Heat flow in nonlinear molecular junctions

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Abstract

We investigate the heat conduction properties of molecular junctions comprising anharmonic interactions. We find that nonlinear interactions can lead to novel phenomena: 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 anharmonic interactions, strengths of 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, diode like behavior is expected for a highly anharmonic molecule with an inherent structural asymmetry. Anharmonic interactions are also necessary for manifesting Fourier type transport. We briefly present an extension of our model system that can lead to this behavior.

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I. INTRODUCTION

Understanding and controlling heat flow in nanoscale structures is of interest both from the fundamental aspect [1] and for device applications [2, 3, 4, 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 (\( h = 1 \)) [7, 9, 10]

\[
J = \int d\omega \omega T(\omega) [n_L(\omega) - n_R(\omega)].
\] (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 \( T(\omega) \) for phonons of frequency \( \omega \). 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, \( \nabla T \), as asserted by the Fourier law of conductivity,

\[
J = -\mathcal{K} \mathcal{A} \nabla T.
\] (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. An outstanding problem in statistical physics is to find out the necessary and sufficient conditions for attaining this normal (Fourier) law of heat conductivity in low dimensional systems [11, 12, 13, 14, 15, 16]. Among the crucial requirements explored is that the molecular potential energy should constitute strong anharmonic interactions.
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 [17, 18]. Intramolecular vibrational energy flow in bridged azulene-anthracene compounds could be explained by assuming ballistic energy transport in the chain connecting both chromophores [19]. In contrast, calculations of heat flow through proteins show substantial contribution of anharmonic interactions leading to an enhancement of the energy current in comparison to the (artificial) purely harmonic situation [20].

Anharmonic (nonlinear) interactions are also a tool for controlling heat flow in molecular junctions with potential technological applications, e.g. a thermal diode [21, 22, 23] and a thermal transistor [24]. 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 [23].

In this paper we generalize the model developed in Ref. [23], and present a comprehensive analysis of the heat conduction properties of molecular junctions taking into account anharmonic interactions in the system. 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 diode like behavior. We also follow the transition from the elastic Landauer formula to the Fourier law of conduction as anharmonic interactions are turned on.

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. Under additional conditions, the nonlinear models extended to a $l$ sites system satisfy the Fourier law of conductivity as explained in Section V. Section VI provides concluding remarks.
II. MODEL

The model system consists 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 ($MB$)

$$H = H_M + H_B + H_{MB}. \tag{3}$$

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

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

where $\omega_0$ 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. 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

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

$a_j^\dagger$, $a_j$ 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-reservoirs interaction

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

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 Section IV.
The probabilities $P_n$ to occupy the $n$ state of the molecular oscillator satisfy the master equation

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

(7)

where the occupations are normalized $\sum_n P_n = 1$. Within second order perturbation theory the rates are given by

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

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

(8)

where the average is done over the baths thermal distributions, irrespective of the fact that it may involve two distributions of different temperatures. In Section IV we demonstrate that these rates also apply 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

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

(9)

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-baths 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) $T_L = T_s$

$$
T_R = T_s - \Delta T.
$$

(10)

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

(B) $T_L = T_s + \Delta T/2$

$$
T_R = T_s - \Delta T/2.
$$

(11)
The main difference between these two situations is that the average temperature is decreasing steadily with $\Delta T$ 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 \[23\]. The Hamiltonian is given by Eqs. (3)-(6) with linear (harmonic) system-bath interactions

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

$$B = B_L + B_R,$$

where the bath operators $B_K$ satisfy

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

$$x_j = (2\omega_j)^{-1/2}(a_j^\dagger + a_j); \quad K = L, R. \quad (13)$$

In the present linear coupling model, no correlations persist between the thermal baths and the rate constants \[23\] are additive in the $L$ and $R$ baths

$$k_d = k_L + k_R$$

$$k_u = k_L e^{-\beta_L \omega_0} + k_R e^{-\beta_R \omega_0}, \quad (14)$$

with

$$k_K = \Gamma_K(\omega_0)(1 + n_K(\omega_0)); \quad K = L, R. \quad (15)$$

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} \quad \[23\], where $m$ and $\omega_0$ 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. (14)-(15). The steady-state heat flux calculated,
e.g. at the right contact, is given by the sum

\[ J = \omega_0 \sum_{n=1}^{N-1} n \left( k_R P_n - k_R P_{n-1} e^{-\beta R \omega_0} \right), \]  

(16)

where positive sign indicates current going from left to right.

A. Harmonic molecule

For the harmonic model \((N \to \infty)\), putting \(\dot{P}_n = 0\) in (17), and searching a solution of the form \(P_n \propto y^n\) we get a quadratic equation for \(y\) whose physically acceptable solution is

\[ y = \frac{k_L e^{-\beta_L \omega_0} + k_R e^{-\beta_R \omega_0}}{k_L + k_R}, \]  

(17)

which leads to the normalized state population

\[ P_n = y^n (1 - y). \]  

(18)

Using Eq. (17) we obtain the heat current (16)

\[ J = \omega_0 \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} (n_L - n_R). \]  

(19)

In the classical limit, \(\omega_0 / T_K \ll 1 (K = L, R)\), it reduces to

\[ J = \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} (T_L - T_R). \]  

(20)

This is a special case (with \(T(\omega) = \Gamma_L \Gamma_R (\Gamma_L + \Gamma_R)^{-1} \delta(\omega - \omega_0)\) consistent with our resonance energy transfer assumption) of the Landauer expression, Eq. (1). It is also consistent with the standard expression for the heat current through a perfect harmonic chain.

We emphasize on three important features of this result: (i) The heat current depends (classically) on the temperature difference between the two reservoirs, leading to divergent heat conductivity. Note that there is no need to introduce here the concept of the molecular temperature \(T_M\). (ii) The current is the same when exchanging \(\Gamma_L\) by \(\Gamma_R\), 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, (10)-(11), irrespective of the system symmetry. We can verify it by studying the \(\Delta T\) derivative of the current (19)

\[ \frac{\partial J}{\partial \Delta T} \propto \frac{\partial n_L}{\partial \Delta T} - \frac{\partial n_R}{\partial \Delta T} = \frac{\partial n_L}{\partial \Delta T} + \frac{\partial n_R}{\partial (-\Delta T)}. \]  

(21)
Since the term
\[ \frac{\partial n_L}{\partial \Delta T} = \frac{\omega_0 e^{\beta L_0 \omega_0}}{T_0^2 (e^{\beta L_0 \omega_0} - 1)^2} \frac{\partial T_L}{\partial \Delta T} \] (22)
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 -possible 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)-(16), except that we take \( n=0,1 \) only. Following Eqs. (7)-(8) we obtain the steady state levels population
\[ P_1 = \frac{k_u}{k_u + k_d}; \quad P_0 = \frac{k_d}{k_u + k_d}. \] (23)
We substitute it into Eq. (16) with \( N=2 \) and find the heat current \[ J = \omega_0 \frac{\Gamma_L \Gamma_R (n_L - n_R)}{\Gamma_L (1 + 2n_L) + \Gamma_R (1 + 2n_R)}. \] (24)
Next we calculate the molecular temperature \( T_M \) in the weak coupling-TLS case by substituting the population (23) into Eq. (9) using Eqs. (14)-(15). In the classical limit this results in
\[ T_M = \frac{\Gamma_L T_L + \Gamma_R T_R}{\Gamma_L + \Gamma_R}. \] (25)
We can now study the implications of the different models for the temperature bias, Eqs. (10)-(11), on the conductance: In Model A the molecular temperature decreases monotonically with the temperature difference
\[ T_M^{(A)} = T_s - \Delta T \frac{\Gamma_R}{\Gamma_L + \Gamma_R}. \] (26)
In Model B we find
\[ T_M^{(B)} = T_s + \frac{\Delta T}{2} \frac{(\Gamma_L - \Gamma_R)}{\Gamma_L + \Gamma_R}, \] (27)
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 \( \Delta T \), depending on the sign of \( \Gamma_L - \Gamma_R \).
In terms of the molecular temperature (Eq. (25)), going into the classical limit, the heat current (24) reduces into the simple form

\[ J = (T_L - T_R) \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \frac{\omega_0}{2T_M}. \] (28)

This relationship differs from the harmonic expression, (20), by its implicit dependence on the internal molecular temperature. As we show next, this opens up the door for heat rectification and can also lead to the applicability of the Fourier law of conduction. 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 \( T(\omega, T_L, T_R) \propto 1/T_M \delta(\omega - \omega_0) \).

In Fig. 1 we display the current (Eq. (24)) for a representative set of parameters. It increases monotonically with \( \Delta T \) and saturates at high temperature gaps. We can verify this trend analytically as

\[ \frac{\partial J}{\partial \Delta T} = \left[ \frac{\partial n_L}{\partial \Delta T}(1 + 2n_R) - \frac{\partial n_R}{\partial \Delta T}(1 + 2n_L) \right] \times \frac{\omega_0 \Gamma_L \Gamma_R \Gamma_L + \Gamma_R}{\left[ \Gamma_L(1 + 2n_L) + \Gamma_R(1 + 2n_R) \right]^2} > 0, \] (29)

which indicates that NDTC can not take place. However, Eq. (24) implies that the system can rectify heat current, i.e. the current can be different (in absolute values) when exchanging the reservoirs temperatures. Following [23], defining the asymmetry parameter \( \chi \) such that \( \Gamma_L = \Gamma(1 - \chi) ; \Gamma_R = \Gamma(1 + \chi) \) with \(-1 \leq \chi \leq 1\) we get

\[ \Delta J \equiv J(T_L = T_h, T_R = T_c) + J(T_L = T_c, T_R = T_h) \]
\[ = \frac{\omega_0 \Gamma \chi(1 - \chi^2)(n_L - n_R)^2}{(1 + n_L + n_R)^2 - \chi^2(n_L - n_R)^2}. \] (30)

Here \( T_c \) (\( T_h \)) relates to the cold (hot) bath. Eq. (30) implies that for small \( \Delta T = T_L - T_R, \Delta J \) grows like \( \Delta T^2 \), 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 at 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 anharmonic interactions with the thermal baths, which may result in an effective nonlinear temperature dependent molecule-bath coupling term, see section IV. Therefore, there is no direct correspondence between these two phenomena.
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).

C. General expression for the heat current

We can generalize the harmonic [20] and anharmonic [28] results and revise the current in the weak coupling limit ($W$) as

$$J_W = \omega_0 \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \frac{(T_L - T_R)}{T_M} f_{S,B},$$

where

$$f_{S,B} = \begin{cases} 
1/2, & \text{Anharmonic TLS case ("Spin")}, \\
T_M/\omega_0, & \text{Harmonic case ("Boson")}. 
\end{cases}$$

For an intermediate anharmonicity we expect this function to attain an intermediate value, $1/2 < f_{S,B} < T_M/\omega_0$. Note that $f_{S,B}$ can be retrieved by going into the classical limit of $f_{S,B} = (\exp(\omega_0/T_M) \pm 1)^{-1}$. Here the ”spin” case takes the plus sign, and the ”boson” situation 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 $\omega_0/T_M$ which includes
internal molecular properties: frequency and effective temperature, and (iii) the molecular occupation factor \( f_{S,B} \) that varies between 1/2 for the strictly anharmonic system and \( T_M/\omega_0 \) 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),

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

(33)

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 Appendix A 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 parameters that depend on the level index and the reservoir mode, see Appendix A. The Hamiltonian (33) is similar to that defined in Eqs. (4)-(13), except that the \( L \) and \( R \) system-baths couplings appear as multiplicative rather than additive factors in the interaction term, implying non-separable transport at the two contacts [23]. The dynamics is still readily handled. For small \( V \) (the "non-adiabatic limit") the Hamiltonian (33) leads again to the rate equation (7) with

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

(34)

where

\[
C(\omega_0) = \int_{-\infty}^{\infty} dt e^{i\omega_0 t} \tilde{C}(t),
\]

(35)
and

$$\tilde{C}(t) = \langle e^{i[\Omega_n(t) - \Omega_{n-1}(t)]} e^{-i[\Omega_n(0) - \Omega_{n-1}(0)]} \rangle = \langle e^{i[\Omega^L_n(t) - \Omega^R_{n-1}(t)]} e^{-i[\Omega^L_n(0) - \Omega^R_{n-1}(0)]} \rangle_L$$

$$\times \langle e^{i[\Omega^R_n(t) - \Omega^R_{n-1}(t)]} e^{-i[\Omega^R_n(0) - \Omega^R_{n-1}(0)]} \rangle_R.$$

(36)

This may be evaluated explicitly to produce

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

(37)

with

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

$$- (1 + n_K(\omega_j)) e^{-i\omega_j t} - n_K(\omega_j) e^{i\omega_j t}].$$

(38)

Note that we have omitted the $n$ dependence from the rates above. This is supported by

(i) taking all the inter-levels 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 Appendix A.

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

$$C(\omega_0) = \sqrt{\frac{2\pi}{\left(D^2_L + D^2_R\right)}} \exp\left[ -\frac{\omega_0 - E^L_M - E^R_M}{2(D^2_L + D^2_R)} \right],$$

(39)

where

$$E^K_M = \sum_{j \in K}(\lambda_{n,j} - \lambda_{n-1,j})^2 \omega_j,$$

$$D^2_K = \sum_{j \in K}(\lambda_{n,j} - \lambda_{n-1,j})^2 \omega_j^2 (2n_K(\omega_j) + 1).$$

(40)

$E^K_M$ can be considered as the reorganization energy associated with the structural distortions

do reservoirs modes around the isolated molecular vibration. In the classical limit ($\omega_0/T_K \to 0$),

$D^2_K = 2T_K E^K_M$.

Following Ref. [23] we calculate the steady state heat current utilizing

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

$$-C_R(-\omega)C_L(-\omega_0 + \omega)P_{n-1}]n,$$

(41)
where

\[
C(\omega_0) = \int_{-\infty}^{\infty} d\omega C_L(\omega_0 - \omega)C_R(\omega),
\]
\[
C_K(\omega) = \frac{1}{\sqrt{2E^*_M T^*_K}} e^{-\left(\omega - E^*_K\right)^2/4T^*_K E^*_M}.
\]

Eq. (41) views the process \(|n\rangle \rightarrow |n - 1\rangle\) in which the molecular mode looses energy \(\omega_0\) as a combination of processes in which the system gives energy \(\omega\) (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. (34)-(40). The heat current (41) is computed by first making the summation over \(n\)

\[
\sum_{n=0}^{\infty} nP_n = \frac{C(-\omega_0)}{C(\omega_0) - C(-\omega_0)},
\]
\[
\sum_{n=0}^{\infty} nP_{n-1} = \frac{C(\omega_0)}{C(\omega_0) - C(-\omega_0)}.
\]

Next, performing the integrals over frequency yields

\[
J = \frac{2\sqrt{\pi} |V|^2 E^*_L E^*_R (T_L - T_R)}{(E^*_L T_L + E^*_R T_R)^{3/2}} \times e^{-\left(\omega_0 - (E^*_L + E^*_R)\right)^2/(4E^*_L T_L + E^*_R T_R)} \times f_B,
\]

where

\[
f_B = \left[e^{\omega_0(E^*_L + E^*_R)/(E^*_L T_L + E^*_R T_R)} - 1\right]^{-1}.
\]

Before we discuss the heat conduction properties of this model we examine the anharmonic system.
FIG. 2: Conduction properties of the TLS system in the strong coupling limit $T_R = T_L - \Delta T$ (model A), $E^{K}_M=300$ meV, $(K = L, R) V=1$ meV, $\omega_0=10$ meV.

**B. Anharmonic molecule**

The anharmonic model is described by the Hamiltonian (33) with $n = 0, 1$. The steady state current is therefore obtained by reducing Eq. (41) to

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

(46)

Here $P_0 = C(\omega_0)/\left(C(\omega_0) + C(-\omega_0)\right)$ and $P_1 = 1 - P_0$ are established from the steady state solution of (7) with the rates given by (34). By following the same steps as for the harmonic system, the heat current (46) is obtained as

$$J = \frac{2\sqrt{\pi}|V|^2E^{K}_L E^{R}_M(T_L - T_R)}{(E^{K}_M T_L + E^{R}_M T_R)^{3/2}} \times e^{-\left(\omega_0 - (E^{K}_L + E^{R}_L)\right)^2/4(E^{K}_M T_L + E^{R}_M T_R)} \times f_S,$$

(47)

with the occupation factor

$$f_S = \left[e^{\omega_0(E^{K}_L + E^{R}_L)/(E^{K}_M T_L + E^{R}_M T_R)} + 1\right]^{-1}.$$

(48)
C. General expression for the heat current

Next the harmonic (44) and anharmonic results (47) are reduced into a common form. We begin by evaluating the internal molecular temperature (9). In the present strong coupling case, for both harmonic and anharmonic molecular modes, it is given by (34)

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

(49)

Using Eq. (39) we obtain the explicit expression

\[ T_M = \frac{D_L^2 + D_R^2}{2(E_M^L + E_M^R)} \text{lim}_{\omega_0/T_M \rightarrow 0} \frac{(E_M^L T_L + E_M^R T_R)}{(E_M^L + E_M^R)}. \]  

(50)

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

\[ J_S = |V|^2 \sqrt{\frac{4\pi}{T_M(E_M^L + E_M^R)}} e^{-(\omega_0 - E_M^L - E_M^R)^2/(4T_M(E_M^L + E_M^R))} \times \frac{E_M^L E_M^R}{E_M^L + E_M^R} \times \frac{T_L - T_R}{T_M} \times f_{S,B}, \]  

(51)
where

\[ f_{S,B} \equiv \left[ e^{\omega_0(E_M^L+E_M^R)/(E_M^LT_L+E_M^RT_R)} \pm 1 \right]^{-1} = \left( e^{\omega_0/T_M} \pm 1 \right)^{-1}. \] (52)

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

We analyze next the conduction properties of this model. Diode like 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 (nonlinear) 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. (11)), NDTC occurs for an asymmetric \( E_M^L \neq E_M^R \) system. In model A the molecular temperature depends on \( \Delta T \) even for a symmetric junction, providing NDTC.

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 \( \Delta T = T_L - T_R \sim 100 \text{ K} \) 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).

We can also investigate the effect of asymmetrical contacts. We define the asymmetry parameter \( \chi \) such as \( E_M^L = E_M(1 - \chi) \), \( E_M^R = E_M(1 + \chi) \), \( 0 < \chi < 1 \). Figure 3 presents the heat current when \( \chi \neq 0 \). (a) For small \( \chi \) the current is almost the same for both forward and reversed operation modes. (b) At intermediate \( \chi \) values we find that for \( T_L = 100 \text{ K}, T_R = 300 \text{ K} \) there is a maximal heat flow (dashed), while for the reversed operation (\( T_R = 100 \text{ K}, T_L = 300 \text{ K} \)) 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 (31)

\[ J_W = \omega_0 \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} \frac{(T_L - T_R)}{T_M} f_{S,B}. \] (53)
Comparing it to Eq. (51) guides us to the compact expression

$$J = C \frac{f_{S,B}}{T_M} \Delta T.$$  

(54)

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 "Spin-Boson" factor $f_{S,B}$. 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-baths interactions.

V. FOURIER LAW OF CONDUCTION

The validity of Fourier’s law of heat conduction (2) in 1D lattices is an open issue [13]. This law is a macroscopic consequence of ordinary diffusion at the microscopic level. Here we extend our single mode model and present a realization of a molecular chain that can lead to normal Fourier conduction, provided that the molecule is highly anharmonic, independently of the molecule-baths coupling strengths. We emphasize that we bypass the difficult task of showing how normal diffusion emerges in the system [16], and simply assume non-correlated hopping motion between molecular units. Our sole mission here is to construct from the single mode result (54) a model that supplies normal conduction.

Figure 4 depicts the system: We envision an array of $I + 2$ local heat baths where heat transfers along the chain of bath, single mode, bath, single mode...: $L \rightarrow B_1 \rightarrow B_2 \rightarrow \ldots \rightarrow B_I \rightarrow R$. The intermediate thermal baths $B_i$ might be realized by large molecular groups where full thermalization to a local temperature occurs. This implies that anharmonic
interactions govern the dynamics within the intermediate baths. We also assume that the temperature difference $T_L - T_R$ falls linearly on the system, i.e. the temperature at the $i$-th bath is

$$T_i = T_s + \delta T[i - (I + 1)/2], \quad \Delta T = \delta T(I + 1), \quad (55)$$

where $i = (0, 1, 2...I, I + 1)$. The $L$ and $R$ bath are indexed by 0 and $I + 1$ respectively, and $\delta T$ is the temperature difference between neighboring reservoirs. The resulting effective temperature of a molecular mode located in between each two baths $i - 1$ and $i$ is

$$T^{(i)}_M = T_s + \delta T[2i - 1 - (I + 1)]/2, \quad (56)$$

assuming equal coupling along the chain ($\Gamma_i = \Gamma$ or $E^i_M = E_M$).

The conductance $\kappa_i$ of the unit $B_{i-1} \leftrightarrow B_i$ is defined through the relation $J = \kappa_i(T_i - T_{i-1})$. In the diffusional hopping regime, the total conductance $\kappa_T$ is established by inverting the sum of all units resistances, $\kappa_T = (\sum_i 1/\kappa_i)^{-1}$. In the linear coupling-TLS model (31) it becomes

$$\kappa_T = \frac{\omega_0 \Gamma}{4} \left( \sum_{i=1}^{I+1} T^{(i)}_M \right)^{-1} = \frac{\Gamma \omega_0}{4T_s l}, \quad (57)$$

where $l = I + 1$ is the actual length of the system, given by the number of internal molecular modes. This equation implies the validity of the Fourier law of heat conduction, $J \propto (T_L - T_R)/l$. In addition, the prefactor depends on the inverse temperature $T_s^{-1}$ as expected in the high temperature limit [27] where interactions among phonons are dominant. The same result holds when the temperature falls mainly on the contacts whereas the temperature distribution along the central baths is almost constant. Strong molecule-bath interactions contribute a temperature dependent prefactor, but do not modify the $l^{-1}$ form assuming $\Delta T/T_s \ll 1$. A possible realization of this system is a fullerene polymer [28].

VI. CONCLUSIONS

Using a simple theoretical model we have investigated the effect of anharmonic interactions on heat flow through molecular junctions. Our general expressions for the heat current (31) and (51) clearly manifest the interplay between the system anharmonicity, system-bath coupling and junction asymmetry. We have also extended our model into a chain of $l$ local
FIG. 5: An overview of the parameter ranges providing negative differential thermal conductance (NDTC) and diode like 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.

molecular sites, and indicated that anharmonicity is a crucial requirement for achieving normal conductance. We have found that nonlinear interactions can lead to novel phenomena: negative differential thermal conductance and heat rectification. NDTC takes place when the molecular mode is strongly coupled to the thermal environment. In contrast, diode like behavior originates from the combination of substantial molecular anharmonicities with a structural asymmetry. 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\textsubscript{60} could be explained due to a voltage dependent tunneling barrier \cite{29}. Rectification of electron current was theoretically exhibited in one-dimensional asymmetric electronic conductors with screened electron-electron interactions \cite{30}.

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 \cite{31}. Engineering good thermal contacts and cooling of the the junction \cite{32} 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\(^\text{[33]}\). Finally, we propose building technological devices based on heat flow, in analogy with electron current devices\(^\text{[34]}\).

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**APPENDIX A: Microscopic model for the strong coupling Hamiltonian**

The strong coupling Hamiltonian Eq. (33) can be derived from the following microscopic model

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

(A1)

which describes a forced oscillator of frequency \(\omega_0\) 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 \(\propto x_j x^2\), with \(x\) as the molecular coordinate. Here \(x_j\) and \(p_j\) are the displacement and momentum of the reservoirs harmonic modes with frequency \(\omega_j\), \(\alpha_{n,j}\) is the system-bath coupling parameter and \(V_{n,n-1}\) is the effective inter-level matrix element. We can expand the quadratic term in (A1) and obtain

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

(A2)
Here \( x_j = (a_j^\dagger + a_j)/\sqrt{2\omega_j} \) and \( p_j = i \sqrt{\omega_j/2}(a_j^\dagger - a_j) \). Use of the small polaron transformation \[35\], \( \tilde{H} = UHU^{-1}, \) leads to

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

(A3)

where

\[
U = \Pi_{n=0}^{N-1} U_n, \quad U_n = \exp(-i\Omega_n |n\rangle\langle n|),
\]

(A4)

and where

\[
\begin{align*}
\Omega_n &= \Omega_n^L + \Omega_n^R, \quad \Omega_n^K = i \sum_{j \in K} \lambda_{n,j} \left( a_j^\dagger - a_j \right), \quad (K = L, R), \\
\lambda_{n,j} &= (2\omega_j^3)^{-1/2} n\alpha_{n,j}.
\end{align*}
\]

(A5)

The term

\[
H_{\text{shift}} = -\frac{1}{2} \sum_{n=0}^{N-1} \sum_{j} \frac{n^2 \alpha_{n,j}^2}{\omega_j^2} |n\rangle\langle n|
\]

(A6)

exactly cancels the \( \propto n^2 \) term in Eq. (A3), and we finally recover the strong coupling Hamiltonian \[33\].

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The general formulation of Ref. \cite{10} yields
\[ T(\omega) = \frac{1}{(2/\pi)\omega^2\Gamma_L\Gamma_R \left[ (\omega^2 - \omega_0^2)^2 + (\Gamma_L + \Gamma_R)^2\omega^2 \right]}^{-1}. \]