

Heat flow in nonlinear molecular junctions: Master equation analysis

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(Received 22 December 2005; revised manuscript received 17 February 2006; published 19 May 2006)

We investigate the heat conduction properties of molecular junctions comprising nonlinear interactions. We find that these interactions can lead to phenomena such as negative differential thermal conductance and heat rectification. Based on analytically solvable models we derive an expression for the heat current that clearly reflects the interplay between internal molecular anharmonic interactions, the strength of molecular coupling to the thermal reservoirs, and junction asymmetry. This expression indicates that negative differential thermal conductance shows up when the molecule is strongly coupled to the thermal baths, even in the absence of internal molecular nonlinearities. In contrast, diodelike behavior is expected for a highly anharmonic molecule with an inherent structural asymmetry.

DOI: [10.1103/PhysRevB.73.205415](https://doi.org/10.1103/PhysRevB.73.205415)

PACS number(s): 63.20.Ry, 44.10.+i, 05.60.-k, 66.70.+f

I. INTRODUCTION

Understanding and controlling heat flow in nanoscale structures is of interest both from the fundamental aspect¹ and for device applications.²⁻⁵ The influential role of quantum effects and geometrical constrictions in low dimensional systems often results in fundamentally interesting behavior.⁶ Recent theoretical and experimental studies demonstrated that the thermal transport properties of nanowires can be very different from the corresponding bulk properties.^{7,8} In the low temperature *ballistic* regime the phonon thermal conductance of a one-dimensional (1D) quantum wire is quantized, with $g = \pi^2 k_B^2 T / 3h$ as the universal quantum conductance unit,⁷ where k_B and h are the Boltzmann and Planck constants, respectively, and T is the temperature. Reflections from the boundaries and disorder in the wire can be further treated by considering a Landauer type expression for the heat current ($\hbar = 1$)^{7,9,10}

$$J = \int d\omega \omega \mathcal{T}(\omega) [n_L(\omega) - n_R(\omega)]. \quad (1)$$

This relationship describes energy transfer between two [left (L), right (R)] thermal reservoirs maintained at equilibrium with the temperatures T_L and T_R , respectively, in terms of the temperature independent transmission coefficient $\mathcal{T}(\omega)$ for phonons of frequency ω . Here $n_K(\omega) = (e^{\beta_K \omega} - 1)^{-1}$; $\beta_K = 1/k_B T_K$ ($K=L, R$), is the Bose-Einstein distribution characterizing the reservoirs. This expression assumes the absence of inelastic scattering processes, and the two opposite phonon flows of different temperatures are out of equilibrium with each other. This leads to an anomalous transport of heat, where (classically) the energy flux is proportional to the temperature difference, $\Delta T = T_L - T_R$, rather than to the temperature gradient ∇T as asserted by the Fourier law of conductivity

$$J = -\mathcal{K} \mathcal{A} \nabla T. \quad (2)$$

In this equation \mathcal{A} is the cross section area normal to the direction of heat propagation and \mathcal{K} is the coefficient of thermal conductivity.

Heat conductance experiments on short molecules or highly ordered structures provide results consistent with the

Landauer expression. A micron length individual carbon nanotube conducts heat ballistically without showing signatures of phonon-phonon scattering for temperatures up to 300 K.^{11,12} Intramolecular vibrational energy flow in bridged azulene-anthracene compounds could be explained by assuming ballistic energy transport in the chain connecting both chromophores.¹³ In contrast, calculations of heat flow through proteins show substantial contribution of anharmonic interactions leading to the diffusion of energy, and to an enhancement of the energy current in comparison to the (artificial) purely harmonic situation.¹⁴

An outstanding problem in statistical physics is to find out the necessary and sufficient conditions for attaining the normal (Fourier) law of heat conductivity (2) in low dimensional systems. While classical dynamical systems were intensively investigated in the last fifty years, usually by means of computer simulations,¹⁵⁻¹⁹ there is also an ongoing effort in deriving the Fourier law from quantum dynamics. In a series of papers Michel *et al.* had recently investigated heat conductance in modular quantum systems, e.g., spin chains, within the level of Lindblad theory, and later by using pure Schrödingerian dynamics, demonstrating normal heat conduction for a large class of systems' parameters.²⁰⁻²³ Similar results were presented in Ref. 24 using the Green-Kubo formula for thermal conductivity.²⁵ For quantum spin chains it was numerically demonstrated that the Fourier law holds in correlation with the onset of quantum chaos.²⁶

These studies suggest that one of the crucial requirements for showing normal transport in molecular chains is that the molecular potential energy constitutes anharmonic interactions.²⁷ Nonlinear interactions are also a tool for controlling heat flow in molecular junctions with potential technological applications, e.g., a thermal diode²⁸⁻³⁰ and a thermal transistor.³¹ We have recently demonstrated that when nonlinear interactions govern heat conduction, the heat current is asymmetric for forward and reversed temperature biases, provided the junction has some structural asymmetry.³⁰

In this paper we generalize the model developed in Ref. 30, and present a comprehensive analysis of the heat conduction properties of molecular junctions taking into account nonlinear interactions in the system. Our treatment is done at the level of the master equation for the vibrational states occupation, assuming dephasing processes die out at the rel-

evant timescale for transport. We discuss the influence of the following effects on heat flow through the junction: (i) interparticle potential, specifically the degree of molecular anharmonicity, (ii) molecule-thermal reservoirs contact interactions, and (iii) junction asymmetry with respect to the L and R ends. We derive an exact analytic expression for the heat current that clearly reflects the role of each of these factors in determining phonon dynamics. More specifically, we analyze the necessary conditions for demonstrating negative differential thermal conductance (NDTC) and diodelike behavior.

The paper is organized as follows. Section II presents our model system. Section III begins with a fully harmonic model and shows that it satisfies the Landauer formula. We then proceed and show that an asymmetric anharmonic molecule linearly coupled to thermal reservoirs, can rectify heat. Section IV further presents strong coupling models that exhibit NDTC. Section V provides concluding remarks.

II. MODEL

The model system consists of a molecular unit connecting two thermal reservoirs left (L) and right (R) of inverse temperatures $\beta_L = T_L^{-1}$ and $\beta_R = T_R^{-1}$, respectively. Henceforth we take the Boltzmann constant as $k_B = 1$. The general Hamiltonian includes three contributions: the molecular part (M), the two reservoirs (B), and the system-bath interaction (MB)

$$H = H_M + H_B + H_{MB}. \quad (3)$$

For simplicity we assume that heat transfer is dominated by a specific single mode. The molecular term in the Hamiltonian is therefore given by

$$H_M = \sum_{n=0}^{N-1} E_n |n\rangle\langle n|; \quad E_n = n\omega_0, \quad (4)$$

where ω_0 is the frequency of the molecular oscillator ($\hbar \equiv 1$). We shall consider two situations: harmonic model, and a two-level system (TLS) that simulates a highly anharmonic vibrational mode. For a harmonic molecule N is taken up to infinity. Strong anharmonicity is enforced by limiting n to 0,1. We emphasize that in our model molecular anharmonicity is included only by truncating the spectrum of the single molecular mode. We do not include other phonon-phonon scattering processes, e.g., umklapp processes, that can lead to normal conductivity as in the Peierls model.³²

The molecular mode is coupled either linearly (weakly) or nonlinearly (strongly) to the L and R thermal baths represented by sets of independent harmonic oscillators

$$H_B = H_L + H_R; \quad H_K = \sum_{j \in K} \omega_j a_j^\dagger a_j; \quad K = L, R. \quad (5)$$

a_j^\dagger , a_j are boson creation and annihilation operators associated with the phonon modes of the harmonic baths. The L and R thermal baths are not coupled directly, only through their interaction with the molecular mode. We use the following model for the molecule-reservoir interaction

$$H_{MB} = \sum_{n=1}^{N-1} (B|n-1\rangle\langle n| + B^\dagger|n\rangle\langle n-1|) \sqrt{n}, \quad (6)$$

where B are bath operators. This model assumes that transitions between molecular levels occur due to the environment excitations. Note that in general this interaction does not need to be additive in the thermal baths, i.e., we may consider situations in which $B \neq B_L + B_R$, see Sec. IV.

Under the assumption of weak system-bath interactions and when going into the Markovian limit, the probabilities P_n to occupy the n state of the molecular oscillator are found to satisfy the master equation³³

$$\dot{P}_n = -[nk_d + (n+1)k_u]P_n + (n+1)k_d P_{n+1} + nk_u P_{n-1}, \quad (7)$$

where the occupations are normalized $\sum_n P_n = 1$, and k_d and k_u are the vibrational relaxation and excitation rates, respectively. In second order perturbation theory the relaxation rate is given by the Fermi golden rule, adjusted here to include two independent thermal baths

$$k_d = \frac{2\pi}{Q_L Q_R} \sum_{l,r} \sum_{l',r'} e^{-\beta_L \omega_l} e^{-\beta_R \omega_{r'}} |\langle l', r' | B | l, r \rangle|^2 \times \delta(\omega_{r'} + \omega_{l'} - \omega_r - \omega_l - \omega_0), \quad (8)$$

where l, r (l', r') are initial (final) states of the L and R reservoirs, respectively, and Q_L , Q_R are the partition functions of the thermal baths. We can write the delta function in its Fourier representation and get

$$k_d = \frac{1}{Q_L Q_R} \sum_{l,r} \sum_{l',r'} e^{-\beta_L \omega_l} e^{-\beta_R \omega_{r'}} \int_{-\infty}^{\infty} d\tau e^{-i(\omega_{l'} + \omega_{r'} - \omega_r - \omega_l - \omega_0)\tau} \times \langle l, r | B^\dagger | l', r' \rangle \langle l', r' | B | l, r \rangle. \quad (9)$$

Next we use of the Heisenberg representation of the bath operators $B^\dagger(\tau) = e^{iH_B \tau} B^\dagger e^{-iH_B \tau}$ and the completeness relation $I = |k\rangle\langle k|$ ($k = l', r'$), and obtain the standard expression for the relaxation rate

$$k_d = \int_{-\infty}^{\infty} d\tau e^{i\omega_0 \tau} \langle B^\dagger(\tau) B(0) \rangle. \quad (10)$$

Similar analysis leads to the excitation rate

$$k_u = \int_{-\infty}^{\infty} d\tau e^{-i\omega_0 \tau} \langle B(\tau) B^\dagger(0) \rangle. \quad (11)$$

In both expressions the average is done over the baths thermal distributions, irrespective of the fact that it may involve two distributions of different temperatures. In Sec. IV we demonstrate that Eq. (7) and the corresponding rates (10) and (11) can be also utilized in the strong molecule-baths interaction limit.

A useful concept in the following discussion is the notion of an effective molecular temperature. It can be defined through the relative population of neighboring molecular levels

$$T_M \equiv - \frac{\omega_0}{\ln(P_{n+1}/P_n)}. \quad (12)$$

At steady state this ratio does not depend on n , see Eq. (7). We show below that the molecular temperature is given in terms of the reservoirs temperatures weighted by the molecule-bath coupling strengths.

Given the reservoirs temperatures T_L and T_R , we can define two other related parameters: the temperature difference $\Delta T = T_L - T_R$ and the average temperature $T_a = (T_L + T_R)/2$. The temperature difference can be experimentally imposed in various ways. Here we consider two situations: We may fix the temperature at the left reservoir while varying the temperature at the right side

$$(A) \quad T_L = T_s, \quad T_R = T_s - \Delta T. \quad (13)$$

For the same temperature difference we can also build a symmetric situation where the temperatures of both reservoirs are equally shifted

$$(B) \quad T_L = T_s + \Delta T/2, \quad T_R = T_s - \Delta T/2. \quad (14)$$

The main difference between these two situations is that the average temperature is decreasing steadily with ΔT in the first case, while it is constant (T_s) in (B). We will show below that these boundary conditions determine the effective molecular temperature which implies on the conduction properties of the system. Next we present the model Hamiltonians in the weak and strong molecule-bath interaction limits for either purely harmonic or a TLS molecular mode, and discuss the implications on the junction thermal conductance.

III. WEAK SYSTEM-BATH COUPLING

We begin by analyzing the heat conduction properties of a molecule coupled linearly to two thermal reservoirs of different temperatures.³⁰ The Hamiltonian is given by Eqs. (3)–(6) with linear (harmonic) system-bath interactions

$$H_{MB} = \sum_{n=1}^{N-1} (B|n-1\rangle\langle n| + B^\dagger|n\rangle\langle n-1|)\sqrt{n};$$

$$B = B_L + B_R, \quad (15)$$

where the bath operators B_K satisfy

$$B_K = \sum_{j \in K} \bar{\alpha}_j x_j;$$

$$x_j = (2\omega_j)^{-1/2}(a_j^\dagger + a_j); \quad K = L, R. \quad (16)$$

We restrict ourselves to the weak system-bath coupling regime, namely, we assume that the energy shift due to the coupling is small in comparison to the bare molecular vibrational energy, $\sum_j \frac{\bar{\alpha}_j^2}{\omega_j^2} \ll \omega_0$.¹⁰ We can therefore apply the master equation (7) on the present model. The rate constants (10) and (11) are additive in the L and R reservoirs, since no correlations persist between the thermal baths

$$k_d = k_L + k_R, \quad k_u = k_L e^{-\beta_L \omega_0} + k_R e^{-\beta_R \omega_0}, \quad (17)$$

with

$$k_K = \Gamma_K(\omega_0)[1 + n_K(\omega_0)]; \quad K = L, R. \quad (18)$$

Here $n_K(\omega) = (e^{\beta_K \omega} - 1)^{-1}$, $\Gamma_K(\omega) = \frac{\pi}{2m\omega^2} \sum_{j \in K} \alpha_j^2 \delta(\omega - \omega_j)$, and $\alpha_j = \bar{\alpha}_j \sqrt{2m\omega_0}$,³⁰ where m and ω_0 are the molecular oscillator mass and frequency, respectively.

The heat conduction properties of this model are obtained from the steady state solution of Eq. (7) with the rates specified by Eqs. (17) and (18). The steady-state heat flux calculated, e.g., at the right contact, is given by the sum

$$J = \omega_0 \sum_{n=1}^{N-1} n(k_R P_n - k_R P_{n-1} e^{-\beta_R \omega_0}), \quad (19)$$

where positive sign indicates current going from left to right. In this expression the first term denotes the energy flux going out of the molecular mode into the R reservoir. The second term provides the oppositely going current from the R reservoir into the system. The current could be equivalently calculated at the L contact.

A. Harmonic molecule

For the harmonic model ($N \rightarrow \infty$), putting $\dot{P}_n = 0$ in Eq. (7), and searching a solution of the form $P_n \propto y^n$ we get a quadratic equation for y whose physically acceptable solution is

$$y = \frac{k_L e^{-\beta_L \omega_0} + k_R e^{-\beta_R \omega_0}}{k_L + k_R}, \quad (20)$$

which leads to the normalized state population

$$P_n = y^n (1 - y). \quad (21)$$

Using Eq. (18) we obtain the heat current (19)

$$J = \omega_0 \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} (n_L - n_R). \quad (22)$$

The distribution functions n_K ($K=L, R$) are evaluated at the molecular frequency ω_0 unless otherwise mentioned. In the classical limit $\omega_0/T_K \ll 1$ ($K=L, R$), the current reduces to

$$J = \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} (T_L - T_R). \quad (23)$$

This is a special case [with $\mathcal{T}(\omega) = \Gamma_L \Gamma_R (\Gamma_L + \Gamma_R)^{-1} \delta(\omega - \omega_0)$ consistent with our resonance energy transfer assumption]³⁴ of the Landauer expression, (1). It is also consistent with the standard expression for the heat current through a perfect harmonic chain.³⁵ Note that there is no need to introduce here the concept of the molecular temperature T_M .

We emphasize on three important features of this result. (i) The heat current depends (classically) on the temperature difference between the two reservoirs. (ii) The current is the same when exchanging Γ_L by Γ_R , i.e., rectification cannot take place. (iii) The system cannot show the NDTC behavior, i.e., it is impossible to observe a decrease of the current with increasing temperature difference. This is true considering both models for the temperature drop—A and B, (13) and (14), irrespective of the system symmetry. We can verify it by studying the ΔT derivative of the current (22)

$$\frac{\partial J}{\partial \Delta T} \propto \frac{\partial n_L}{\partial \Delta T} - \frac{\partial n_R}{\partial \Delta T} = \frac{\partial n_L}{\partial \Delta T} + \frac{\partial n_R}{\partial (-\Delta T)}. \quad (24)$$

Since the term

$$\frac{\partial n_L}{\partial \Delta T} = \frac{\omega_0 e^{\beta_L \omega_0}}{T_L^2 (e^{\beta_L \omega_0} - 1)^2} \frac{\partial T_L}{\partial \Delta T} \quad (25)$$

is always positive (or zero), and similarly the second right hand side term, NDTC cannot show up in the fully harmonic model, and the heat current increases monotonically with the temperature difference.

B. Anharmonic molecule

We proceed to the case of a highly anharmonic molecule coupled—possibly asymmetrically—but linearly, to two thermal reservoirs of different temperatures. We simulate strong anharmonicity by modeling the molecular mode by a two levels system (TLS). The Hamiltonian for this model and the resulting rates are the same as presented throughout Eqs. (3)–(19), except that we take $n=0,1$ only. Following Eqs. (7)–(11) we obtain the steady state levels population

$$P_1 = \frac{k_u}{k_u + k_d}; \quad P_0 = \frac{k_d}{k_u + k_d}. \quad (26)$$

We substitute it into Eq. (19) with $N=2$ and get for the heat current³⁰

$$J = \omega_0 \frac{\Gamma_L \Gamma_R (n_L - n_R)}{\Gamma_L (1 + 2n_L) + \Gamma_R (1 + 2n_R)}. \quad (27)$$

Next we calculate the molecular temperature T_M in the weak coupling-TLS case by substituting the population (26) into Eq. (12) using Eqs. (17) and (18). In the classical limit this results in

$$T_M = \frac{\Gamma_L T_L + \Gamma_R T_R}{\Gamma_L + \Gamma_R}. \quad (28)$$

We can now study the implications of the different models for the temperature bias, Eqs. (13) and (14), on the conductance: In model A the molecular temperature decreases monotonically with the temperature difference

$$T_M^{(A)} = T_s - \Delta T \frac{\Gamma_R}{\Gamma_L + \Gamma_R}. \quad (29)$$

In model B we find

$$T_M^{(B)} = T_s + \frac{\Delta T (\Gamma_L - \Gamma_R)}{2 (\Gamma_L + \Gamma_R)}, \quad (30)$$

which implies that for a symmetric ($\Gamma_L = \Gamma_R$) system, the molecular temperature is constant, whereas in the asymmetric situation it can either increase or decrease with ΔT , depending on the sign of $\Gamma_L - \Gamma_R$.

In terms of the molecular temperature [Eq. (28)], going into the classical limit, the heat current (27) reduces into the simple form

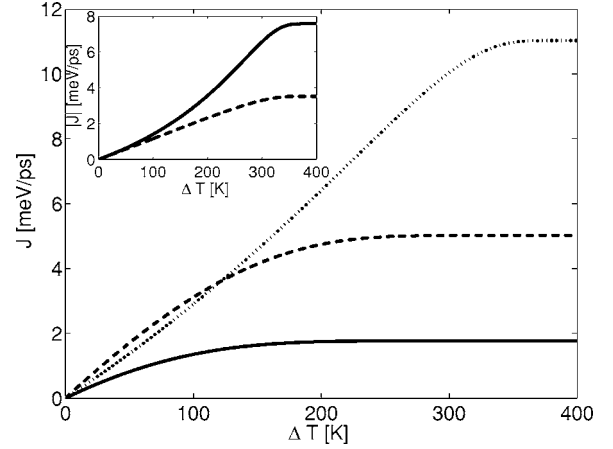


FIG. 1. Conduction properties of a TLS system in the weak coupling limit. $\omega_0=150$ meV (full), 100 meV (dashed), 25 meV (dotted). $T_s=400$ K (model A), $\Gamma_K=1.2$ meV. Inset: Rectifying behavior of this model, $\omega_0=25$ meV, $\chi=0.75$ and $T_L=400$ K, $T_R = T_L - \Delta T$ (full); $T_R=400$ K, $T_L=T_R - \Delta T$ (dashed).

$$J = (T_L - T_R) \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \frac{\omega_0}{2T_M}. \quad (31)$$

This relationship differs from the harmonic expression (23) by its implicit dependence on the internal molecular temperature. If we still try to fit this expression into the Landauer form (1), we find that we have to define an effective temperature dependent transmission coefficient $\mathcal{T}(\omega, T_L, T_R) \propto 1/T_M \delta(\omega - \omega_0)$.

In Fig. 1 we display the current [Eq. (27)] for a representative set of parameters. It increases monotonically with ΔT and saturates at high temperature gaps. We can verify this trend analytically as

$$\frac{\partial J}{\partial \Delta T} = \left[\frac{\partial n_L}{\partial \Delta T} (1 + 2n_R) - \frac{\partial n_R}{\partial \Delta T} (1 + 2n_L) \right] \times \frac{\omega_0 \Gamma_L \Gamma_R (\Gamma_L + \Gamma_R)}{[\Gamma_L (1 + 2n_L) + \Gamma_R (1 + 2n_R)]^2} > 0, \quad (32)$$

which indicates that NDTC can not take place. However, Eq. (27) implies that the system can rectify heat current, i.e., the current can be different (in absolute values) when exchanging the reservoirs temperatures. Following, Ref. 30 defining the asymmetry parameter χ such that $\Gamma_L = \Gamma(1 - \chi)$; $\Gamma_R = \Gamma(1 + \chi)$ with $-1 \leq \chi \leq 1$ we get

$$\Delta J \equiv J(T_L = T_h; T_R = T_c) + J(T_L = T_c; T_R = T_h) = \frac{\omega_0 \Gamma \chi (1 - \chi^2) (n_L - n_R)^2}{(1 + n_L + n_R)^2 - \chi^2 (n_L - n_R)^2}. \quad (33)$$

Here T_c (T_h) relates to the cold (hot) bath. Equation (33) implies that for small $\Delta T = T_L - T_R$, ΔJ grows as ΔT^2 , and that the current is larger (in absolute value) when the cold bath is coupled more strongly to the molecular system. We exemplify this behavior in the inset of Fig. 1.

We found therefore that a system consisting of an anharmonic molecular mode coupled linearly (harmonically) and asymmetrically to two thermal reservoirs of different temperatures can rectify heat, though it cannot manifest the NDTC effect. NDTC requires nonlinear interactions with the thermal baths, which may result in an effective nonlinear temperature dependent molecule-bath coupling term, see Sec. IV. Therefore, there is no direct correspondence between these two phenomena.

C. General expression for the heat current

We can generalize the harmonic (23) and anharmonic (31) results and revise the current in the weak coupling limit (W) as

$$J_W = \omega_0 \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \frac{(T_L - T_R)}{T_M} f_{A,H}, \quad (34)$$

where

$$f_{A,H} = \begin{cases} 1/2, & \text{anharmonic TLS case,} \\ T_M/\omega_0, & \text{harmonic case.} \end{cases} \quad (35)$$

For an intermediate anharmonicity we expect this function to attain an intermediate value $1/2 < f_{A,H} < T_M/\omega_0$. Note that $f_{A,H}$ can be retrieved by going into the classical limit of the function $[\exp(\omega_0/T_M) \pm 1]^{-1}$. Here the TLS case takes the plus sign, and the harmonic model acquires the minus. It can be therefore interpreted as an effective molecular occupation factor.

We can now clearly trace the influence of the different factors on the heat conductance. The thermal current is given by multiplying three terms. (i) A symmetric prefactor that includes the influence of the system-baths coupling. (ii) The factor ω_0/T_M which includes internal molecular properties: frequency and effective temperature. (iii) The molecular occupation factor $f_{A,H}$ that varies between 1/2 for the strictly anharmonic system and T_M/ω_0 in the harmonic case. As we show next the energy current has the same structure when system-bath interactions are strong.

IV. STRONG SYSTEM-BATH COUPLING

We turn now to the situation where the molecular mode is *strongly* coupled to the thermal reservoirs. As before, we discuss two limits, the harmonic case, and the anharmonic TLS situation. In both limits the model Hamiltonian includes the following terms, as in Eqs. (3)–(6),

$$H = \sum_{n=0}^{N-1} E_n |n\rangle\langle n| + \sum_{n=1}^{N-1} \sqrt{n} V_{n-1,n} |n-1\rangle\langle n| e^{i(\Omega_n - \Omega_{n-1})} + \text{c.c.} \\ + \sum_{j \in L,R} \omega_j a_j^\dagger a_j, \quad (36)$$

where $E_n = n\omega_0$, $\Omega_n = \Omega_n^L + \Omega_n^R$, and $\Omega_n^K = i \sum_{j \in K} \lambda_{n,j} (a_j^\dagger - a_j)$ ($K = L, R$). In the Appendix we demonstrate that this model Hamiltonian equivalently represents a displaced molecular mode coupled nonlinearly to two thermal reservoirs. The coefficients $\lambda_{n,j}$ are the effective system-bath interaction pa-

rameters that depend on the level index and the reservoir mode. Strong coupling is imposed by assuming $\sum_j \lambda_{n,j}^2 \omega_j \geq \omega_0$, for details see the Appendix. The Hamiltonian (36) is similar to that defined in Eqs. (4)–(16), except that the L and R system-baths couplings appear as multiplicative rather than additive factors in the interaction term, implying inseparable transport at the two contacts.³⁰ The dynamics is still readily handled. For small V (the “nonadiabatic limit”) the Hamiltonian (36) leads again to the rate equation (7) with

$$k_d = |V|^2 C(\omega_0); \quad k_u = |V|^2 C(-\omega_0), \quad (37)$$

where

$$C(\omega_0) = \int_{-\infty}^{\infty} dt e^{i\omega_0 t} \tilde{C}(t) \quad (38)$$

and

$$\tilde{C}(t) = \langle e^{i[\Omega_n(t) - \Omega_{n-1}(t)]} e^{-i[\Omega_n(0) - \Omega_{n-1}(0)]} \rangle \\ = \langle e^{i[\Omega_n^L(t) - \Omega_{n-1}^L(t)]} e^{-i[\Omega_n^L - \Omega_{n-1}^L]} \rangle_L \\ \times \langle e^{i[\Omega_n^R(t) - \Omega_{n-1}^R(t)]} e^{-i[\Omega_n^R - \Omega_{n-1}^R]} \rangle_R. \quad (39)$$

This may be evaluated explicitly to produce

$$\tilde{C}(t) = \tilde{C}_L(t) \tilde{C}_R(t); \quad \tilde{C}_K(t) = \exp[-\phi_K(t)], \quad (40)$$

with

$$\phi_K(t) = \sum_{j \in K} (\lambda_{n,j} - \lambda_{n-1,j})^2 \{ [1 + 2n_K(\omega_j)] - [1 + n_K(\omega_j)] e^{-i\omega_j t} \\ - n_K(\omega_j) e^{i\omega_j t} \}. \quad (41)$$

Note that we have omitted the n dependence from the rates above. This is supported by (i) taking all the interlevels couplings to be equal, i.e., $|V_{n-1,n}| = V$ and (ii) assuming that $(\lambda_{n,j} - \lambda_{n-1,j})^2$ is the same for all n , e.g., $\lambda_{n,j} \propto n$, see the Appendix.

Explicit expressions may be obtained using the short time approximation [valid for $\sum_{j \in K} (\lambda_{n,j} - \lambda_{n-1,j})^2 \gg 1$ and/or at high temperature] whereupon $\phi(t)$ is expanded in powers of t keeping terms up to order t^2 . This leads to

$$C(\omega_0) = \sqrt{\frac{2\pi}{(D_L^2 + D_R^2)}} \exp\left[\frac{-(\omega_0 - E_M^L - E_M^R)^2}{2(D_L^2 + D_R^2)}\right], \quad (42)$$

where

$$E_M^K = \sum_{j \in K} (\lambda_{n,j} - \lambda_{n-1,j})^2 \omega_j, \\ D_K^2 = \sum_{j \in K} (\lambda_{n,j} - \lambda_{n-1,j})^2 \omega_j^2 [2n_K(\omega_j) + 1]. \quad (43)$$

E_M^K can be considered as the reorganization energy associated with the structural distortions of reservoirs modes around the isolated molecular vibration. In the classical limit ($\omega_0/T_K \rightarrow 0$), $D_K^2 = 2T_K E_M^K$.

Following Ref. 30 we calculate the steady state heat current utilizing

$$J = |V|^2 \sum_{n=1}^{N-1} \int_{-\infty}^{\infty} d\omega \omega [C_R(\omega) C_L(\omega_0 - \omega) P_n - C_R(-\omega) C_L(-\omega_0 + \omega) P_{n-1}], \quad (44)$$

where

$$C(\omega_0) = \int_{-\infty}^{\infty} d\omega C_L(\omega_0 - \omega) C_R(\omega),$$

$$C_K(\omega) = \frac{1}{\sqrt{2E_M^K T_K}} e^{-(\omega - E_M^K)^2 / 4T_K E_M^K}. \quad (45)$$

Equation (44) views the process $|n\rangle \rightarrow |n-1\rangle$ in which the molecular mode loses energy ω_0 as a combination of processes in which the system gives energy ω (or gains it if $\omega < 0$) to the right bath and energy $\omega_0 - \omega$ to the left one, with probability $nC_L(\omega_0 - \omega)C_R(\omega)$. A similar analysis applies to the process $|n-1\rangle \rightarrow |n\rangle$.

A. Harmonic molecule

The levels population of an harmonic molecule ($N \rightarrow \infty$) are calculated from the steady state solution of Eq. (7), leading to $P_n = y^n(1-y)$, $y = k_u/k_d$, with the rates conveyed by Eqs. (37)–(43). We compute the heat current (44) by first making the summation over n

$$\sum_{n=0}^{\infty} n P_n = \frac{C(-\omega_0)}{C(\omega_0) - C(-\omega_0)},$$

$$\sum_{n=0}^{\infty} n P_{n-1} = \frac{C(\omega_0)}{C(\omega_0) - C(-\omega_0)}, \quad (46)$$

then performing the integrals over frequency

$$J = \frac{2\sqrt{\pi}|V|^2 E_M^L E_M^R (T_L - T_R)}{(E_M^L T_L + E_M^R T_R)^{3/2}} \times e^{-[\omega_0 - (E_M^L + E_M^R)]^2 / 4(E_M^L T_L + E_M^R T_R)} \times f_H, \quad (47)$$

with

$$f_H = [e^{\omega_0(E_M^L + E_M^R)/(E_M^L T_L + E_M^R T_R)} - 1]^{-1}. \quad (48)$$

Before we discuss the heat conduction properties of this model we examine the anharmonic system.

B. Anharmonic molecule

The anharmonic model is described by the Hamiltonian (36) with $n=0,1$. The steady state current is therefore obtained by reducing Eq. (44) to

$$J = |V|^2 \int_{-\infty}^{\infty} d\omega \omega [C_R(\omega) C_L(\omega_0 - \omega) P_1 - C_R(-\omega) C_L(-\omega_0 + \omega) P_0]. \quad (49)$$

Here $P_0 = C(\omega_0)/[C(\omega_0) + C(-\omega_0)]$ and $P_1 = 1 - P_0$ are estab-

lished from the steady state solution of Eq. (7) with the rates given by Eq. (37). By following the same steps as for the harmonic system, the heat current (49) is obtained as³⁰

$$J = \frac{2\sqrt{\pi}|V|^2 E_M^L E_M^R (T_L - T_R)}{(E_M^L T_L + E_M^R T_R)^{3/2}} \times e^{-[\omega_0 - (E_M^L + E_M^R)]^2 / 4(E_M^L T_L + E_M^R T_R)} \times f_A, \quad (50)$$

with the occupation factor

$$f_A = [e^{\omega_0(E_M^L + E_M^R)/(E_M^L T_L + E_M^R T_R)} + 1]^{-1}. \quad (51)$$

C. General expression for the heat current

Next the harmonic (47) and anharmonic results (50) are reduced to a common form. We begin by evaluating the internal molecular temperature (12). In the present strong coupling case, for both harmonic and anharmonic molecular modes, it is given by [see Eq. (37)]

$$e^{-\omega_0/T_M} \equiv P_{n+1}/P_n = \frac{C(-\omega_0)}{C(\omega_0)}. \quad (52)$$

Using Eq. (42) we obtain the explicit expression

$$T_M = \frac{D_L^2 + D_R^2}{2(E_M^L + E_M^R)} \xrightarrow{\omega_0/T_K \rightarrow 0} \frac{(E_M^L T_L + E_M^R T_R)}{(E_M^L + E_M^R)}. \quad (53)$$

The effective temperature in the strong coupling limit is therefore given by the algebraic average of the L and R temperatures weighted by the coupling strengths, here conveyed by the reservoirs reorganization energies.

In terms of this quantity we write a general expression for the current in the strong (S) coupling limit as

$$J_S = |V|^2 \sqrt{\frac{4\pi}{T_M(E_M^L + E_M^R)}} e^{-(\omega_0 - E_M^L - E_M^R)^2 / 4T_M(E_M^L + E_M^R)} \times \frac{E_M^L E_M^R}{E_M^L + E_M^R} \frac{T_L - T_R}{T_M} \times f_{A,H}, \quad (54)$$

where

$$f_{A,H} \equiv [e^{\omega_0(E_M^L + E_M^R)/(E_M^L T_L + E_M^R T_R)} \pm 1]^{-1} = (e^{\omega_0/T_M} \pm 1)^{-1}. \quad (55)$$

The plus sign relates to the anharmonic case, the minus stands for the harmonic situation.

We analyze next the conduction properties of this model. Diodelike behavior is expected when $E_M^L \neq E_M^R$, since then the resulting molecular temperature T_M is not the same when exchanging T_L with T_R . Note that in the present strong (non-linear) coupling limit the molecule does not need to be strictly anharmonic for demonstrating this behavior, in contrast to the weak coupling situation.

NDTC can also take place in the system, depending on the system asymmetry and the specific model for the applied temperature gradient. When the temperature bias is applied symmetrically at the L and R sides [model B, Eq. (14)], NDTC occurs for an *asymmetric* $E_M^L \neq E_M^R$ system. In model A the molecular temperature depends on ΔT even for a symmetric junction, providing NDTC.

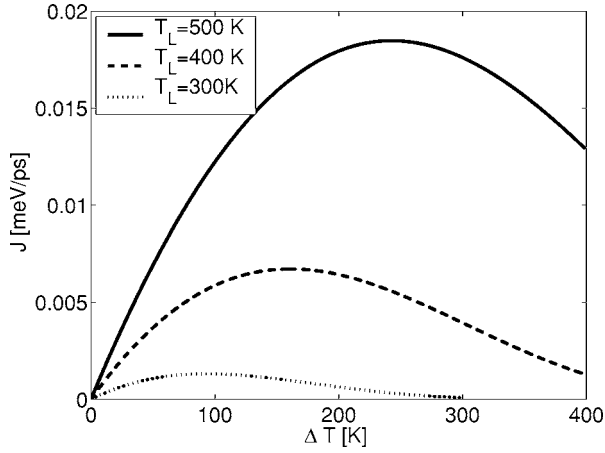


FIG. 2. Conduction properties of the TLS system in the strong coupling limit $T_R = T_L - \Delta T$ (model A), $E_M^K = 300$ meV ($K=L,R$), $V = 1$ meV, $\omega_0 = 10$ meV, $T_L = 500$ K (full), $T_L = 400$ K (dashed), $T_L = 300$ K (dotted).

Figure 2 depicts an example of NDTC behavior in the system. The left reservoir is held at a constant temperature, while the temperature of the R reservoir is decreasing. We find that up to $\Delta T = T_L - T_R \sim 100$ K the current increases with the temperature bias, while above it, i.e., for lower T_R , the current goes down, and even diminishes (dotted line). Figure 3 shows that NDTC takes place in the strong interaction limit, for $E_M^K \gg \omega_0$ (dotted). For weaker system-bath interactions the NDTC effect becomes less significant (dashed), while it completely disappears when $E_M^K \sim \omega_0$ (full).

We can also investigate the effect of asymmetrical contacts. We define the asymmetry parameter χ such as $E_M^L = E_M(1 - \chi)$, $E_M^R = E_M(1 + \chi)$, $0 < \chi < 1$. Figure 4 presents the heat current when $\chi \neq 0$. (a) For small χ the current is almost the same for both forward and reversed operation modes. (b) At intermediate χ values we find that for $T_L = 100$ K, $T_R = 300$ K there is a maximal heat flow (dashed), while for the

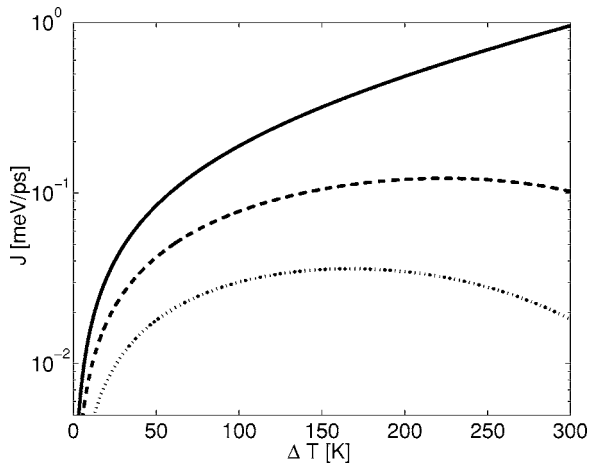


FIG. 3. Controlling NDTC by modifying system-baths interaction strengths for a TLS model in the strong coupling limit. $T_R = T_L - \Delta T$ (model A), $T_L = 300$ K, $V = 1$ meV, $\omega_0 = 10$ meV, $E_M^K = 10$ (full), $E_M^K = 100$ (dashed), $E_M^K = 150$ (dotted).

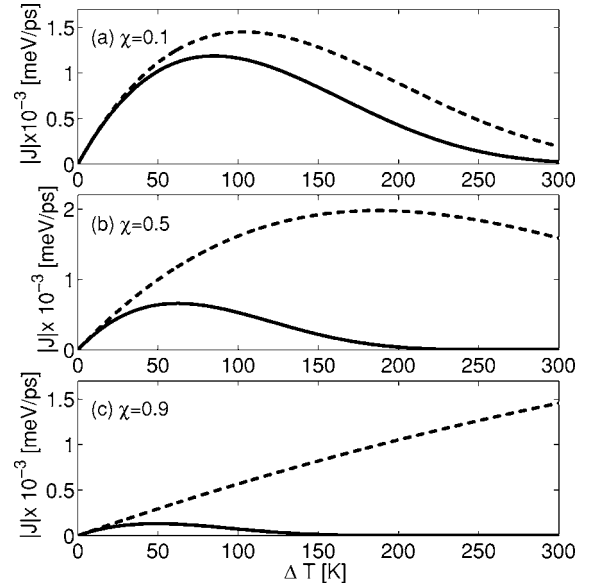


FIG. 4. Rectification in the strong coupling limit for a TLS system. $E_M = 300$ meV, $V = 1$ meV, $\omega_0 = 10$ meV, $T_L = 300$ K, $T_R = T_L - \Delta T$ (full); $T_R = 300$ K, $T_L = T_R - \Delta T$ (dashed).

reversed operation ($T_R = 100$ K, $T_L = 300$ K) heat current is blocked (full). (c) For a highly asymmetric system heat flows predominantly in one direction.

We can further formulate a general expression for the current that holds in *both* strong and weak interaction regimes and for either harmonic or anharmonic systems. For convenience, we copy here the weak (W) linear coupling result (34)

$$J_W = \omega_0 \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \frac{(T_L - T_R)}{T_M} f_{A,H}. \quad (56)$$

Comparing it to Eq. (54) guides us to the compact expression

$$J = C \frac{f_{A,H}}{T_M} \Delta T. \quad (57)$$

Here C includes the contact contribution, which is different in the weak and strong coupling regimes. It may depend on the molecule-baths microscopic couplings, molecular vibrational frequency and the reservoirs temperatures. It is not influenced by the degree of molecular harmonicity which affects only the occupation factor $f_{A,H}$. The temperature T_M provides the effective temperature of the molecular system that is irrelevant in the fully harmonic case. We can therefore clearly distinguish in this expression between the role of the system harmonicity and the effect of molecule-bath interactions.

V. CONCLUSIONS

Using a simple theoretical model we have investigated the effect of nonlinear interactions on heat flow through molecular junctions. Our general expressions for the heat current (34) and (54) clearly manifest the interplay between the system anharmonicity, system-bath coupling and junction asymmetry. We have found that nonlinear interactions can lead to

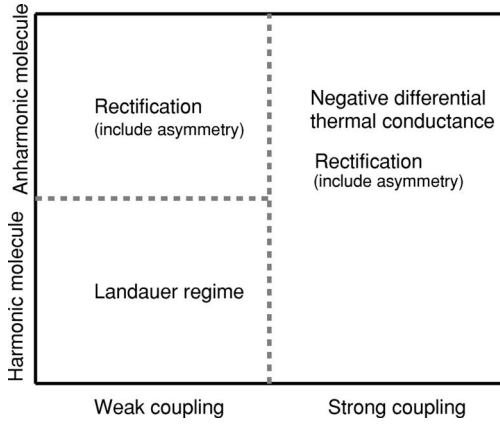


FIG. 5. An overview of the parameter ranges providing negative differential thermal conductance (NDTC) and diodelike behavior. The x axis (weak and strong coupling) relates to the system-bath interaction model. In order to obtain rectification the system should be asymmetric with respect to the L and R ends.

phenomena such as negative differential thermal conductance and heat rectification. NDTC takes place when the molecular mode is strongly coupled to the thermal environment. In contrast, diodelike behavior originates from the combination of substantial molecular anharmonicities with a structural asymmetry. These effects might be observed in mesoscopic-scale magnetic systems.³⁶ Figure 5 presents an overview of the different regimes studied, and the nonlinear effects observed in each case.

We would also like to draw an analogy between the nonlinear behavior discussed in this paper and some nonlinear effects discovered in molecular level *electron* carrying systems: The negative differential resistance observed in molecular films of C_{60} could be explained due to a voltage dependent tunneling barrier.³⁷ Rectification of electron current was theoretically exhibited in one-dimensional asymmetric electronic conductors with screened electron-electron interactions.³⁸

Control of heat flow through molecules by employing nonlinear interactions might be useful for different applications. In molecular electronic local heating of nanoscale devices might cause structural instabilities undermining the junction integrity.³⁹ Engineering good thermal contacts and cooling of the the junction⁴⁰ are necessary for a stable and reliable operation mode. Control of vibrational energy transfer in molecules affects chemical processes, e.g., reaction pathways, bond breaking processes, and folding dynamics.⁴¹ Finally, we propose building technological devices based on heat flow, in analogy with electron current devices.⁴²

ACKNOWLEDGMENTS

The author would like to thank A. Nitzan for his comments. This project was supported by the Feinberg graduate school of the Weizmann Institute.

APPENDIX: MICROSCOPIC MODEL FOR THE STRONG COUPLING HAMILTONIAN

The strong coupling Hamiltonian (36) can be derived from the following microscopic model:

$$H = \sum_{n=0}^{N-1} n \omega_0 |n\rangle\langle n| + \sum_{j \in L,R} \frac{\omega_j^2}{2} \left(x_j - \sum_{n=0}^{N-1} \frac{n \alpha_{n,j}}{\omega_j^2} |n\rangle\langle n| \right)^2 + \sum_{n=1}^{N-1} \sqrt{n} V_{n,n-1} |n\rangle\langle n-1| + \sqrt{n} V_{n-1,n} |n-1\rangle\langle n| + \sum_{j \in L,R} \frac{p_j^2}{2}, \quad (\text{A1})$$

which describes a forced oscillator of frequency ω_0 strongly interacting with the L and R thermal baths. The nonlinear contributions are concealed in the second element of (A1) providing high order terms such as $\propto x_j^2$, with x as the molecular coordinate. Here x_j and p_j are the displacement and momentum of the reservoirs harmonic modes with frequency ω_j , $\alpha_{n,j}$ is the system-bath coupling parameter and $V_{n,n-1}$ is the effective interlevel matrix element. We can expand the quadratic term in Eq. (A1) and obtain

$$H = \sum_{n=0}^{N-1} n \left(\omega_0 - \sum_{j \in L,R} x_j \alpha_{n,j} \right) |n\rangle\langle n| + \sum_{n=1}^{N-1} \sqrt{n} V_{n,n-1} |n\rangle\langle n-1| + \sqrt{n} V_{n-1,n} |n-1\rangle\langle n| + \sum_{j \in L,R} \omega_j a_j^\dagger a_j + \sum_{n=0}^{N-1} \sum_{j \in L,R} \frac{n^2 \alpha_{n,j}^2}{2 \omega_j^2} |n\rangle\langle n|. \quad (\text{A2})$$

Here $x_j = (a_j^\dagger + a_j) / \sqrt{2 \omega_j}$ and $p_j = i \sqrt{\omega_j} / 2 (a_j^\dagger - a_j)$. Strong coupling is imposed by assuming the energy shift due to the system-bath coupling is large, i.e., $\sum_j (n^2 \alpha_{n,j}^2 / 2 \omega_j^2) \approx \omega_0$. Use of the small polaron transformation,⁴³ $\tilde{H} = U H U^{-1}$, leads to

$$\tilde{H} = \sum_{n=0}^{N-1} n \omega_0 |n\rangle\langle n| + \sum_{n=0}^{N-1} \sum_{j \in L,R} \frac{n^2 \alpha_{n,j}^2}{2 \omega_j^2} |n\rangle\langle n| + H_{\text{shift}} + \sum_{n=1}^{N-1} \sqrt{n} V_{n-1,n} |n-1\rangle\langle n| e^{i(\Omega_n - \Omega_{n-1})} + \text{c.c.} + \sum_{j \in L,R} \omega_j a_j^\dagger a_j, \quad (\text{A3})$$

where

$$U = \prod_{n=0}^{N-1} U_n, \quad U_n = \exp(-i \Omega_n |n\rangle\langle n|), \quad (\text{A4})$$

and where

$$\Omega_n = \Omega_n^L + \Omega_n^R, \quad \Omega_n^K = i \sum_{j \in K} \lambda_{n,j} (a_j^\dagger - a_j) \quad (K = L, R),$$

$$\lambda_{n,j} = (2 \omega_j^3)^{-1/2} n \alpha_{n,j}. \quad (\text{A5})$$

The term

$$H_{\text{shift}} = - \frac{1}{2} \sum_{n=0}^{N-1} \sum_j \frac{n^2 \alpha_{n,j}^2}{\omega_j^2} |n\rangle\langle n| \quad (\text{A6})$$

exactly cancels the $\propto n^2$ term in Eq. (A3), and we finally recover the strong coupling Hamiltonian (36).

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