thermal average,

$$\langle\cdots\rangle = \mathrm{Tr}(e^{-\beta H}\cdots)/\mathrm{Tr}(e^{-\beta H}) \tag{8}$$

($\beta = 1/kT$), and

$$\mathbf{S}(t) = e^{iHt/\hbar}\mathbf{S}e^{-iHt/\hbar}. \tag{9}$$

The current operator $\mathbf{S}$ is given by

$$\mathbf{S} = \int d\boldsymbol{x}\, \mathbf{s}(\boldsymbol{x}), \tag{10}$$

where the heat current density operator $\mathbf{s}(\boldsymbol{x})$ is defined by the condition of local energy conservation,

$$\dot{h}(\boldsymbol{x}) + \frac{\partial}{\partial \boldsymbol{x}}\mathbf{s}(\boldsymbol{x}) = 0. \tag{11}$$

Here $h(\boldsymbol{x})$ is the Hamiltonian density,

$$h(\boldsymbol{x}) = \sum_m H_m \delta(\boldsymbol{x} - \mathbf{R}_m), \tag{12}$$

and the Hamiltonian is $H = \int d\boldsymbol{x}\, h(\boldsymbol{x})$.

Fourier transforming Eq. (11) and dropping the longitudinal projection, $\mathbf{S} = \mathbf{s}(\mathbf{k} = 0)$ becomes

$$\mathbf{S} = i\frac{\mathbf{k}}{|\mathbf{k}|^2}\dot{h}(\mathbf{k})\Big|_{\mathbf{k}=0}, \tag{13}$$

where

$$\dot{h}(\mathbf{k}) = \frac{i}{\hbar}\sum_m [H, H_m]e^{-i\mathbf{k}\cdot\mathbf{R}_m}. \tag{14}$$

For the model of Sec. II, by means of Eq. (13) we find

$$\mathbf{S} = \mathbf{S}_{\text{ph}} + \mathbf{S}_{\text{op}} + \mathbf{S}_{\text{int}}, \tag{15}$$

where

$$\mathbf{S}_{\text{ph}} = \sum_{\mathbf{q}} \frac{\partial \omega_{\mathbf{q}}}{\partial \mathbf{q}}\hbar\omega_{\mathbf{q}} b_{\mathbf{q}}^\dagger b_{\mathbf{q}} \tag{16}$$

and

$$\begin{aligned}\mathbf{S}_{\text{op}} + \mathbf{S}_{\text{int}} &= \left\{ i\frac{\mathbf{k}}{|\mathbf{k}|^2}\sum_{ll'mm'}\frac{i}{\hbar}\left[\hat{J}_{mm'}a_m^\dagger a_{m'}, \hat{J}_{ll'}a_l^\dagger a_{l'}\right]\right\}_{\mathbf{k}=0} \\ &\simeq \frac{i}{\hbar}\sum_m \mathbf{R}_m\epsilon_m[H, a_m^\dagger a_m] \\ &\quad + \frac{i}{\hbar}\sum_m \mathbf{R}_m\hat{E}_m[H, a_m^\dagger a_m].\end{aligned} \tag{17}$$

Here

$$\hat{J}_{mm'} = \begin{cases} \hat{\epsilon}_m = \epsilon_m + \hat{E}_m & \text{for} \quad m = m', \\ J_{mm'} & \text{for} \quad m \neq m', \end{cases} \tag{18}$$

where

$$\hat{E}_m = \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}}\left\{u_m(\mathbf{q})b_{\mathbf{q}} + u_m^*(\mathbf{q})b_{\mathbf{q}}^\dagger\right\}. \tag{19}$$

The operator $\mathbf{S}_{\text{ph}}$ governs the conventional heat transport by propagating acoustic phonons, while $\mathbf{S}_{\text{op}}$ governs hopping transport of optical phonons, which is expected to dominate at sufficiently high temperatures.

In what follows, we study heat transport by retaining only $\mathbf{S}_{\text{op}}$ in Eq. (15). The corresponding contribution to the heat current can be expressed through the one-particle density matrix, similarly as the electrical current in the case of electron hopping (cf. Appendix A). This can be shown by making use of the nonequilibrium statistical operator[42] (see also Ref. 43)

$$\hat{\rho}(t) = Q^{-1}\exp\left(-\int d\boldsymbol{x}\, B(\boldsymbol{x}, t)\right), \tag{20}$$

where

$$B(\boldsymbol{x}, t) = \epsilon\int_{-\infty}^{0} dt_1\, e^{\epsilon t_1}\beta(\boldsymbol{x}, t + t_1)h(\boldsymbol{x}, t_1), \quad \epsilon \to +0, \tag{21}$$

and Q is determined by

$$\mathrm{Tr}\,\hat{\rho}(t) = 1. \tag{22}$$

Here $\beta(\boldsymbol{x}, t) = 1/kT(\boldsymbol{x}, t)$ and $h(\boldsymbol{x}, t)$ is $h(\boldsymbol{x})$ in the Heisenberg representation [cf. Eq. (9)].

Assuming weak temperature modulation $\delta T(\boldsymbol{x},t)$, then $\beta(\boldsymbol{x},t)$ can be written as $\beta[1-\delta T(\boldsymbol{x},t)/T]$, where $(k\beta)^{-1}$ is the average temperature T. Integrating in Eq. (21) by parts, using Eq. (11), and assuming the temperature gradient ∇T to be spatially constant, one finds to the linear order in the temperature gradient

$$\hat{\rho}(t) \simeq Q^{-1}\left\{1+\int_0^1 d\lambda \int_{-\infty}^{0} dt_1\, e^{\epsilon t_1}\mathbf{S}(t_1+i\hbar\beta\lambda) \right. \\ \left. \times\, \nabla\beta(t+t_1)\right\} e^{-\beta H}, \quad \epsilon \to +0, \tag{23}$$

which is the expression for the statistical operator needed for getting the thermal Kubo formula (7) (cf. Ref. 41).

The one-particle density matrix is defined as

$$\rho_m(t) = \mathrm{Tr}\left[\hat{\rho}(t)a_m^\dagger a_m\right], \tag{24}$$

and, according to Eq. (17), $\mathbf{S}_{\rm op}$ is given by

$$\mathbf{S}_{\rm op} \simeq \frac{i}{\hbar}\sum_m \mathbf{R}_m\epsilon_m[H, a_m^\dagger a_m] \\ = \sum_m \mathbf{R}_m\epsilon_m \frac{d}{dt}a_m^\dagger a_m. \tag{25}$$

Making use of Eqs. (23)–(25), the heat current density $\bar{\mathbf{S}}$,

$$\bar{\mathbf{S}}(t) = \frac{1}{\Omega}\mathrm{Tr}\left[\hat{\rho}(t)\mathbf{S}_{\rm op}\right] \tag{26}$$

(Ω volume of the system), can be expressed as

$$\bar{\mathbf{S}}(t) = \frac{1}{\Omega}\sum_m \mathbf{R}_m\epsilon_m\frac{d}{dt}\rho_m(t), \tag{27}$$

where

$$\rho_m(t) = N_m + \frac{i}{\hbar\beta}e^{i\omega t}\sum_{m'}\mathbf{R}_{m'}\epsilon_{m'}\int_{-\infty}^{0} dt_1\, e^{i(\omega-i\epsilon)t_1} \\ \times \mathrm{Tr}\left\{e^{-\beta H}[(a_m^\dagger a_m),(a_{m'}^\dagger a_{m'})_{t_1}]\right\} \\ \times \nabla\beta/\mathrm{Tr}\left\{e^{-\beta H}\right\}, \epsilon \to +0, \tag{28}$$

with

$$N_m = \mathrm{Tr}\left\{e^{-\beta H}a_m^\dagger a_m\right\}/\mathrm{Tr}\left\{e^{-\beta H}\right\} \tag{29}$$

and $(a_{m'}^\dagger a_{m'})_t$ denotes $a_{m'}^\dagger a_{m'}$ in the Heisenberg representation [cf. Eq. (9)].

It can be readily verified that $\bar{\mathbf{S}}(t)$ from Eqs. (27), (28) agrees with $\bar{\mathbf{S}}(t) = \boldsymbol{\kappa}(\omega)(-\nabla T)e^{i\omega t}$, where $\boldsymbol{\kappa}$ is determined by the Kubo formula (7), with $\mathbf{S}_{\rm op}$ as the heat current operator. Furthermore, the expression for the heat current density, Eqs. (27) – (29), agrees with that for the electron (hopping) current density (in the case of linear response), Eqs. (A1), (A3), and (A4), provided that in the latter expression one makes the replacements

$$e\mathbf{E} \to \epsilon_m\nabla\beta/\beta, \tag{30a}$$

Fermi operators $a_m^\dagger$ $(a_m) \to$ Bose operators a_m^+ (a_m), (30b)

and

$$F_m \to N_m. \tag{30c}$$

Here e is the electron charge, $\mathbf{E}$ is the electrical field, and F_m and N_m are given by Eqs. (A4) and (29), respectively.

Hence, on studying vibrational hopping, we may employ the technique commonly used for electron hopping, which is well developed.

IV. RATE EQUATIONS

In response theory, the stationary current regime may be described by switching on the external field $\mathbf{E}$ either adiabatically at $t \to -\infty$ or suddenly at $t = 0$ (and examining the system at large t). Adopting the latter procedure, electron hopping has been studied (cf. Refs. 36, 37) by means of the density-matrix formalism, which allows electrical fields of any strength to be considered. In this formalism, if necessary, linearization with respect to $\mathbf{E}$ may be carried out at the level of the kinetic (rate) equations (cf. Refs. 36, 38).

Owing to the mathematical equivalence between the problems of electron and vibrational hopping [cf. Eq. (30)], the density-matrix formalism may formally also be applied to vibrational hopping in the presence of a temperature gradient ∇T of any strength, which is switched on at $t = 0$. However, only after linearization the relations obtained become physically relevant.

To study vibrational hopping along this line, we introduce the following generalized one-particle density matrix

$$\rho_m^{m'}(t) = \langle U^\dagger(t)a_m^\dagger a_{m'}U(t)\rangle, \tag{31}$$

where $U(t)$ is the time evolution operator,

$$U(t) = T\exp\left\{-i/\hbar\int_0^t dt'\,\mathcal{H}(t')\right\}, \tag{32}$$

with

$$\mathcal{H}(t) = H + H'(t). \tag{33}$$

Here T is the time-ordering operator, H is the canonically transformed Hamiltonian (3), the symbol $\langle\cdots\rangle$ indicates the thermal average (8) performed with this Hamiltonian, and $H'(t)$ describes the effect of the external perturbation given by [cf. Eq. (30)]

$$H'(t) = -\frac{\nabla\beta(t)}{\beta}\sum_m \epsilon_m\mathbf{R}_m a_m^\dagger a_m. \tag{34}$$

The diagonal elements of the density matrix (31), $\rho_m \equiv \rho_m^m$, are needed for calculating the current density (27). Recall that the polaron canonical transformation does not affect the operator $a^\dagger_m a_m$ and, therefore, we can use the canonically transformed Hamiltonian in Eqs. (24) and (A2).

The equation governing the diagonal elements $\rho_m(t)$ in general also contains off-diagonal elements $\rho^m_{m'}(t)$ with $m \neq m'$. For the latter ones, we find that

$$\rho^m_{m'} \sim \frac{\tilde{J}_{m'm}}{i(\tilde{\epsilon}_{m'} - \tilde{\epsilon}_m)}(\rho_m - \rho_{m'}), \tag{35}$$

where $\tilde{J}_{m'm}$ denotes the quantity $J_{m'm}$ renormalized by the interaction with the acoustic phonons (cf. Ref. 36). Thus, for most of the pairs of sites we have $\rho^m_{m'} \sim (\tilde{J}/\Gamma)(\rho_m - \rho_{m'})$, where Γ is the width of the spread of the oscillator energies. Anderson localization requires $\tilde{J}/\Gamma \ll 1$ and, therefore, in a hopping system it holds that $\rho^m_{m'} \ll \rho_m, \rho_{m'}$. Neglecting the off-diagonal elements of the density matrix, we obtain (in the Markovian limit) the following rate equation:

$$\frac{d\rho_m(t)}{dt} = \sum_{m_1} \{\rho_{m_1}(1 + \rho_m)W_{m_1 m}(t) - \rho_m(1 + \rho_{m_1})W_{m m_1}(t)\}, \tag{36}$$

where

$$W_{m_1 m}(t) = \frac{|\tilde{J}_{m_1 m}|^2}{\hbar^2} \int_{-\infty}^{\infty} dt_1 \exp\left\{\left(\frac{\beta}{2} + \frac{it_1}{\hbar}\right)\left[\tilde{\epsilon}_{m_1} - \tilde{\epsilon}_m - \frac{\nabla\beta(t)}{\beta}(\tilde{\epsilon}_{m_1}\mathbf{R}_{m_1} - \tilde{\epsilon}_m \mathbf{R}_m)\right]\right\} \times \left\{\exp\left[\sum_{\mathbf{q}} \frac{|\gamma(\mathbf{q})|^2[1 - \cos \mathbf{q}(\mathbf{R}_{m_1} - \mathbf{R}_m)]}{N \sinh(\hbar\omega_{\mathbf{q}}\beta/2)} \cos \omega_{\mathbf{q}} t_1\right] - 1\right\}. \tag{37}$$

The hopping probabilities $W_{m_1 m}$ have the symmetry property

$$W_{m_1 m}/W_{m m_1} = \exp\left\{\beta\left[\tilde{\epsilon}_{m_1} - \tilde{\epsilon}_m - \frac{\nabla\beta(t)}{\beta}(\tilde{\epsilon}_{m_1}\mathbf{R}_{m_1} - \tilde{\epsilon}_m \mathbf{R}_m)\right]\right\}, \tag{38}$$

which reflects the principle of detailed balance.

Setting $\nabla\beta$ equal to zero in Eq. (36), we find that

$$\sum_{m_1}\left\{\rho^{(0)}_{m_1}(1 + \rho^{(0)}_m)W^{(0)}_{m_1 m} - \rho^{(0)}_m(1 + \rho^{(0)}_{m_1})W^{(0)}_{m m_1}\right\} = 0, \tag{39}$$

where the superscript (0) denotes the zeroth-order term with respect to $\nabla\beta$ of the corresponding quantity. From Eqs. (38) and (39), we obtain

$$n_m \equiv \rho^{(0)}_m = \left[e^{\beta\tilde{\epsilon}_m} - 1\right]^{-1}, \tag{40}$$

which is the equilibrium occupation number of the oscillator at site m (for $\nabla\beta = 0$ and $J_{mm'} = 0$).

Let us now linearize Eq. (36) with respect to $\nabla\beta$. To this end we write

$$\rho_m(t) = n_m + \rho^{(1)}_m(t), \tag{41a}$$

$$W_{m_1 m}(t) = W^{(0)}_{m_1 m} + W^{(1)}_{m_1 m}(t), \tag{41b}$$

where the superscript (1) denotes the first order in $\nabla\beta$ terms.

Inserting Eq. (41) into Eq. (36) and taking into account Eq. (39) and

$$W^{(1)}_{m_1 m}(t) = -\frac{1}{2}\nabla\beta(t)\,(\tilde{\epsilon}_{m_1}\mathbf{R}_{m_1} - \tilde{\epsilon}_m \mathbf{R}_m)\,W^{(0)}_{m_1 m}, \tag{42}$$

we find that

$$\frac{d\rho^{(1)}_m(t)}{dt} = \sum_{m_1}\Gamma_{m_1 m}\{(\tilde{\epsilon}_m \mathbf{R}_m - \tilde{\epsilon}_{m_1}\mathbf{R}_{m_1})\nabla\beta(t) + \rho^{(1)}_{m_1}/n_{m_1}(1 + n_{m_1}) - \rho^{(1)}_m/n_m(1 + n_m)\}, \tag{43}$$

where $\Gamma_{m_1 m} = \Gamma_{m m_1}$ is the symmetrized hopping probability,

$$\Gamma_{m_1 m} = W^{(0)}_{m_1 m} n_{m_1}(1 + n_m). \tag{44}$$

Assuming $\nabla\beta(t) = \nabla\beta e^{i\omega t}$ and writing

$$\rho^{(1)}_m(t) = \beta n_m(1 + n_m)\delta\mu_m e^{i\omega t}, \tag{45}$$

the linearized rate equation (43) becomes

$$i\omega n_m(1 + n_m)\delta\mu_m = \sum_{m_1}\Gamma_{m_1 m}\left\{(\tilde{\epsilon}_m \mathbf{R}_m - \tilde{\epsilon}_{m_1}\mathbf{R}_{m_1})\frac{\nabla\beta}{\beta} + \delta\mu_{m_1} - \delta\mu_m\right\}, \tag{46}$$

where

$$\Gamma_{m_1 m} = |\tilde{J}_{m_1 m}|^2\left[4\hbar^2\left(\sinh\frac{\beta\tilde{\epsilon}_{m_1}}{2}\right)\left(\sinh\frac{\beta\tilde{\epsilon}_m}{2}\right)\right]^{-1} \times \int_{-\infty}^{\infty} dt \exp\left\{\frac{it}{\hbar}(\tilde{\epsilon}_{m_1} - \tilde{\epsilon}_m)\right\} \times \left\{\exp\left[\sum_{\mathbf{q}}\frac{|\gamma(\mathbf{q})|^2[1 - \cos \mathbf{q}(\mathbf{R}_{m_1} - \mathbf{R}_m)]}{N \sinh(\hbar\omega_{\mathbf{q}}\beta/2)} \times \cos \omega_{\mathbf{q}} t\right] - 1\right\}. \tag{47}$$

In two limiting cases, the time integral in Eq. (47) can be evaluated analytically: (i) for $\delta \equiv \sum_{\mathbf{q}} |\gamma(\mathbf{q})|^2/[N \sinh(\hbar\omega_{\mathbf{q}}\beta/2)] \ll 1$, i.e., weak interaction between the optical and acoustic phonons, $\gamma \ll 1$, and not too high temperatures, and (ii) for $\delta > 1$, i.e., strong interaction, $\gamma > 1$–2, and/or sufficiently high temperatures.

In case (i) we obtain

$$\Gamma_{m_1m} = |\tilde{J}_{m_1m}|^2 \left[(\hbar^2/2\pi) \left(\sinh \frac{\beta\tilde{\epsilon}_{m_1}}{2} \right) \left(\sinh \frac{\beta\tilde{\epsilon}_m}{2} \right) \times \left(\sinh \beta \frac{|\tilde{\epsilon}_{m_1} - \tilde{\epsilon}_m|}{2} \right) \right]^{-1} \times \frac{1}{N} \sum_{\mathbf{q}} |\gamma(\mathbf{q})|^2 [1 - \cos \mathbf{q}(\mathbf{R}_{m_1} - \mathbf{R}_m)] \times \delta(\omega_{\mathbf{q}} - |\tilde{\epsilon}_{m_1} - \tilde{\epsilon}_m|/\hbar), \quad (48)$$

and in case (ii), by means of the method of the steepest descent, we find that

$$\Gamma_{m_1m} = |J_{m_1m}|^2 \sqrt{\pi} \times \left[4\hbar\sqrt{4kTE_a} \left(\sinh \frac{\beta\tilde{\epsilon}_{m_1}}{2} \right) \left(\sinh \frac{\beta\tilde{\epsilon}_m}{2} \right) \right]^{-1} \times \exp(-\beta E_a) \exp\left(-\frac{(\tilde{\epsilon}_{m_1} - \tilde{\epsilon}_m)^2}{16E_a kT} \right), \quad (49)$$

where E_a (the high-temperature small polaron activation energy) is given by

$$E_a = \frac{1}{4N} \sum_{\mathbf{q}} |\gamma(\mathbf{q})|^2 \hbar\omega_{\mathbf{q}} [1 - \cos \mathbf{q}(\mathbf{R}_{m_1} - \mathbf{R}_m)]. \quad (50)$$

As will be discussed in Sec. VI, the expressions (48) and (49) lead to $\kappa \propto T$ and $\kappa \propto 1/\sqrt{T}$, respectively.

V. HEAT CARRIER NONCONSERVATION

To get a first insight into effects of optical phonon nonconservation in hopping transport, we introduce, *ad hoc*, the following additional term to the canonically transformed Hamiltonian (3):

$$H'' = \sum_{m \neq m'} K_{mm'} (a_m^\dagger + a_{m'}) \Phi_{mm'}, \quad (51)$$

where the quantities $K_{mm'}$ are assumed to be proportional to $J_{mm'}$. Such a term can be easily incorporated in our diagrammatic technique (Appendix B).

Equation (51) leads to the following additional term on the right hand side of the rate equation (36):

$$\rho_m(t)[W_1^m(t) + W_2^m(t)] + W_2^m(t). \quad (52)$$

Here

$$W_k^m(t) = (-1)^k \frac{1}{\hbar} \sum_{m_1m_2} \tilde{K}_{m_1m} \tilde{K}_{mm_2} \times \int_{-\infty}^{\infty} dt' \exp\left[-(-1)^k Q_m(t)\, (\beta/2 + it'/\hbar) \right] \left\{ \exp\left[\sum_{\mathbf{q}} \frac{|\gamma(\mathbf{q})|^2}{N \sinh(\hbar\omega_{\mathbf{q}}\beta/2)} a_{mm_1}^{m_2m} \cos \omega_{\mathbf{q}} t' \right] - 1 \right\}, \quad (53)$$

where $k = 1, 2$; $Q_m(t) = \tilde{\epsilon}[1 + \mathbf{R}_m \cdot \boldsymbol{\nabla}\beta(t)/\beta]$, $\tilde{K}_{m'm}$ is the quantity $K_{m'm}$ renormalized by the interaction with the acoustic phonons, similar to $\tilde{J}_{m'm}$ and $J_{m'm}$, and

$$a_{m_km_k'}^{m_im_i'} = \tfrac{1}{2} \{ \cos \mathbf{q}(\mathbf{R}_{m_i} - \mathbf{R}_{m_k'}) + \cos \mathbf{q}(\mathbf{R}_{m_i'} - \mathbf{R}_{m_k}) - \cos \mathbf{q}(\mathbf{R}_{m_i} - \mathbf{R}_{m_k}) - \cos \mathbf{q}(\mathbf{R}_{m_i'} - \mathbf{R}_{m_k'}) \}. \quad (54)$$

Setting $\boldsymbol{\nabla}\beta$ equal to zero, we find that the expression (52) vanishes for the equilibrium occupation number $\rho_m^{(0)} = n_m$ [Eq. (40)]. Furthermore, to the first order in $\boldsymbol{\nabla}\beta$, from Eqs. (36) and (52) we now obtain, instead of Eq. (46),

$$[i\omega + 1/\tau_m] n_m (1 + n_m) \delta\mu_m = -(1/\tau_m) n_m (1 + n_m) \tilde{\epsilon}_m \mathbf{R}_m (\boldsymbol{\nabla}\beta/\beta) + \sum_{m_1} \Gamma_{m_1m} \left\{ (\tilde{\epsilon}_m \mathbf{R}_m - \tilde{\epsilon}_{m_1} \mathbf{R}_{m_1})(\boldsymbol{\nabla}\beta/\beta) + \delta\mu_{m_1} - \delta\mu_m \right\}, \quad (55)$$

where

$$1/\tau_m = [n_m(1 + n_m)\hbar^4]^{-1/2} \times \sum_{m_1m_2} \tilde{K}_{m_1m} \tilde{K}_{mm_2} \int_{-\infty}^{\infty} dt\, e^{\frac{i}{\hbar} t \epsilon_m} \left\{ \exp\left[\sum_{\mathbf{q}} \frac{|\gamma(\mathbf{q})|^2}{N \sinh(\hbar\omega_{\mathbf{q}}\beta/2)} a_{mm_1}^{m_2m} \cos \omega_{\mathbf{q}} t' \right] - 1 \right\}. \quad (56)$$

As compared to Eq. (36), Eq. (55) contains new terms, which describe the decay and generation of optical phonons due to processes governed by the Hamiltonian (51).

VI. RESULTS AND DISCUSSION

A. Parameters and computational procedure

To illustrate the rate equations (46) and (55), we calculate the hopping current (27) on the basis of these equations and study its dependence on the various parameters characterizing the model system in question.

We solve the rate equations numerically for two-dimensional (2D) systems with site (optical oscillator) energies $\tilde{\epsilon}_m$ and positions $\mathbf{R}_m$ distributed at random.

The acoustic phonons are described by a Debye model with Debye frequency ω_D.

The "hopping integral" $J_{mm'}$ between sites m and m' is assumed to decrease exponentially with the distance $|\mathbf{R}_m - \mathbf{R}_{m'}|$ between the sites, $J_{mm'} = J_0 \exp(-2\alpha|\mathbf{R}_m - \mathbf{R}_{m'}|)$, where the parameter α^{-1} characterizes the range of interaction between the oscillators m and m' and J_0 is some constant.

The other parameters characterizing the model system are the mean oscillator energy $\bar{\epsilon}$, the spread of the oscillator energies $\Delta\epsilon$, the constant γ governing the strength of the interaction between optical (carrier) and acoustic phonons, the concentration of sites (optical oscillators) $\mathcal{N}$, and the temperature T. Anderson localization, the prerequisite of hopping (at least for small γ), requires that $\Delta\epsilon > J$, where J is some typical value of $J_{mm'}$.

Heat conduction due to hopping is expected to be relevant for $kT > \hbar\omega_D$.

In what follows, all the energies are given in units of $\hbar\omega_D$, and the temperatures in units of $\hbar\omega_D/k$.

The integral in Eq. (47) is solved using (48) as the first-order approximation and then integrating the difference between (47) and (48) numerically. To calculate the sum over the wave vector $\mathbf{q}$ in Eq. (47) the coupling strength γ is assumed to be independent of $\mathbf{q}$ and the expression $[1 - \cos \mathbf{q}(\mathbf{R}_{m_1} - \mathbf{R}_m)]$ is approximated by $(1/2)[\mathbf{q}(\mathbf{R}_{m_1} - \mathbf{R}_m)]^2$.

Figure 1 shows the temperature dependence of the time integral in Eq. (47) (curve I). For comparison, the analytically obtained values in the limits of weak and strong interaction, corresponding to Eqs. (48) and (49), respectively, are given, too (curves II and III). The parameters chosen are $\tilde{\epsilon}_{m_1} - \tilde{\epsilon}_m = 0.5\,\hbar\omega_D$, $|\mathbf{R}_{m_1} - \mathbf{R}_m| = c/\omega_D$, where c is the sound velocity, and $\gamma^2 = 0.05$. In contrast to the electronic hopping case, where the temperature is usually small as compared to $\hbar\omega_D$, so that the limit of weak interaction is a good approximation, here we have to compute the time integral in (47) numerically to obtain the right temperature dependence of the hopping rates.

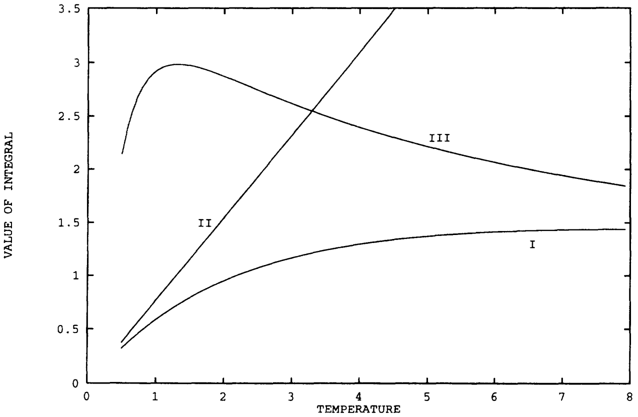

FIG. 1. The numerically computed time integral in the expression for the hopping probability (47) compared with its approximations leading to (48) and (49). Curve I is the numerically computed integral, curve II corresponds to the approximation leading to (48), and curve III corresponds to that one leading to (49). The coupling strength is $\gamma^2 = 0.05$. The temperature T is given in units of $\hbar\omega_D/k$.

The systems studied for calculating the thermal conductivity consist of $\mathcal{N}L^2 = 700$ optical oscillators, where L is the linear size of the system, the site energies $\tilde{\epsilon}_m$ are equally distributed between $2\hbar\omega_D$ and $3\hbar\omega_D$, and $\alpha = 50/L$, except for the two curves in the case of strong disorder discussed in Sec. VI C, for which $\alpha = 200/L$.

On two parallel sides of the system, an area of a tenth of the total system size is considered as a heat bath. The heat baths are simulated by setting $\delta\mu_m - \tilde{\epsilon}_m \mathbf{R}_m \nabla\beta/\beta$ equal to $-\bar{\epsilon}(\beta_B - \beta)/\beta$ at the sites m which are inside these areas, where β_B denotes the corresponding reciprocal heat bath temperature. With these $\delta\mu_m$ as boundary conditions, the remaining quantities $\delta\mu_m$ are calculated by using the systems of equations (46) or (55) with $\omega = 0$.

The magnitude of the calculated heat conductivity of different configurations varies by about a factor of 2 for the system size considered here, but the resulting temperature dependence remains qualitatively unchanged. Thus, for reasons of short computational time, no configurational averaging is performed.

On studying particle nonconservation, the time integrals in Eqs. (47) and (56) are evaluated by means of the method of the steepest descent [cf. Eq. (49)], because the actual temperature dependence of these integrals is irrelevant, if one is interested only in the qualitative effect of the decay rate on the heat conductivity. In this case, the temperature is fixed at $4\,\hbar\omega_D/k$.

Inclusion of particle-nonconserving terms requires a careful choice of the reference temperature $1/(k\beta)$, which is in between the (nearly equal) temperatures of the cold and the warm heat baths. Due to the finiteness of the considered systems, the number of produced optical phonons may not be equal to the number of decaying optical phonons per time unit. This corresponds to a net energy transfer between the subsystem of the acoustic phonons and the subsystem of the optical phonons. To guarantee that heat transport is only due to hopping, the quantity β is chosen such that the net production of optical phonons in the finite system vanishes.

To obtain the magnitude of the ratio between the characteristic decay rate and the hopping probability, the mean decay rate τ^{-1} is calculated as the arithmetic mean of the decay rates τ_m^{-1} of all oscillators in the system, and the mean hopping probability W is calculated as $W_{m_1 m}$ with an energy difference equal to half the width of the optical band. This underestimates the true characteristic ratio τ^{-1}/W but should give the right order of magnitude.

B. Temperature dependence of the heat conductivity

The temperature dependence of the hopping contribution κ to the heat conductivity resulting from Eqs. (27), (45), and (46) (for $\omega = 0$) is illustrated in Fig. 2.

As shown in Fig. 2, curve III, for a strong interaction between optical (carrier) and acoustic phonons ($\gamma > 1$–2; small polaron model) the heat conductivity κ decreases at

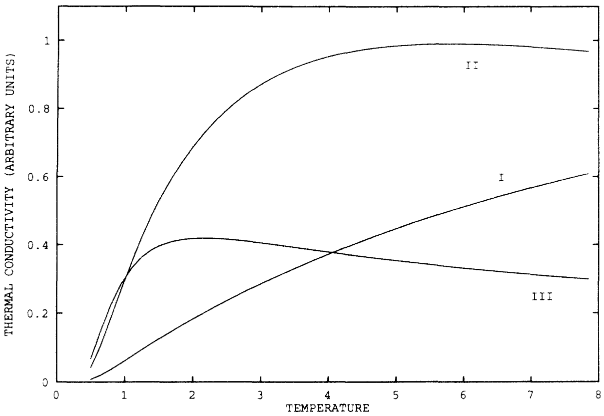

FIG. 2. Temperature dependence of the hopping contribution to the heat conductivity κ for varying strength of the coupling between optical and acoustical phonons; the coupling constant γ is 0.01 for curve I, 0.05 for curve II, and 1.0 for curve III. The temperature T is given in units of $\hbar\omega_D/k$ and the heat conductivity in arbitrary units.

high temperatures with increasing T as $1/\sqrt{T}$. This behavior qualitatively agrees with results of calculations[35] for explaining experimental heat conductivity data of boron carbides.[22]

Furthermore, Fig. 2 shows results for a weak interaction between optical and acoustic phonons ($\gamma < 1$). For a sufficiently small parameter γ (one-phonon hopping processes), the heat conductivity κ increases at high T nearly linearly with T, without changing to a "saturated" value (curve I). Such a behavior has been experimentally observed in certain silica glasses and interpreted as an indication for vibrational hopping transport.[27] On the other hand, using suitable values of the parameters (such that $\sum_{\mathbf{q}} \gamma^2/[N \sinh(\hbar\omega_{\mathbf{q}}/2kT)] > 1$), for a weak interaction ($\gamma < 1$), we can also obtain a linear increase of κ with T at moderate temperatures ($kT \approx \tilde{\epsilon}$) and, at higher temperatures, a change of κ to a saturated value (curve II). Such a behavior has been experimentally observed[21,24] in certain amorphous materials.

According to the fracton-hopping conception,[3,4,10] a linear increase of κ with T may be due to hopping and a crossover to a saturated level due to anharmonicity induced lifetime broadening of the localized vibrational states (fractons), which quenches the hopping mechanism. By contrast, we do not need such a quenching effect for explaining saturation of κ at high temperatures.

In our study, a crossover of κ to saturation results from a careful examination of the integral (47) governing the hopping transitions.

C. Effect of disorder on hopping heat transport

The parameters $\Delta\epsilon$ and $\alpha\mathcal{N}^{-1/d}$ (d dimension of the system), respectively, characterize the energetic and positional disorders in the hopping system under consideration.

To discuss the effect of changing the amount of disorder on vibrational hopping, let us write the heat current $\mathbf{S}$ given by Eqs. (27), (45), and (46) as a sum of two terms,

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2, \tag{57}$$

where

$$\mathbf{S}_1 = \frac{\beta}{2\Omega} \sum_{mm_1} \Gamma_{m_1 m}(\epsilon_m \mathbf{R}_m - \epsilon_{m_1} \mathbf{R}_{m_1}) \times [(\tilde{\epsilon}_{m_1} \mathbf{R}_{m_1} - \tilde{\epsilon}_m \mathbf{R}_m)(-\nabla\beta/\beta)] \tag{58}$$

and

$$\mathbf{S}_2 = \frac{\beta}{2\Omega} \sum_{mm_1} \Gamma_{m_1 m}(\epsilon_m \mathbf{R}_m - \epsilon_{m_1} \mathbf{R}_{m_1})(\delta\mu_{m_1} - \delta\mu_m). \tag{59}$$

Apart from energetic weighting of the hopping distance, the term $\mathbf{S}_1$ has in essence the form (hopping probability times hopping distance squared) obtained for fracton hopping[6,10] by means of the golden rule.

The novel second term $\mathbf{S}_2$ may be viewed of as a diffusive contribution to the heat current, because it is proportional to the quantity $\delta\mu_m$, which describes the redistribution of vibrational energy at site m caused by the temperature gradient. In an ordered system (small polaron model) $\delta\mu_m$ and therefore $\mathbf{S}_2$ vanish.

Figure 3 illustrates the influence of the diffusive contribution $\mathbf{S}_2$ on the heat transport.

For strong disorder ($\alpha\mathcal{N}^{-1/d} \approx 8$ in this case), this contribution may considerably reduce the total heat conductivity. Here the conductivity calculated with inclusion of the diffusive contribution (curve IV) is about two orders of magnitude smaller than the conductivity calculated without the diffusive contribution (curve III). This effect is even more pronounced in 1D than in 2D sys-

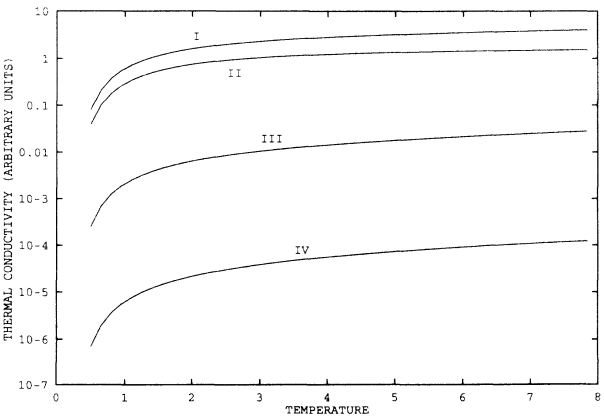

FIG. 3. Hopping contribution to the thermal conductivity κ calculated with and without the diffusive part of the current. Curves I and II are calculated for a system with $\alpha\mathcal{N}^{-1/2} \approx 2$ and curves III and IV for a system with $\alpha\mathcal{N}^{-1/2} \approx 8$. Curves I and III represent the thermal conductivity without the diffusive contribution whereas curves II and IV are calculated with inclusion of the diffusive contribution. The temperature T is given in units of $\hbar\omega_D/k$ and the heat conductivity in arbitrary units. Note that the conductivity axis is logarithmic.

tems, because in one dimension "hard hops" cannot be bypassed by the heat current, in contrast to two dimensions.

For weak disorder ($\alpha\mathcal{N}^{-1/d} \approx 2$), the diffusive current $\mathbf{S}_2$ is small as compared to $\mathbf{S}_1$, so that in this case the total hopping current $\mathbf{S}$ (curve II) is well described solely by $\mathbf{S}_1$ (curves I). They differ by about half an order of magnitude in this case.

Note that in the theory of electron hopping it has been shown that, at least in the one-electron approximation, in the "high-density limit" ($\alpha\mathcal{N}^{-1/d} \approx 1$) the diffusive contribution to the total current may be neglected (cf. Ref. 36).

In contrast to electron hopping, vibrational hopping is in general only weakly affected by energetic disorder. This is due to the high temperatures needed for getting a relevant contribution of hopping to heat transport.

At high temperatures, in a hopping event there is no competition between the spatial and the energetic hopping distances, because all sites are thermally accessible for a jumping vibrational quantum. Such competition, however, may be important for energy redistribution due to hopping in a band of localized modes after locally exciting these modes at low temperatures, for example, by a laser pulse. Note that for large disorder, the time dependence of such energy redistribution process should be intimately related to the frequency dependence of the heat conductivity and, therefore, also to the diffusive current $\mathbf{S}_2$.

Let us yet consider the magnitude of the parameter $\alpha\mathcal{N}^{-1/d}$. For the molecular system discussed in Sec. II, the parameter $\alpha\mathcal{N}^{-1/d}$ is in general of order unity, except for a strongly distorted system.

A large parameter $\alpha\mathcal{N}^{-1/d}$ may be characteristic of a hopping system with a narrow acoustic band but a very broad spectrum of localized optical modes. In such a system, hopping should occur in narrow frequency bands of width $\hbar\omega_D$, which implies a large spread of nearest-neighbor distances between the hopping centers.

Furthermore, the parameter $\alpha\mathcal{N}^{-1/d}$ is also large in systems with a low concentration of optical oscillators (light impurities). In such a system, there will be no relevant hopping contribution to heat conductivity, because the heat capacity of the low concentration of localized modes is small (cf. Ref. 27). However, hopping may be important for energy redistribution in the band of localized states.

D. Effect of heat-carrier nonconservation

Figure 4 shows the heat conductivity κ, calculated by means of Eqs. (27), (46), and (55), in dependence of the decay rate τ^{-1}, which results from particle (carrier) number nonconservation.

As expected, the hopping mechanism is gradually quenched with increasing rate τ^{-1}. At sufficiently large τ^{-1}, the hopping contribution to the heat current vanishes and even becomes negative. To understand the latter fact, we must keep in mind that our theory assumes a fixed temperature gradient $\nabla\beta$ in the system quoted, which requires a diffusive transport mechanism. Such mechanisms are hopping of optical phonons and propagation of scattered acoustic phonons. Thus, in the case that both mechanisms are operative, a large relaxation rate τ^{-1} may lead to a negative hopping contribution, whereas in the case of only a hopping current, the relaxation rate must be small as compared to the hopping rate, in order to justify the assumption of a fixed temperature gradient. Note that only the term $\mathbf{S}_{\mathrm{op}}$ [cf. Eq. (15)] was taken into consideration on calculating the curve shown in Fig. 4.

For a sufficiently small temperature gradient, the first term on the right hand side of Eq. (55) may be approximately written as $-(1/\tau_m)\,n_m(1+n_m)\tilde{\epsilon}_m\,[\beta(\mathbf{R}_m)-\beta]$, where $\beta(\mathbf{R}_m) = 1/kT(\mathbf{R}_m)$, with $T(\mathbf{R}_m)$ the temperature at site $\mathbf{R}_m$. Accordingly, for $T(\mathbf{R}_m) > T$ ($< T$) this term describes generation (annihilation) of additional carrier (optical) phonons.

The second term on the left hand side of Eq. (55) governs the decay of the carrier phonons.

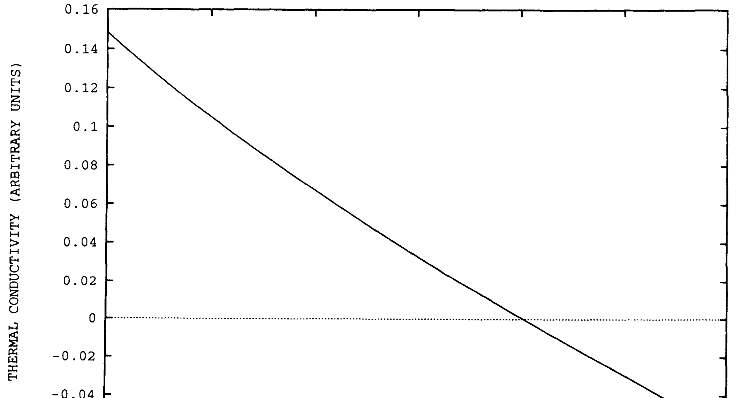

FIG. 4. Influence of the particle-number-nonconserving term on the hopping contribution to the thermal conductivity. The value of $(K_0/J_0)^2$ is proportional to a characteristic τ^{-1}/W, which is in this case by about a factor of 30 larger than $(K_0/J_0)^2$. The heat conductivity κ is in arbitrary units.

VII. CONCLUSIONS

We have shown that, changing the carrier statistics, the model Hamiltonian and the density-matrix formalism used in the theory of electron hopping may, with success, also be applied to vibrational hopping.

Our study is based on the assumption that disorder is strong enough to localize the optical (carrier) phonons. This enables us to neglect the off-diagonal elements of the density matrix on deriving the rate equation for hopping transport.

Off-diagonal elements should be included, if one is interested in effects of anharmonicity induced broadening of the localized states, such as tunneling processes in addition to hopping ones.

We have shown that particle (carrier) number nonconservation leads to a quenching of the hopping mechanism. So far, we have only studied an ad hoc introduced particle-number-nonconserving term in the canonically transformed Hamiltonian, which can be easily incorporated in our density-matrix formalism. A more realistic, but likewise manageable, particle-nonconserving term would be desirable.

On the basis of a careful inspection of the integral governing the hopping probabilities, we have shown that a linear in T increase and a subsequent crossover to a "saturated" level[21,24] of heat conductivity can be explained by heat transport due to vibrational hopping without the necessity of invoking[3,4,10] additional lifetime broadening of the localized states.

But with the aid of a suitable choice of the parameters involved, we can also obtain a linear in T increase of heat conduction over a large temperature range without tendency to saturation.[27] Thus, we expect that our study is not only of purely theoretical interest, but also of interest for experimentalists.

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APPENDIX A: CURRENT DENSITY FOR ELECTRON HOPPING

The current density $\mathbf{j}(t)$ in the case of electron hopping in the presence of an electrical field, as obtained in Ref. 36, is

$$\mathbf{j}(t) = \frac{e}{\Omega} \sum_m \mathbf{R}_m \frac{d\rho_m(t)}{dt}, \tag{A1}$$

where

$$\rho_m(t) = \frac{\mathrm{Tr}\left\{e^{-\beta(H-\mu N)} U^\dagger(t) a_m^\dagger a_m U(t)\right\}}{\mathrm{Tr}\left\{e^{-\beta(H-\mu N)}\right\}}. \tag{A2}$$

Here $N = \sum_m a_m^\dagger a_m$ is the particle number operator, μ is the chemical potential, and $U(t)$ is the time evolution operator (which includes the external electrical field $\mathbf{E}$ as a perturbation). H is the Hamiltonian in zero electrical field.

From Eq. (A2), with $\mathbf{E}(t) = \mathbf{E} e^{\epsilon t} e^{i\omega t}$, we find that

$$\begin{aligned}\rho_m = F_m &+ \frac{ie}{\hbar} e^{i\omega t} e^{\epsilon t} \sum_{m'} \mathbf{R}_{m'} \int_{-\infty}^{0} dt_1\, e^{i(\omega - i\epsilon)t_1} \\ &\times \mathrm{Tr}\left\{e^{-\beta(H-\mu N)} \left[(a_m^\dagger a_m), (a_{m'}^\dagger a_{m'})_{t_1}\right]\right\} \\ &\times \mathbf{E}/\mathrm{Tr}\left(e^{-\beta(H-\mu N)}\right),\end{aligned} \tag{A3}$$

where

$$F_m = \mathrm{Tr}\left(e^{-\beta(H-\mu N)} a_m^\dagger a_m\right) / \mathrm{Tr}\left(e^{-\beta(H-\mu N)}\right). \tag{A4}$$

The expression for the current density from Eqs. (A1) and (A3) agrees with that obtained by means of the Kubo formula (cf. Ref. 40).

APPENDIX B: DIAGRAMMATIC TECHNIQUE

The diagrammatic technique required for evaluating Eq. (31) is similar to that used in the theory of electron hopping, which is explained in Ref. 36. The carrier statistics is now bosonic and the replacements (30) are to be taken into account. By means of this technique, we obtain a hierarchy of equations for $\rho_m^{m'}$ and many-particle density matrices, which require a decoupling.

We include irreducible blocks of second order in J. For the two-particle density matrix

$$R_{m_2 m_4}^{m_1 m_3}(t) = \langle U^\dagger(t) a_{m_4}^\dagger a_{m_3} a_{m_2}^\dagger a_{m_1} U(t)\rangle, \tag{B1}$$

occurring in the equation for $\rho_m^{m'}$, the Hartree-Fock decoupling yields

$$R_{m_2 m_4}^{m_1 m_3} = \delta_{m_2 m_3} \rho_{m_4}^{m_1} + \rho_{m_2}^{m_3} \rho_{m4}^{m_1} + \rho_{m_2}^{m_1} \rho_{m4}^{m_3}. \tag{B2}$$

Note that, in contrast to the electron case, intersections of optical phonon lines do not provide an additional factor in the diagrammatic technique (cf. Ref. 36).

The particle-number-nonconserving term (51) in the Hamiltonian leads to additional interaction points which include either an operator $a_{m_i}^\dagger$ or $a_{m_i'}$ and are associated with factors of the form $\pm \frac{i}{\hbar} \tilde{K}_{m_i m_i'} \exp[\pm \frac{i}{\hbar} \int_0^{t_i} d\tau\, V_{m_i}(\tau)]$, where $V_m(t) = \tilde{\epsilon}_m - \boldsymbol{\nabla}\beta(t) \epsilon_m \mathbf{R}_m / \beta$.

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