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# Nonlinear thermal control in an $N$-terminal junction

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We demonstrate control over heat flow in an $N$-terminal molecular junction. Using simple model Hamiltonians we show that the heat current through two terminals can be tuned by the temperature and coupling parameters of external gating reservoirs. We discuss two models: A fully harmonic system and a model incorporating anharmonic interactions. For both models the control reservoirs induce thermal fluctuations of the transition elements between molecular vibrational states. We find that a fully harmonic model does not show any controllability, while for an anharmonic system the conduction properties of the junction strongly depend on the parameters of the gates. Realizations of the model system within nanodevices and macromolecules are discussed.

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Control over vibrational energy flow in nanoscale structures and single molecules is a long standing goal in many parts of physical science and nanotechnology. Historically, intramolecular vibrational redistribution (IVR) was a topic of great interest in chemistry and physics. IVR processes must be reckoned for understanding, and ultimately controlling, molecular dynamics and chemical kinetics [1]. The efficiency of these processes is the basic assumption behind the well validated Rice-Ramsperger-Kassel-Marcus reaction rate theory [2,3]. From a different perspective, the unexpected results of the computer experiment of Fermi-Pasta-Ulam [4], showing no equipartition of energy among normal modes in harmonic chains including small nonlinear terms, lead to extensive research of IVR in nonlinear systems [5].

Recurrent theoretical interest in this field is due to the impressive progress in probing thermal properties of nanoscale systems such as nanotubes [6–8], self-assembled monolayers [9–11], and thin films [12], and due to the development of more tunable systems [13,14]. Recent progress in molecular electronics and nanomechanics has raised further interest in exploring mechanisms of energy flow in nanolevel systems. In molecular electronics, local heating of nanoscale devices might cause structural instabilities undermining the junction integrity [15–17]. Engineering good thermal contacts and cooling of the junction are necessary for a stable operation mode. Minimization of mechanical devices, e.g., refrigerators [18] and pumps [19], to the molecular scale is a topic of great interest for technologies such as chemical sensing, power generation, and energy conversion [12,20–22]. In this context, it is crucial to understand, and ultimately control, the dynamics of phonons in nanoscale structures or, analogously, vibrational modes in molecular systems.

The heat conduction properties of molecular chains can be tuned either by manipulating the internal molecular parameters, or by externally gating the system. We refer to the first mode of control as "static," or "internal," while, as we explain below, we consider gating as a "dynamical," or "external," control scheme.

Static control is realized by adjusting internal system parameters, e.g., atomic masses and interatomic potential energy, with the goal of an increase or decrease of the system thermal conductivity [23]. This type of control problem has been extensively discussed in the context of Fourier transport. Here the main challenge is to identify the necessary and sufficient conditions for the validity of the Fourier law of heat conductivity $J \propto -\nabla T$ in low dimensions and for quantum systems [24–27]. By engineering the molecular system, one can also build functional devices, for example, a thermal rectifier, where the nanojunction allows heat flux in one direction, while it acts similar to an insulator when the temperature gradient is reversed [13,28–35], and logic gates [36].

In this context we would like to emphasize that tuning the thermal conductance of harmonic chains is also feasible, though these systems demonstrate abnormal (non-Fourier) thermal current. In the language of the thermal Landauer formula [37], this can be accomplished by manipulating the transmission coefficient for phononic heat flow through the device, e.g., by introducing impurities into the structure [38].

In this paper we present a simple model that illustrates an external control over thermal current in molecular systems. The generic setup includes a molecule (subsystem) coupled to $N$ thermal baths of different temperatures. Heat current flowing through the system may be modified by a control reservoir, where, in general, more than one gate may couple to the subsystem. Typical control parameters are the gate temperature and its coupling to the molecular unit. A schematic representation of a three-bath scenario is shown in Fig. 1. We refer to the energetically hot group as $L$, while the $R$ group is the energy accepting side group. We will show here that the current in the $L,R$ terminals can be modulated by tuning the parameters of the $G$ (gate) reservoir.

We consider two realizations of this standard setup. (i) Artificial nanodevices operating as thermal amplifiers or transistors [39]. Here the generic system includes three segments, source, drain, and gate, following the notation used in semiconductor transistors. In such systems one would try to manifest strong gated controllability of the current in the source and drain terminals, while negligible current leaks to the gate. This device may be realized by fabricating branched nanotubes with $T$, $Y$, and $X$ shapes [40,41]. (ii) Macromolecules, e.g., proteins and dendriemds with spatially separated side groups. Energy may be funneled between the molecular groups by a control unit, for example a protein, that can

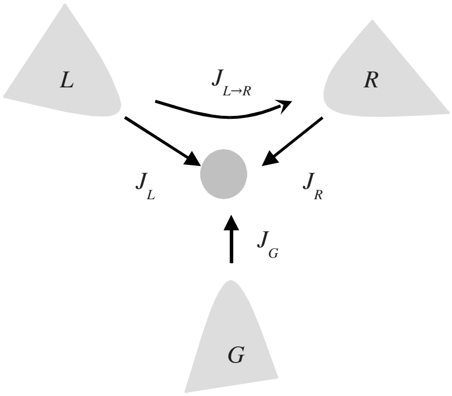

FIG. 1. A schematic representation of the model studied in this work, exemplified on a three-bath system. The molecular units (central part) interacts with multiple thermal reservoirs maintained at constant temperatures. Heat current is defined as positive when flowing into the central molecular segment.

temporarily bind to the system. In such systems we are not necessarily focused on minimizing the energy current from the subsystem to the gating group.

The role of the gate ($G$) may be modeled as inducing thermal fluctuations of the $L$-$R$ transition element [42], thus we refer to this mode of control as dynamical. The control element can also be identified as the solvent itself, modulating system parameters. Inserting a molecule in different mediums may therefore modify its heat conduction properties. In this context this work provides a simple framework for investigating IVR in solutions [43].

The main question to be addressed in this paper is what is the role of anharmonic interactions, specifically, nonbilinear molecule-surface interactions, in controlling the thermal properties of a gated system. It is widely accepted that nonlinear interactions are essential for showing normal (Fourier) transport in molecular chains [25,44]. Anharmonic interactions are also necessary for bringing in rectifying behavior [28–35], and for manifesting nonlinear thermal conductance characteristics [39,45]. We show next that anharmonic interactions are also a crucial element for realizing dynamical control of heat current.

We consider two models. The first system is a prototype for transport in harmonic chains. The second model incorporates anharmonic interactions in the molecule, and also assumes nonbilinear system-bath couplings. For both models we focus on two quantities: (i) We calculate the heat current at the terminal $\nu$, $J_\nu$ and (ii) we investigate the net heat current flowing between two surfaces $J_{\nu\to\mu}$. The objective of our calculation is to demonstrate that these quantities strongly depend on the parameters of the gate reservoirs (temperature and energetics) for the anharmonic model only.

We begin with the harmonic model. In this case both the reservoirs (inverse temperatures $\beta_\nu = T_\nu^{-1}$, $\nu = 1\cdots N$) and the molecular unit are modeled by a set of noninteracting bosons coupled via a bilinear term. For simplicity, we assume that heat transfer in the molecular unit is dominated by a specific single mode

$$H_{\rm BB} = \omega_0 b^\dagger b + \sum_{j,\nu} \omega_j a_{j,\nu}^\dagger a_{j,\nu} + (b^\dagger + b)\sum_{j,\nu} \lambda_{j,\nu}(a_{j,\nu}^\dagger + a_{j,\nu}). \tag{1}$$

Here $b^\dagger$ ($b$) are creation (annihilation) operators for the molecular mode of frequency $\omega_0$. Similarly, $a_{j,\nu}^\dagger$ ($a_{j,\nu}$) are the operators for the mode $j$ of the $\nu$ reservoir. Since system-bath interaction is bilinear, the model Hamiltonian can be exactly diagonalized, to be represented in terms of a set of noninteracting phonons. We refer to model (1) as the boson-boson (BB) Hamiltonian.

The dynamics of the subsystem can be exactly solved using various techniques, e.g., the generalized Langevin equation [38,44] and Master equation formalism [30,45,46]. The result of these calculations is the "thermal Landauer formula" [37,38], where in the classical limit the heat current (for $N=2$) linearly depends on the temperature difference between the two thermal baths. We briefly follow here the derivation within the Master equation formalism, generalizing the results of Refs. [30,45]. for an $N$-terminal system.

Under the assumption of weak system-bath interactions, going into the Markovian limit, the probabilities $P_n$ to occupy the $n$ state of the molecular oscillator satisfy the master equation [45,46]

$$\dot{P}_n = nk_u P_{n-1}(t) + (n+1)k_d P_{n+1}(t) - [nk_d + (n+1)k_u]P_n(t). \tag{2}$$

The nonadiabatic relaxation and excitation rates $k_d$ and $k_u$, respectively, are given by summing up contributions from each reservoir, as no correlations exist between the different baths ($\nu = 1\cdots N$),

$$k_u = \sum_\nu k_u^\nu, \quad k_d = \sum_\nu k_d^\nu. \tag{3}$$

It can be shown that

$$k_d^\nu = \Gamma_\nu(\omega_0)[1 + \bar{n}_\nu(\omega_0)], \quad k_u^\nu = \Gamma_\nu(\omega_0)\bar{n}_\nu(\omega_0), \tag{4}$$

where

$$\Gamma_\nu(\omega_0) = 2\pi \sum_j \lambda_{j,\nu}^2 \delta(\omega_j - \omega_0). \tag{5}$$

Here $\bar{n}_\nu(\omega) = [e^{\omega/T_\nu} - 1]^{-1}$ is the Bose-Einstein distribution function for the $\nu$ reservoir. The heat current properties of this model are obtained from the steady state solution of Eq. (2) with the nonadiabatic rates (3) and (4). The steady state heat flux at the $\nu$ terminal is given by calculating the difference between heat flow from the $\nu$ bath into the molecular mode, leading to vibrational excitations within the molecule, and the outgoing molecule-reservoir energy current, resulting from relaxation processes inside the molecule

$$J_\nu^{(\rm BB)} = -\omega_0 \sum_n n(k_d^\nu P_n - k_u^\nu P_{n-1}). \tag{6}$$

The current is defined positive when flowing from the contact into the molecule. In the classical limit ($T_\nu > \omega_0$) we get [45]

$$J_\nu^{(\mathrm{BB})} = \frac{\Gamma_\nu \sum_\mu \Gamma_\mu (T_\nu - T_\mu)}{\sum_\mu \Gamma_\mu}. \tag{7}$$

Considering this expression, we can identify the directed current $\nu \to \mu$ as

$$J_{\nu\to\mu}^{(\mathrm{BB})} = \frac{\Gamma_\nu \Gamma_\mu (T_\nu - T_\mu)}{\sum_\mu \Gamma_\mu}. \tag{8}$$

We refer next to two specific terminals as source ($L$) and drain ($R$), while all other $N-2$ baths are referred to as gates ($G$). When currents in the $G$ terminals are zero $J_{\nu\neq L,R}=0$, the gates acquire the same temperature in the steady state $T_G =(\Gamma_L T_L+\Gamma_R T_R)/(\Gamma_L+\Gamma_R)$. The current at the $L/R$ contact is then given by

$$J_L^{(\mathrm{BB})} = \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R}(T_L - T_R), \quad J_R = -J_L, \tag{9}$$

which is the same result as obtained when $\Gamma_G=0$, see Eq. (7). We also find that the current $J_{L\to R}$ decays with the number of thermal reservoirs as

$$J_{L\to R}^{(\mathrm{BB})} = \frac{\Gamma_L \Gamma_R}{\sum_\nu \Gamma_\nu}(T_L - T_R) \quad (J_G = 0) \tag{10}$$

due to additional decay channels. To summarize, we find that in the harmonic limit the effect of gate terminals is simply to effectively increase the broadening $\Gamma$, while the gates' temperatures cannot modify the current in the system. Thus, there is no control over the heat dissipated (or absorbed) from the contacts in a purely harmonic system.

Next we show that in a model consisting nonlinear interactions heat current can be strongly controlled by the temperature of a gate terminal. As a case study we consider the spin-boson (SB) model, generalized to include $N$ bosonic reservoirs (creation operators $a_{j,\nu}^\dagger$, $\nu=1\cdots N$) linearly coupled to a spin (two-level) system

$$H_{\mathrm{SB}} = \frac{\Delta}{2}\sigma_x + \frac{\omega_0}{2}\sigma_z + \sum_{j,\nu} \omega_j a_{j,\nu}^\dagger a_{j,\nu} + \frac{\sigma_z}{2}\sum_{j,\nu} \kappa_{j,\nu}(a_{j,\nu}^\dagger + a_{j,\nu}). \tag{11}$$

Here $\omega_0$ is the energy difference between the spin levels with tunneling splitting $\Delta$. In this model internal molecular anharmonicity is introduced by truncating the spectrum of the single molecular mode to include only the lowest two energy states. We do not allow for other phonon-phonon scattering processes, e.g., umklapp processes, that can lead to normal conductivity as in the Peierls model [47]. Using the small polaron transformation [48] it can be shown that this model represents a molecular mode coupled nonbilinearly to the harmonic reservoirs [30],

$$H_{\mathrm{SB}} = \frac{\omega_0}{2}\sigma_z + \sum_{j,\nu} \omega_j a_{j,\nu}^\dagger a_{j,\nu} + \frac{\Delta}{2}(e^{i\Omega}\sigma_+ + e^{-i\Omega}\sigma_-) + H_{\mathrm{shift}}. \tag{12}$$

Here $\Omega=\Sigma_\nu \Omega_\nu$, $\Omega_\nu = i\Sigma_j \frac{\kappa_{j,\nu}}{\omega_j}(a_{j,\nu}^\dagger - a_{j,\nu})$, $H_{\mathrm{shift}}=\Sigma_{j,\nu}\frac{-\kappa_{j,\nu}^2}{4\omega_j}$ is an energy shift henceforth incorporated into the zero order energies. Equation (12) shows that the role of the thermal reservoirs is to modulate the transition elements between molecular vibrational levels. The important feature of this model is that system-bath couplings [Eq. (12)] are multiplicative in the bath degrees of freedom, rather than additive as is the linear harmonic model (3). We do not distinguish in this model between the role of the different reservoirs (source, drain, and gates). One could construct variants of this model, where the gates interact in a distinct functional form. For small $\Delta$ the Hamiltonian leads again to nonadiabatic dynamics, Eq. (2), with $n=0,1$. The rate constants are given by

$$k_u = \frac{\Delta^2}{4}C(-\omega_0), \quad k_d = \frac{\Delta^2}{4}C(\omega_0). \tag{13}$$

Here

$$C(\omega_0) = \int_{-\infty}^{\infty} dt e^{i\omega_0 t} C(t), \quad C(t) = \Pi_\nu C_\nu(t),$$

$$C_\nu(t) = \langle e^{i\Omega_\nu(t)} e^{-i\Omega_\nu(0)}\rangle_\nu. \tag{14}$$

The trace is performed over the $\nu$ reservoir degrees of freedom. For convenience, in what follows we disregard the prefactor $(\Delta/2)^2$. Using the convolution theorem, it can be shown that the function $C(\omega_0)$ can be decomposed in terms of the $N$ reservoirs correlation functions

$$C(\omega_0) = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \cdots \int_{-\infty}^{\infty} d\omega_{N-1} \times C_1(\omega_1) C_2(\omega_2) \cdots C_N(\omega_0 - \omega_1 - \omega_2 - \cdots - \omega_{N-1}), \tag{15}$$

where $C_\nu(\omega)=\int_{-\infty}^{\infty} e^{i\omega t} C_\nu(t) dt$ is identified as the rate constant affected from the $\nu$ thermal bath. The heat flux at the $\nu$ terminal can be formally written for an $N$-terminal system by considering combinations of all processes in which the reservoirs exchange energy with the subsystem [30]

$$\begin{aligned} J_\nu^{(\mathrm{SB})} = -\int_{-\infty}^{\infty} & \omega_\nu d\omega_1 d\omega_2 \cdots d\omega_\nu \cdots d\omega_{N-1} \Pi_{k\neq \nu,N} C_k(\omega_k) \\ & \times [C_\nu(\omega_\nu) C_N(\omega_0 - \omega_1 - \omega_2 \cdots - \omega_\nu \cdots - \omega_{N-1}) P_1 \\ & - C_\nu(-\omega_\nu) C_N(-\omega_1 - \omega_2 \cdots + \omega_\nu \cdots - \omega_{N-1} - \omega_0) P_0]. \end{aligned} \tag{16}$$

For clarity, we include the explicit expression for the heat flux in a three-terminal junctions, measured at terminal "1"

$$J_1^{(\mathrm{SB})}(N=3) = -\int_{-\infty}^{\infty}\omega_1 d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \times[C_1(\omega_1)C_2(\omega_2)C_3(\omega_0-\omega_1-\omega_2)P_1 - C_1(-\omega_1)C_2(\omega_2)C_3(-\omega_0+\omega_1-\omega_2)P_0]. \tag{17}$$

The population of the spin levels is given by $P_0=1-P_1=C(\omega_0)/[C(\omega_0)+C(-\omega_0)]$. Assuming strong coupling, going into the high-temperature classical limit ($T_\nu > \omega_0$), the kernel $C_\nu(t)$ [Eq. (14)] can be calculated in the short time limit [48]

$$C_\nu(t) = e^{-\phi_\nu(t)}, \quad \phi_\nu(t) = iE_M^\nu t + T_\nu E_M^\nu t^2, \tag{18}$$

where $E_M^\nu=\sum_j \frac{\kappa_{j,\nu}^2}{\omega_j}$ is the reorganization energy of the $\nu$ reservoir. In frequency domain we find that

$$C(\omega_0) = \sqrt{\frac{\pi}{T_M E_M}}\exp\left[-\frac{(\omega_0-E_M)^2}{4T_M E_M}\right],$$

$$C_\nu(\omega) = \frac{1}{\sqrt{2T_\nu E_M^\nu}}\exp\left[-\frac{(\omega-E_M^\nu)^2}{4T_\nu E_M^\nu}\right], \tag{19}$$

where $E_M$ is the total ($N$ baths) reorganization energy and $T_M$ is an effective temperature for the subsystem

$$E_M = \sum_\nu E_M^\nu, \quad T_M = \frac{\sum_\nu E_M^\nu T_\nu}{E_M}. \tag{20}$$

Integrating Eq. (16) utilizing Eq. (19) yields the heat current at the $\nu$ contact (ignoring a multiplicative numeric factor of $\sqrt{4\pi}$),

$$J_\nu^{(\mathrm{SB})} = E_M^\nu \frac{\sum_\mu E_M^\mu (T_\nu - T_\mu)}{(E_M T_M)^{3/2}(1+e^{\omega_0/T_M})} e^{-(\omega_0-E_M)^2/4E_M T_M}. \tag{21}$$

The current flowing between the terminals $\nu$ and $\mu$ is given by

$$J_{\nu\to\mu}^{(\mathrm{SB})} = \frac{E_M^\nu E_M^\mu (T_\nu - T_\mu)}{(E_M T_M)^{3/2}(1+e^{\omega_0/T_M})} e^{-(\omega_0-E_M)^2/4E_M T_M}. \tag{22}$$

The temperatures of the gating terminals and their couplings to the molecule appear in a nontrivial way in this expression, leading to strong controllability, as opposed to the harmonic results, Eqs. (7) and (8).

We exemplify control over the heat current in the system by studying a source-drain-gate setup, where two reservoirs are considered as source ($L$) and drain ($R$), while $N-2$ baths are identified as gates ($G$). Under the condition of zero current in the gating terminals ($J_G=0$), the gates temperatures can be determined self consistently to yield $T_G=T_M=(E_M^L T_L + E_M^R T_R)/(E_M^L+E_M^R)$. The current at the source-drain contact then becomes

$$J_L^{(\mathrm{SB})} = -J_R^{(\mathrm{SB})} = (T_L-T_R)\frac{E_M^L E_M^R}{E_M^L+E_M^R}\frac{E_M}{(E_M T_G)^{3/2}}\frac{e^{-(\omega_0-E_M)^2/4E_M T_G}}{(1+e^{\omega_0/T_G})}. \tag{23}$$

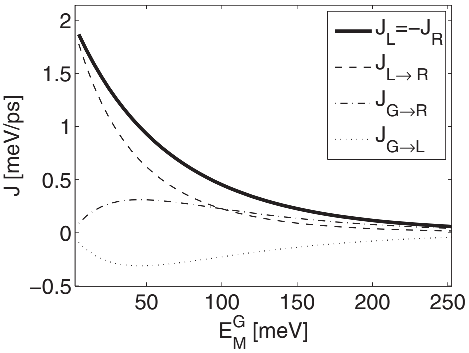

FIG. 2. Control over heat current in a three-terminal configuration under the condition of zero current at the gate $J_G^{(\mathrm{SB})}=0$. The heat current at the $L$ contact (full) strongly decays with $E_M^G$. Also shown are the directed currents $J_{L\to R}^{(\mathrm{SB})}$ (dashed), $J_{G\to R}^{(\mathrm{SB})}$ (dashed-dotted), and $J_{G\to L}^{(\mathrm{SB})}$ (dotted). Other parameters are $T_L=300$ K, $T_R=200$ K, $T_G=250$ K, $E_M^L=E_M^R=50$ meV.

When all gates evenly couple to the subsystem $E_M^\nu=E_M^0$ and for $E_M=NE_M^0>\omega_0$, we find that the current exponentially decays with $N$, corrected by a power law $J_L^{(\mathrm{SB})} \propto \Delta T N^{-1/2} e^{-NE_M^0/4T_G}$, $\Delta T=T_L-T_R$. We can also calculate the $L\to R$ current, again taking $J_G=0$,

$$J_{L\to R}^{(\mathrm{SB})} = (T_L-T_R)\frac{E_M^L E_M^R}{(E_M T_G)^{3/2}}\frac{e^{-(\omega_0-E_M)^2/4E_M T_G}}{(1+e^{\omega_0/T_G})}. \tag{24}$$

In the limit of strong coupling $NE_M^0>\omega_0$, we find that $J_{L\to R}^{(\mathrm{SB})} \propto \Delta T N^{-3/2} e^{-NE_M^0/4T_G}$. Therefore, the temperature $T_G$ serves as an effective activation temperature, exponentially enhancing the directed current, $E_M$ is the energy gap for transport. Note that $J_L/J_{L\to R}=E_M/(E_M^L+E_M^R)$, in analogy with the behavior of the fully harmonic model, Eqs. (9) and (10).

We present next numerical results calculated by applying Eqs. (21) and (22) on a three-terminal ($L$, $R$, and $G$) configuration. The control parameters are the coupling strength of the gate to the subsystem, given in terms of reorganization energy $E_M^G$ and the temperature of the $G$ reservoir. For simplicity we take $\Delta/2=1$ meV.

Figure 2 displays results in the absence of (net) energy flow between the gate and the subsystem. Taking all coupling strengths to be equal sets the gate temperature to $T_G=(T_L+T_R)/2$. Simulating Eq. (23) we find that the current at the $L/R$ interfaces strongly decays with $E_M^G$. We also show strong control over the directed $L\to R$ current using Eq. (24).

Next we modulate the temperature of the gate reservoir, and manifest that the system can act as a good thermal conductor or an insulator, depending on the gate temperature. Figure 3 shows that the system behaves as a bad thermal conductor at low gating temperature $T_G\sim 100$ K, while at $T_G=250$ K (where $J_G=0$) the current is amplified by a factor

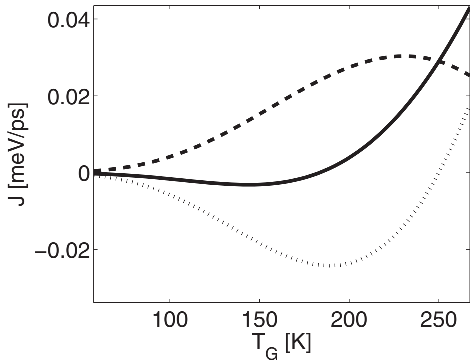

FIG. 3. Switching the heat current in a three-terminal setup: The system behaves as an insulator for low control temperatures, while for high $T_G$ the system becomes a good thermal conductor. $J_L^{(\mathrm{SB})}$ (dashed) and $-J_R^{(\mathrm{SB})}$ (full) are equal at $T_G=250$ K, where $J_G^{(\mathrm{SB})}$ (dotted) diminishes. Other parameters are $T_L=300$ K, $T_R=200$ K, $E_M^L=E_M^R=50$ meV, $E_M^G=300$ meV.

of ∼10. The system can thus act as a switch, with an off-state at low gate temperatures and on-state at high $T_G$. A similar behavior was looked at in nonlinear molecular chains using Langevin dynamics [39].

We can also expose the nonlinear controllability in this model by studying the directed current $J_{\nu\to\mu}$ as a function of the gate temperature. While the experimental observables are in general the $J_\nu$ currents, it is still instructive to show the directed components, manifesting nontrivial behavior.

Figure 4 shows that the $J_{L\to R}^{(\mathrm{SB})}$ flux is strongly enhanced, by two orders of magnitudes, when the gate terminal is strongly coupled to the molecular mode (dashed-dotted line). In contrast, at weak coupling (full line), $J_{L\to R}^{(\mathrm{SB})}$ is insensitive to the presence of the $G$ channel. Since $T_L$ and $T_R$ are higher than $T_G$, energy from both $L,R$ reservoirs is transferred into the gate. However, this process nonlinearly depends on the temperature of the control unit (inset), in contrast to the harmonic behavior $J_{L\to G}^{(\mathrm{BB})}=(T_L-T_G)\Gamma_L\Gamma_G/(\Gamma_L+\Gamma_R+\Gamma_G)$, Eq. (8).

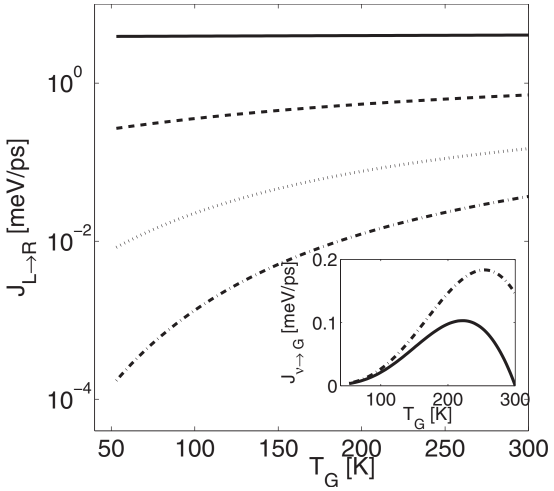

FIG. 4. Control of heat current in a three-terminal configuration. The current $J_{L\to R}^{(\mathrm{SB})}$ can be strongly manipulated by the control bath at strong coupling. $T_L=350$ K, $T_R=300$ K, $E_M^L=E_M^R=50$ meV, $E_M^G=10$ meV (full), 100 (dashed), 200 (dotted), and 300 meV (dashed-dotted). Inset: The energy flow into the gate strongly depends on its temperature $J_{L\to G}^{(\mathrm{SB})}$ (dashed-dotted) and $J_{R\to G}^{(\mathrm{SB})}$ (full), $E_M^G=300$ meV.

As discussed above, the model Hamiltonian (11) could also be introduced for describing transport between two side-groups in a macromolecule immersed in a solvent. In this context, Fig. 4 reveals that changing the solvent temperature may enhance the $L$ to $R$ current, in analogy with the effect of solvent assisted IVR [43].

In conclusion, we have presented two models for the study of thermal transport in gated systems: A purely harmonic system and an anharmonic model. In both cases the gate terminals induce thermal fluctuations of the transition elements between the molecular vibrational states, leading to dynamical control of heat current. We (trivially) found that the purely harmonic setup cannot bring in a gated behavior. In contrast, in the spin-boson model, incorporating anharmonic interactions, the system can behave either as an insulator, or as a good thermal conductor, depending on the gates parameters: temperatures and molecule-bath coupling strength (binding energy using proteins terminology).

We may also explore other variants of the anharmonic model. For example, the central molecular unit can bilinearly and weakly couple to the $L$ and $R$ surfaces, while the gates may couple nonbilinearly-strongly to the subsystem. Such models should basically display the same characteristics as discussed above.

The effects described in this paper may be also studied using classical molecular dynamics (MD) simulations [39]. The advantage of our formalism over such Langevin equation treatment is twofold. (i) Nonbilinear system-surface couplings are difficult to simulate within Langevin dynamics, leading to a coordinate-dependent friction coefficient [49]. (ii) The net heat current between two reservoirs $J_{\nu\to\mu}$ cannot be resolved within MD simulations, only the current at each terminal can be directly obtained. In contrast, one can clearly identify these currents in the analytical expression (22).

The models presented in this paper can be realized by fabricating an $N$ terminal nanodevice. The heat conductance of suspended two-terminal nanotubes was measured by detecting changes in the electric resistance of the attached heater and detector pads [13]. We suggest employing this method in a three-terminal setup, e.g., by connecting a T-shaped nanotube to three conducting surfaces [40,41]. Macromolecules with spatially localized side-groups also offer a playground for realizing these models [43,50].

Nonlinear electrical devices (rectifiers, switches and transistors) have shaped technology in the last 60 years. Nonlinear nanomechanical devices promise to revolutionize the technology of the future as well, whereas phonons, instead of electrons become the carriers of information and the computation element. This paper, presenting a simple study for the control of heat flow in nanosystems, is a first step in addressing this challenge. Introducing quantum effects will further offer new pathways for energy control at the nanoscale [51,52].

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[1] T. Uzer and W. H. Miller, Phys. Rep. **199**, 73 (1991).
[2] R. A. Marcus, J. Chem. Phys. **20**, 359 (1952).
[3] M. Gruebele and P. G. Wolynes, Acc. Chem. Res. **37**, 261 (2004).
[4] E. Fermi, J. Pasta, and S. Ulam, Los Alamos Report No. LA-1940, 1955 (unpublished).
[5] D. K. Campbell, P. Rosenau, and G. M. Zaslavsky, Chaos **15**, 015101 (2005).
[6] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, Phys. Rev. Lett. **87**, 215502 (2001).
[7] M. Fujii, X. Zhang, H. Xie, H. Ago, K. Takahashi, T. Ikuta, H. Abe, and T. Shimizu, Phys. Rev. Lett. **95**, 065502 (2005).
[8] C. H. Yu, L. Shi, Z. Yao, D. Y. Li, and A. Majumdar, Nano Lett. **5**, 1842 (2005).
[9] Z. B. Ge, D. G. Cahill, and P. V. Braun, Phys. Rev. Lett. **96**, 186101 (2006).
[10] R. Y. Wang, R. A. Segalman, and A. Majumdar, Appl. Phys. Lett. **89**, 173113 (2006).
[11] Z. Wang *et al.*, Science **317**, 787 (2007).
[12] C. Chiritescu *et al.*, Science **315**, 351 (2007).
[13] C. W. Chang, D. Okawa, A. Majumdar, and A. Zettl, Science **314**, 1121 (2006).
[14] C. W. Chang *et al.*, Appl. Phys. Lett. **90**, 193114 (2007).
[15] D. Segal and A. Nitzan, J. Chem. Phys. **117**, 3915 (2002).
[16] R. D'Agosta, N. Sai, and M. Di Ventra, Nano Lett. **6**, 2935 (2006).
[17] M. Galperin, M. A. Ratner, and A. Nitzan, J. Phys.: Condens. Matter **19**, 103201 (2007).
[18] O. P. Saira, M. Meschke, F. Giazotto, A. M. Savin, M. Möttönen, and J. P. Pekola, Phys. Rev. Lett. **99**, 027203 (2007).
[19] D. Segal and A. Nitzan, Phys. Rev. E **73**, 026109 (2006).
[20] D. G. Cahill, K. Goodson, and A. Majumdar, J. Heat Transfer **124**, 223 (2002).
[21] M. Blencowe, Phys. Rep. **395**, 159 (2004).
[22] D. Li, S. T. Huxtable, A. R. Abramson, and A. Majumdar, J. Heat Transfer **127**, 108 (2005).
[23] G. Casati, Chaos **15**, 015120 (2005).
[24] F. Bonetto, J. L. Lebowitz, and L. Rey-Bellet, in *Fourier's Law: A Challenge to Theorists, Mathematical Physics*, edited by A. Fokas, A. Grigoryan, T. Kibble, and B. Zegarlinski (Imperial College Press, London, 2000).
[25] S. Lepri, R. Livi, and A. Politi, Phys. Rep. **377**, 1 (2003).
[26] M. Michel, G. Mahler, and J. Gemmer, Phys. Rev. Lett. **95**, 180602 (2005).
[27] E. Pereira and R. Falcao, Phys. Rev. Lett. **96**, 100601 (2006); F. Barros, H. C. F. Lemos, and E. Pereira, Phys. Rev. E **74**, 052102 (2006).
[28] M. Terraneo, M. Peyrard, and G. Casati, Phys. Rev. Lett. **88**, 094302 (2002).
[29] B. Li, L. Wang, and G. Casati, Phys. Rev. Lett. **93**, 184301 (2004).
[30] D. Segal and A. Nitzan, Phys. Rev. Lett. **94**, 034301 (2005); D. Segal and A. Nitzan, J. Chem. Phys. **122**, 194704 (2005).
[31] B. Li, J. Lan, and L. Wang, Phys. Rev. Lett. **95**, 104302 (2005).
[32] B. Hu, D. He, L. Yang, and Y. Zhang, Phys. Rev. E **74**, 060201(R)(2006).
[33] B. Hu, L. Yang, and Y. Zhang, Phys. Rev. Lett. **97**, 124302 (2006).
[34] N. Yang, N. Li, L. Wang, and B. Li, Phys. Rev. B **76**, 020301(R) (2007).
[35] G. Wu and B. Li, Phys. Rev. B **76**, 085424 (2007).
[36] L. Wang and B. Li, Phys. Rev. Lett. **99**, 177208 (2007).
[37] L. G. C. Rego and G. Kirczenow, Phys. Rev. Lett. **81**, 232 (1998).
[38] D. Segal, A. Nitzan, and P. Hänggi, J. Chem. Phys. **119**, 6840 (2003).
[39] B. W. Li, L. Wang, and G. Casati, Appl. Phys. Lett. **88**, 143501 (2006).
[40] M. Menon and D. Srivastava, Phys. Rev. Lett. **79**, 4453 (1997).
[41] P. Yang, Q. F. Sun, H. Guo, and B. Hu, Phys. Rev. B **75**, 235319 (2007).
[42] G. Trinkunas and A. Holzwarth, J. Phys. Chem. B **101**, 7271 (1997).
[43] R. von Benten, O. Link, B. Abel, and D. Schwarzer, J. Phys. Chem. A **108**, 363 (2004).
[44] Harmonic chains with self-consistent reservoirs can also manifest normal heat conductivity, see, e.g., F. Bonetto, J. L. Lebowitz, and J. Lukkarinen, J. Stat. Phys. **116**, 783 (2004); A. Dhar and D. Roy, *ibid.* **125**, 801 (2006).
[45] D. Segal, Phys. Rev. B **73**, 205415 (2006).
[46] S. H. Lin, J. Chem. Phys. **61**, 3810 (1974).
[47] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, 1955).
[48] G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 2000).
[49] B. Carmeli and A. Nitzan, Chem. Phys. Lett. **102**, 517 (1983).
[50] D. Schwarzer, P. Kutne, C. Schröder, and J. Troe, J. Chem. Phys. **121**, 1754 (2004).
[51] K. C. Schwab and M. L. Roukes, Phys. Today **58**, 36 (2005).
[52] N. Mingo, Phys. Rev. B **74**, 125402 (2006).