Spin-Boson Thermal Rectifier

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Rectification of heat transfer in nanodevices can be realized by combining the system inherent anharmonicity with structural asymmetry. We analyze this phenomenon within the simplest anharmonic system—a spin-boson nanojunction model. We consider two variants of the model that yield, for the first time, analytical solutions: a linear separable model in which the heat reservoirs contribute additively, and a nonseparable model suitable for a stronger system-bath interaction. Both models show asymmetric (rectifying) heat conduction when the couplings to the heat reservoirs are different.

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The heat conduction properties of nanojunctions attract attention for two reasons. First, heating in nanoconductors, a crucial issue for their operation and stability, is determined by both heat release and conduction in such systems. Secondly, as with electronic conduction, the restrictive geometry raises fundamental questions concerning the relationship between transport processes in microscopic systems and their macroscopic counterparts. Indeed thermal transport properties of nanowires can be very different from the corresponding bulk properties as is demonstrated by the recent confirmation [1] of the prediction [2] that the low temperature ballistic phonon conductance in a one-dimensional quantum wire is characterized by a universal quantum unit. Also of considerable interest are studies that confront the macroscopic Fourier law, $J = -K\nabla T$, that connects the heat current J to the temperature gradient ∇T and defines the thermal conductance K, with heat transport on the microscopic scale. Harmonic chains were repeatedly discussed theoretically in these contexts and considerable experimental progress was also made [1]. For reviews see Refs. [3,4].

An intriguing mode of behavior of transport devices is current rectification, allowing larger conduction in one direction than in the opposite one when driven far enough from equilibrium. Such phenomena were extensively studied for electronic conduction in molecular junctions, but much less so for thermal nanoconductors. For a harmonic thermal conductor connecting (by linear coupling) two [left (L), right (R)] harmonic thermal reservoirs that are maintained at equilibrium with the temperatures T_L and T_R, respectively, heat transfer is a ballistic process and the heat current J can be recast into a Landauer-type expression [2]

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

where $\mathcal{T}(\omega)$ is the transmission coefficient for phonons of frequency ω and $n_K(\omega) = (e^{\beta_K\omega} - 1)^{-1}$; $\beta_K = (k_B T_K)^{-1}$; $K = L, R$ ($\hbar \equiv 1$) are Bose-Einstein distribution functions characterizing the reservoirs. Obviously, this expression is symmetric to interchanging the reservoirs temperatures and cannot show rectifying behavior irrespective of any asymmetry in the system structure.

In contrast, Terraneo *et al.* [5] have shown numerically that rectifying behavior is obtained by replacing the interior part of a classical harmonic chain by an anharmonic segment. An example of a similar behavior by a somewhat simpler model is shown in Fig. 1. The model is defined by the N-particle Hamiltonian

$$H = (2m)^{-1}\sum_{i=1}^{N} p_i^2 + \sum_{i=1}^{N-1} D(e^{-\alpha(x_{i+1}-x_i-x_{\mathrm{eq}})} - 1)^2 + D(e^{-\alpha(x_1-a)} - 1)^2 + D(e^{-\alpha(b-x_N)} - 1)^2 \qquad (2)$$

supplemented by damping and noise terms. The equations of motions are $\ddot{x}_i = -(1/m)\partial H/\partial x_i - (\gamma_L\dot{x}_1 - F_L(t))\delta_{i,1} - (\gamma_R\dot{x}_N - F_R(t))\delta_{i,N}$, where $F_K(t)$, $K = L, R$

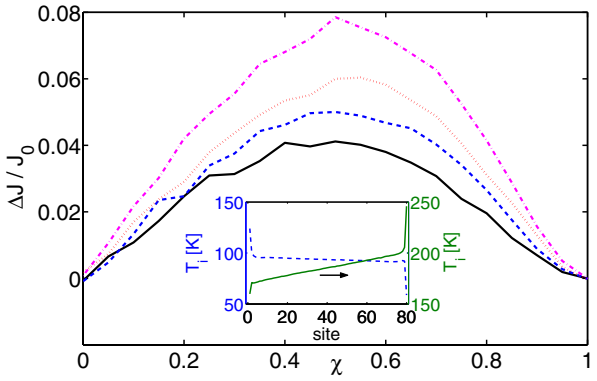

FIG. 1 (color online). The asymmetry in the thermal conduction plotted against χ for a classical N-atom chain. The parameters used, $D = 3.8/\nu^2$ eV, $\alpha = 1.88\nu$ Å^{-1}, $x_{\mathrm{eq}} = 1.538$ Å and $m = 12/6.02 \times 10^{23}$ g, are based on a standard model for the carbon-carbon force field in alkanes [15], for which $\nu = 1$. Here we increase the system anharmonicity by taking $\nu = 6$. Solid, dashed, dotted, and dashed-dotted lines correspond to $N = 10$, 20, 40, and 80, respectively, with $\gamma = 50$ ps^{-1}, $T_h = 300$ K and $T_c = 0$ K. (Inset) The temperature profile for the $N = 80$, $\chi = 0.5$ case with $T_L = T_c$; $T_R = T_h$ (solid line), $T_L = T_h$; $T_R = T_c$ (dashed line).

are Gaussian random forces that satisfy $\langle F_K(t)F_K(0)\rangle = 2\gamma_K k_B T_K \delta(t)/m$. We take $\gamma_L = \gamma(1-\chi)$, $\gamma_R = \gamma(1+\chi)$,$|\chi| \le 1$, and study the ratio between $\Delta J \equiv J(T_L = T_h; T_R = T_c) + J(T_L = T_c; T_R = T_h)$ and $J_0 \equiv |J(\chi = 0)|$, where T_c and T_h denote low and high temperatures and where the heat current J is calculated as the average over sites, at steady state, of $J_i = \langle -\dot{x}_i(\partial H_{i+1,i}/\partial x_i)\rangle$ with $H_{i+1,i} = D(e^{-\alpha(x_{i+1}-x_i-x_{eq})} - 1)^2$. Figure 1 shows that the intrinsic nonlinearity of this model is enough to induce asymmetry in the thermal conduction of the asymmetrically coupled ($\gamma_L \neq \gamma_R$) bridge.

Clearly, in addition to structural asymmetry, nonlinear interactions are essential for rectifying behavior. In this paper we examine the rectifying properties of the simplest nonlinear heat conductor: a two-level system (TLS). The model investigated is a generalization of the spin-boson model that has been widely applied for many physical phenomena [6], where the TLS is now coupled to two equilibrium boson baths maintained at different temperatures. We study two variants of the model and show that if asymmetry is built into either one by employing, e.g., different spin-boson coupling strengths for the two baths, thermal rectification naturally sets in.

The first variant of our spin-boson model is defined by the $N = 2$ case of the Hamiltonian

$$H = \sum_{n=0}^{N-1} E_n |n\rangle\langle n| + H_B + H_{MB} \tag{3}$$

$$H_B = H_L + H_R; \qquad H_K = \sum_{j\in K} \omega_j a_j^\dagger a_j; \qquad K = L, R \tag{4}$$

$$H_{MB} = \sum_{n=1}^{N-1} \sqrt{n}(B|n-1\rangle\langle n| + B^\dagger|n\rangle\langle n-1|); \; B \equiv B_L + B_R, \tag{5}$$

where $a_j^\dagger$ and a_j are boson creation and annihilation operators associated with the phonon modes of the harmonic baths and B_K are bath operators. For linear coupling

$$B_K = \sum_{j\in K} \bar{\alpha}_j x_j; \qquad x_j = (2\omega_j)^{-1/2}(a_j^\dagger + a_j), \tag{6}$$

where asymmetry is incorporated by taking $\bar{\alpha}_{j\in L} \neq \bar{\alpha}_{j\in R}$. This model is characterized by the independent transport processes at the two system-bath interfaces. Note that the N-level system in the model (3)–(6) becomes a standard harmonic oscillator in the limit $N \to \infty$ and for equal energy spacing. Equation (6) corresponds in the latter case to the bilinear coupling model for the oscillator-bath interactions, $H_{MB} = \sum_{j\in K} \alpha_j x_j x$, where x is the coordinate of the bridge oscillator and $\alpha_j = \bar{\alpha}_j (2m\omega_0)^{1/2}$, where m and $\omega_0 = E_1 - E_0$ are the oscillator mass and frequency, respectively.

The reduced dynamics of the N-level system can be derived for weak system-bath coupling using the Redfield approximation [7]. Assuming that the temperature is high enough to make dephasing fast, the resulting kinetic equations for the state probabilities are

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

where $X_n = \delta_{n,0}$ for the two-level ($n = 0, 1$) system and $X_n = 1$ for the harmonic oscillator ($n = 0, \ldots, \infty$) case, and where $k_d = \int_{-\infty}^{\infty} d\tau e^{i\omega_0\tau}\langle B^\dagger(\tau)B(0)\rangle$ and $k_u = \int_{-\infty}^{\infty} d\tau e^{-i\omega_0\tau}\langle B(\tau)B^\dagger(0)\rangle$. The average is over the baths thermal distributions, irrespective of the fact that it may involve two distributions of different temperatures [8]. Specifying to the linear coupling model, and assuming no correlation between the thermal baths, leads to the rates

$$k_d = k_L + k_R; \qquad k_u = k_L e^{-\beta_L\omega_0} + k_R e^{-\beta_R\omega_0}, \tag{8}$$

with

$$k_K = \Gamma_K(\omega_0)(1 + n_K(\omega_0)), \tag{9}$$

$$\Gamma_K(\omega) = \frac{\pi}{2m\omega^2}\sum_{j\in K} \alpha_j^2 \delta(\omega - \omega_j); \qquad K = L, R. \tag{10}$$

The heat conduction properties of this model are obtained from the steady-state solution of Eq. (7) with the rates given in Eqs. (8)–(10). For the harmonic model ($N \to \infty$), putting $\dot{P}_n = 0$, and searching a solution of the form $P_n \propto y^n$ we get a quadratic equation for y whose physically acceptable solution is

$$y = \frac{k_L e^{-\beta_L\omega_0} + k_R e^{-\beta_R\omega_0}}{k_L + k_R}. \tag{11}$$

This leads to the normalized state populations $P_n = y^n(1-y)$. The steady-state heat flux is obtained from

$$J = \omega_0 \sum_{n=1}^{\infty} n(k_R P_n - k_R P_{n-1} e^{-\beta_R\omega_0}) \tag{12}$$

where a positive sign indicates current going from left to right [9]. Using Eqs. (9) and (11) we find

$$J = \omega_0 \frac{\Gamma_L\Gamma_R}{\Gamma_L + \Gamma_R}(n_L - n_R). \tag{13}$$

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] [10] of Eq. (1). Obviously no rectifying behavior is obtained in this limit.

Next consider the two-level case, $N = 2$. The two steady-state equations obtained from (7) yield

$$P_1 = \frac{k_L e^{-\beta_L\omega_0} + k_R e^{-\beta_R\omega_0}}{k_L(1 + e^{-\beta_L\omega_0}) + k_R(1 + e^{-\beta_R\omega_0})}; \qquad P_1 = 1 - P_0, \tag{14}$$

and the analog of Eq. (12) is

$$J = \omega_0 k_R (P_1 - P_0 e^{-\beta_R \omega_0}). \tag{15}$$

Using this with Eq. (9) leads to

$$J = \omega_0 \frac{\Gamma_L \Gamma_R (n_L - n_R)}{\Gamma_L(1 + 2n_L) + \Gamma_R(1 + 2n_R)}, \tag{16}$$

which does have rectifying behavior. Indeed, defining the asymmetry parameter χ such that $\Gamma_L = \Gamma(1 - \chi)$; $\Gamma_R = \Gamma(1 + \chi)$ with $-1 \le \chi \le 1$ we find

$$\Delta J \equiv J(T_L = T_h; T_R = T_c) + J(T_L = T_c; T_R = T_h) = \frac{\omega_0 \Gamma \chi (1 - \chi^2)(n_L - n_R)^2}{(1 + n_L + n_R)^2 - \chi^2 (n_L - n_R)^2}. \tag{17}$$

Equation (17) implies that for small $\Delta T = T_L - T_R$, $|\Delta J|$ grows like ΔT^2. Furthermore, noting that $\mathrm{sgn}(\Delta J) = \mathrm{sgn}(\chi)$ it follows from Eq. (17) that the current is larger when the bridge links more strongly to the colder reservoir than when it links more strongly to the hotter one. Figure 2 shows an example of this behavior.

Next we consider another variant of the two-bath spin-boson model, taking the Hamiltonian to be

$$H = E_0|0\rangle\langle 0| + E_1|1\rangle\langle 1| + V_{0,1}|0\rangle\langle 1| + V_{1,0}|1\rangle\langle 0| + \sum_{j\in L,R} \omega_j a_j^\dagger a_j + \sum_{j\in L,R} x_j(\alpha_{0,j}|0\rangle\langle 0| + \alpha_{1,j}|1\rangle\langle 1|). \tag{18}$$

The L and R boson baths are again maintained at different temperatures T_L and T_R. When $T_L = T_R$, Eq. (18) represents a standard spin-boson Hamiltonian used, e.g, in the electron transfer problem. Using the small polaron transformation [11], $\tilde{H} = UHU^{-1}$, leads to

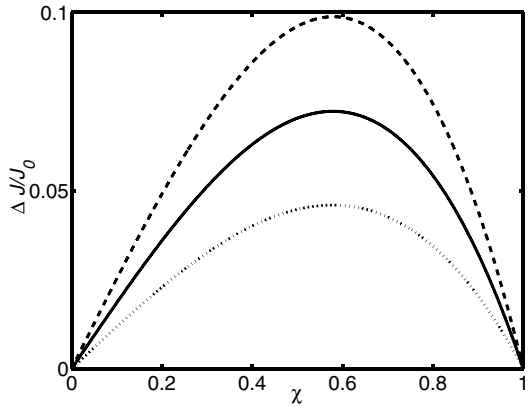

FIG. 2. Heat rectification by a TLS bridge in the linear coupling model, Eqs. (3)–(17). The ratio $\Delta J/J_0$ (with $J_0 \equiv |J(\chi = 0)|$) is plotted against the asymmetry parameter χ for several two-level spacings: $\omega_0 = 0.025$ eV (dashed line); $\omega_0 = 0.05$ eV (solid line); $\omega_0 = 0.075$ eV (dotted line). The temperatures are $T_h = 400$ K, $T_c = 300$ K.

$$\tilde{H} = E_0|0\rangle\langle 0| + E_1|1\rangle\langle 1| + V_{0,1}|0\rangle\langle 1|e^{i\Omega} + V_{1,0}|1\rangle\langle 0|e^{-i\Omega} + \sum_{j\in L,R} \omega_j a_j^\dagger a_j + H_{\mathrm{shift}}, \tag{19}$$

where $U = U_0 U_1$, $U_n = \exp(-i\Omega_n |n\rangle\langle n|)$, $(n = 0, 1)$, $\Omega_n = \Omega_n^L + \Omega_n^R$, $\Omega_n^K = i\sum_{j\in K} \lambda_{n,j}(a_j^\dagger - a_j)$ $(K = L, R)$, $\lambda_{n,j} = (2\omega_j^3)^{-1/2}\alpha_{n,j}$ and $\Omega = \Omega_1 - \Omega_0$. The term $H_{\mathrm{shift}} = -(1/2)\sum_j \omega_j^{-2}(\alpha_{0,j}^2|0\rangle\langle 0| + \alpha_{1,j}^2|1\rangle\langle 1|)$ may be henceforth incorporated into the zero order energies. The Hamiltonian (19) is similar to that defined in Eqs. (3)–(5), except that the system-bath couplings appear as multiplicative rather than additive factors in the interaction term, implying nonseparable transport at the two contacts. The dynamics is still readily handled. For small V (the "nonadiabatic limit") the Hamiltonian (19) leads again to the rate Eq. (7) with

$$k_d = |V_{0,1}|^2 C(\omega_0); \qquad k_u = |V_{0,1}|^2 C(-\omega_0), \tag{20}$$

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

$$\tilde{C}(t) = \langle e^{i(\Omega_1^L(t) - \Omega_0^L(t))} e^{-i(\Omega_1^L - \Omega_0^L)}\rangle_L \times \langle e^{i(\Omega_1^R(t) - \Omega_0^R(t))} e^{-i(\Omega_1^R - \Omega_0^R)}\rangle_R. \tag{21}$$

This may be evaluated explicitly to give

$$\tilde{C}(t) = \tilde{C}_L(t)\tilde{C}_R(t); \qquad \tilde{C}_K(t) = \exp[-\phi_K(t)], \tag{22}$$

$$\phi_K(t) = \sum_{j\in K} (\lambda_{1,j} - \lambda_{0,j})^2 [(1 + 2n_K(\omega_j)) - (1 + n_K(\omega_j))e^{-i\omega_j t} - n_K(\omega_j)e^{i\omega_j t}]. \tag{23}$$

Explicit expressions may be obtained using the short time approximation [valid for $\sum_{j\in K}(\lambda_{1,j} - \lambda_{0,j})^2 \gg 1$ and/or at high temperature] whereupon $\phi(t)$ is expanded in powers of t keeping terms up to order t^2. This leads to

$$C(\omega_0) = \sqrt{\frac{2\pi}{(D_L^2 + D_R^2)}} \exp\left[\frac{-(\omega_0 - E_M^L - E_M^R)^2}{2(D_L^2 + D_R^2)}\right], \tag{24}$$

where $E_M^K = \sum_{j\in K}(\lambda_{1,j} - \lambda_{0,j})^2\omega_j$, $D_K^2 = \sum_{j\in K}(\lambda_{1,j} - \lambda_{0,j})^2\omega_j^2(2n_K(\omega_j) + 1) \overset{\omega/k_B T_K}{\rightarrow} 2k_B T_K E_M^K$. Equations (20)–(24) provide an extension of the Marcus nonadiabatic rate expressions [12] to the case of two reservoirs maintained at different temperatures. E_M^L and E_M^R are the corresponding reorganization energies.

Consider now the steady-state heat current. The nonseparability of the system-bath couplings makes the procedure that leads to Eq. (15) unusable. Instead note that $C_L(\omega_0)$ and $C_R(\omega_0)$ are the rates affected by each thermal reservoir separately and that, from (22), $C(\omega_0) = \int_{-\infty}^{\infty} d\omega C_L(\omega_0 - \omega)C_R(\omega)$. The process $|1\rangle \rightarrow |0\rangle$ in which the TLS loses energy ω_0 can be therefore viewed as a combination of processes in which the system gives energy ω (or gains it if $\omega < 0$) to the right bath and energy

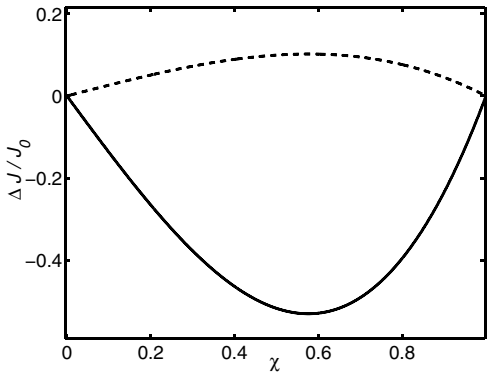

FIG. 3. Heat rectification of a TLS bridge with a nonseparable coupling, Eqs. (18)–(26). $\Delta J/J_0$ is plotted against χ for $\omega_0 = 0.025$ eV and for $E_M = 0.012$ eV (dashed line), $E_M = 0.38$ eV (solid line). The temperatures are $T_h = 400$ K, $T_c = 300$ K.

$\omega_0 - \omega$ to the left one, with probability $C_L(\omega_0 - \omega)C_R(\omega)$. A similar analysis applies to the process $|0\rangle \rightarrow |1\rangle$. The heat flux calculated as the energy transferred per unit time into the right bath is therefore [9]

$$J = |V_{0,1}|^2 \int_{-\infty}^{\infty} d\omega\,\omega[C_R(\omega)C_L(\omega_0 - \omega)P_1 - C_R(-\omega)C_L(-\omega_0 + \omega)P_0], \tag{25}$$

where $P_0 = C(\omega_0)/[C(\omega_0) + C(-\omega_0)]$ and $P_1 = 1 - P_0$ are the steady-state probabilities that the system is in state 0 or 1, respectively. In the short time approximation $C(\omega)$ takes the form $C_K(\omega) = (D_K^2)^{-1/2}\exp[-(\omega - E_M^K)^2/2D_K^2]$. It is convenient also to take $E_M^L = E_M(1 - \chi)$; $E_M^R = E_M(1 + \chi)$ ($|\chi| \leq 1$), which implies $D_L^2 + D_R^2 = 2k_B E_M(T_S - \chi\Delta T)$ where $T_S = T_L + T_R$. Using these relationships in (25) leads to

$$J = \frac{2\sqrt{\pi}|V_{0,1}|^2(1-\chi^2)E_M^2 k_B \Delta T}{[k_B E_M(T_S - \chi\Delta T)]^{3/2}} \frac{e^{-\frac{(\omega_0 - 2E_M)^2}{4k_B E_M(T_s - \chi\Delta T)}}}{1 + e^{2\omega_0/k_B(T_S - \chi\Delta T)}}. \tag{26}$$

Equation (26) again implies asymmetric heat conduction provided symmetry is broken by taking $\chi \neq 0$. This is shown in Fig. 3 where $\Delta J/J_0$ is displayed against χ. It is seen that the heat conduction asymmetry can be quite large, with its magnitude and sign strongly dependent on system parameters. When $E_M \gg \omega_0$ the heat flux is dominated by the term $e^{-(\omega_0 - 2E_M)^2/4k_B E_M(T_s - \chi\Delta T)}$ that is bigger when ΔT is negative than when it is positive, hence the negative asymmetry in ΔJ. The same behavior is seen in the opposite limit, $E_M \ll \omega_0$. However, when $2E_M \approx \omega_0$ and $\omega_0 \approx k_B T$, J is dominated by the term $[k_B E_M(T_S - \chi\Delta T)]^{-3/2}$, implying positive asymmetry as seen in Fig. 3.

In Summary, while rectification of electronic current in molecular junctions is well known, heat flux rectification is a novel concept. Asymmetric anharmonic chains have this property, as shown in Fig. 1. We have presented two simple heat rectifying models where anharmonicity stems from the dynamics of a two-level system and asymmetry is introduced by different interaction strengths with the thermal baths. These models should be considered as simple prototypes of few levels systems such as normally encountered in the vibronic spectra of small molecular systems at and below room temperatures, that indeed show similar rectification behavior [13]. For both models, the calculated heat current shows diodelike behavior that depends on the junction characteristics.

Asymmetric coupling to the two thermal reservoirs can be originated from different chemical bonding, by using reservoirs with different Debye temperatures or from different spatial organization of molecular vibrational states [13]. Heat rectification will be very useful in nanodevices, where efficient heat transfer away from the conductor center is crucial for proper functionality and stability. Similarly, directed energy flow in biomolecules such as proteins [14] may play a role in controlling conformational dynamics.

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[1] K. Schwab, E. A. Henriksen, J. M. Worlock, and M. L. Roukes, Nature (London) **404**, 974 (2000).
[2] L. G. C. Rego and G. Kirczenow, Phys. Rev. Lett. **81**, 232 (1998).
[3] D. Cahill *et al.*, J. Appl. Phys. **93**, 793 (2003).
[4] S. Lepri, R. Livi, and A. Politi, Phys. Rep. **377**, 1 (2003).
[5] M. Terraneo, M. Peyrard, and G. Casati, Phys. Rev. Lett. **88**, 094302 (2002).
[6] See papers in Special issue on The Spin-Boson Problem, edited by H. Grabert and A. Nitzan, [Chem. Phys. **296**, 101 (2004)].
[7] A. G. Redfield, IBM J. Res. Dev. **1**, 19 (1957).
[8] Equation (8) is derived assuming $\langle B\rangle = 0$. This is exact for the linear coupling model (7). In the strong coupling case, Eq. (22), $\langle B\rangle \neq 0$ leads to an additional coherent transfer route that is however strongly damped and may be disregarded. [See, e.g., D. Segal and A. Nitzan, Chem. Phys. **281**, 235 (2002)].
[9] The heat flux can be equivalently calculated at the left contact.
[10] The general formulation of D. Segal, A. Nitzan, and P. Hänggi, J. Chem. Phys. **119**, 6840 (2003) yields $\mathcal{T}(\omega) = (2/\pi)\omega^2\Gamma_L\Gamma_R[(\omega^2 - \omega_0^2)^2 + (\Gamma_L + \Gamma_R)^2\omega^2]^{-1}$.
[11] G. D. Mahan, *Many-Particle Physics* (Plenum Press, New York, 2000).
[12] R. A. Marcus, J. Chem. Phys. **24**, 966 (1956).
[13] D. Segal and A. Nitzan, (to be published).
[14] D. M. Leitner, Phys. Rev. Lett. **87**, 188102 (2001).
[15] S. Lifson and P. S. Stern, J. Chem. Phys. **77**, 4542 (1982).