A spin-boson thermal rectifier

*Dvira Segal and Abraham Nitzan
School of Chemistry, Tel Aviv University, Tel Aviv, 69978, Israel
(Dated: March 22, 2004)

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 non-separable model suitable for a stronger system-bath interaction. Both models show asymmetric (rectifying) heat conduction when the couplings to the heat reservoirs are different.

PACS numbers: 63.22.+m, 44.10.+i, 05.60.-k, 66.70.+f

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 1 dimensional quantum wire is characterized by a universal quantum unit. Also of considerable interest are studies that confront the macroscopic Fourier law, $J = -K \nabla T$, a linear relationship between the heat current $J$ and the temperature gradient $\nabla T$ that defines the thermal conductance $K$, with heat transport on the microscopic scale. $^3, 4, 5, 6, 7, 8$. Harmonic chains were repeatedly discussed theoretically in these contexts and considerable experimental work was also made $^9, 10, 11$. For reviews see Refs. $11, 12$.

An intriguing mode of behavior often addressed in the study 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 are 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 $^2, 13, 14$.

$$ J(\omega) = \int T(\omega) [n_L(\omega) - n_R(\omega)] \omega d\omega, \quad (1) $$

where $T(\omega)$ is the transmission coefficient for phonons of frequency $\omega$ and $n_K(\omega) = (e^{\beta_K \omega} - 1)^{-1}$; $\beta_K = (k_B T)^{-1}$; $K = L, R$ $(h = 1)$ 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. $15$ 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. $11$. The model is defined by the $N$-particle Hamiltonian

$$ H = (2m)^{-1} \sum_{i=1}^{N} \dot{p}_i^2 + \sum_{i=1}^{N-1} D \left( e^{-\alpha(x_{i+1} - x_i - x_{eq})} - 1 \right)^2 + D \left( e^{-\alpha(x_i - a)} - 1 \right)^2 + D \left( e^{-\alpha(b - x_N)} - 1 \right)^2, \quad (2) $$

supplemented by damping and noise terms operating on particle 1 and $N$ to simulate the effect of two thermal baths. The equations of motions are

$$ \dot{x}_i = -(1/m) \partial H / \partial x_i = (\gamma_L \dot{x}_i - F_L(t)) \delta_{i,1} - (\gamma_R \dot{x}_N - F_R(t)) \delta_{i,N}. $$

In these equations, $a$, $b$, $x_{eq}$, $\gamma$ and $m$ are constants and $F_L(t)$, $K = L, R$ are Gaussian random forces that satisfy $\langle F_L(t) F_R(0) \rangle = 2 \gamma_K k_B T K \delta(t)/m$. We take $\gamma_L = \gamma(1 - \chi)$ and $\gamma_R = \gamma(1 + \chi)$, $|\chi| \leq 1$, and study the ratio between $\Delta J \equiv J(L = T_h; R = T_c) + J(T_L = T_c; R = T_h) + J(\chi = 0)$, 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 $H_{i+1,i} = D \left( e^{-\alpha(x_{i+1} - x_i - x_{eq})} - 1 \right)^2$. Fig. 1 shows that the intrinsic non-linearity 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, non-linear interactions are essential for rectifying behavior. In this paper we examine the rectifying properties of the simplest non-linear heat conductor: a two level system (TLS). The model investigated is a generalization of the
the $N \to \infty$ limit corresponds to a harmonic oscillator bridge connecting the baths. Eq. (3) corresponds in the latter case to the bilinear coupling model for the oscillator-baths interactions, $H_{MB} = \sum_{j \in K} \tilde{v}_j x_j$, where $x$ is the coordinate of the bridge oscillator and $\alpha_j = \tilde{\omega}_j (2\omega_0)^{1/2}$, 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 following standard procedures, e.g. the Redfield approximation \cite{Ref18} for the weak system-baths coupling limit. In the limit of fast dephasing the resulting kinetic equations for the state probabilities are

$$\dot{P}_n = -(nk_d + (n+1)k_u X_n) P_n + nk_u P_{n-1} + (n+1)k_d X_n P_{n+1}; \quad P_{-1} = 0,$$

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 $k_d = \int^{\infty}_{-\infty} d\omega e^{i\omega\tau} (B^\dagger(\tau)B(0))$ and $k_u = \int^{\infty}_{-\infty} d\omega e^{i\omega\tau} (B(\tau)B^\dagger(0))$. The average is over the baths thermal distributions, irrespective of the fact that it may involve two distributions of different temperatures \cite{Ref19}.

Specifying to the linear coupling model, and assuming no correlation between the thermal baths leads to the rates

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

with

$$k_L = \Gamma_L (\omega_0)(1 + n_L (\omega_0)); \quad k_R = \Gamma_R (\omega_0)(1 + n_R (\omega_0)).$$

The heat conduction properties of this model are obtained from the steady state solution of Eqs. (3) 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

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

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

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

where positive sign indicates current going from left to right \cite{Ref21}. Using Eqs. (8) and (11) we find

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

This is a special case (with $\tau (\omega) = \Gamma_L \Gamma_R (\Gamma_L + \Gamma_R)^{-1} \delta(\omega - \omega_0)$) consistent with our resonance energy.
transfer assumption) of Eq. 1. Obviously no rectifying behavior is obtained in this limit.

Next consider the two levels case, \( N=2 \). The two steady-state equations obtained from (4) yield

\[
P_1 = \frac{k_L e^{-\beta \omega_0} + k_R e^{-\beta \omega_0}}{k_L (1 + e^{-\beta \omega_0}) + k_R (1 + e^{-\beta \omega_0})}; \quad P_0 = 1 - P_1,
\]

and the analog of Eq. 13 is

\[
J = \omega_0 k_R (P_1 - P_0 e^{-\beta \omega_0}).
\]

Using this with Eq. 6, leads to

\[
J = \omega_0 \Gamma_L \Gamma_R (n_L - n_R) \frac{\Gamma_L (1 + 2n_L) + \Gamma_R (1 + 2n_R)}{(1 + n_L + n_R)^2 - \chi^2 (n_L - n_R)^2},
\]

(16)

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

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

(17)

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

The \( L \) and \( R \) boson baths are again maintained at different temperatures \( T_L \) and \( T_R \). When \( T_L = T_R \), Eq. 15 represents a standard spin-boson Hamiltonian used, e.g., in the electron transfer problem. Using the small polaron transformation \( \tilde{H} = U H U^{-1} \), leads to

\[
\tilde{H} = E_0 |0\rangle \langle 0| + E_1 |1\rangle \langle 1| + V_{0,1} |0\rangle \langle 1| + V_{1,0} |1\rangle \langle 0| + \sum_{j \in \{L, R\}} \omega_j a_j^\dagger a_j + H_{\text{shift}},
\]

(19)

where \( U = U_0 U_1 \), \( U_n = e^{i \Omega |n\rangle \langle n|} \), \( \omega_n = \Omega_n + \Omega_{n'} \), \( \Omega_K = \sum_{J \in K} \lambda_n \langle a_j^\dagger - a_j \rangle (K = L, R) \), \( \lambda_{n_j} = (2\omega_j)^{-1/2} \alpha_n \), and \( \Omega_n = \Omega_1 - \Omega_0 \). The term \( H_{\text{shift}} = -(1/2) \sum \omega_j^{-2} (a_j^\dagger a_j) + \alpha_j^2 |1\rangle \langle 1| \) may be henceforth incorporated into the zero order energies. The Hamiltonian (10) is similar to that defined in Eqs. 13-15, except that the system-baths couplings appear as multiplicative rather than additive factors in the interaction term, implying non-separable transport at the two contacts. The dynamics is still readily handled. For small \( V \) (the “non-adiabatic limit”) the Hamiltonian (19) leads again to the rate equation (17) with

\[
k_d = |V_{0,1}|^2 C(\omega_0); \quad k_{\text{up}} = |V_{0,1}|^2 C(-\omega_0),
\]

(20)

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

\[
\tilde{C}(t) = \frac{e^{i \Omega_1 (t) - \Omega_0 (0)}}{\Omega_1 - \Omega_0} \frac{e^{i \Omega_1 (t) - \Omega_0 (0)}}{\Omega_1 - \Omega_0}.
\]

(21)

This may be evaluated explicitly to give

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

(22)

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

(23)

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

\[
C(\omega_0) = \sqrt{\frac{2 \pi}{D^L_2 + D^R_2}} \exp \left( \frac{-(\omega_0 - E^L_0 - E^R_0)^2}{2(D^L_2 + D^R_2)} \right),
\]

(24)

where \( E^L_0 = \sum_{j \in K} \lambda_{1,j} - \lambda_{0,j} \omega^2, D^L_2 = \sum_{j \in K} (\lambda_{1,j} - \lambda_{0,j})^2 \omega^2 (2n_K \omega_j + 1) / k_B T_K \). Eqs. 20-24 provide an extension of the Marcus non-adiabatic rate expressions 22 to the case of two reservoirs maintained at different temperatures. \( E^L_M \) and \( E^R_M \) are the corresponding reorganization energies.

Consider now the steady state heat current. The non-separability of the system-baths 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 Eq. (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 looses energy $\omega_0$ can be therefore viewed 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 $C_L(\omega_0 - \omega)C_R(\omega)$. 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

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

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 $C_K(\omega) = (D_K^L)^{-1/2} \exp[-(\omega - E_K^L)^2/2D_K^L]$. It is convenient also to take $E_K^R = E_M(1 - \chi)$; $E_K^0 = E_M(1 + \chi)$ $(|\chi| \leq 1)$, which implies $D_J^L + D_J^R = 2k_B E_M(T_S - \chi \Delta T)$ where $T_S = T_L + T_R$. Using these relationships in Eq. (25) leads to

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

Eq. (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 $\chi$. 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 $\Delta T$ is negative than when it is positive, hence the negative asymmetry in $\Delta J$. 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. We have presented a simple heat rectifying model where anharmonicity stems from the dynamics of a two-levels system and asymmetry is introduced by different interaction strengths with the thermal baths. We have considered two cases that yield analytical solutions: a separable model with additive interactions with the bridge, and a non separable model. For both, the calculated heat current shows diode like behavior that depends on the junction characteristics.

Asymmetric coupling to the two thermal reservoirs can be affected by different chemical bonding or by using phonon reservoirs with different Debye temperatures. Alternatively, in a more realistic molecular model, this may result from asymmetric spatial organization of the molecular vibrational states.

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 may play a role in controlling conformational dynamics. From the theory perspective, the efficiency of rectification and its possible optimization are issues for future considerations.

This research was supported by the Israel National Science Foundation and by the U.S. - Israel Binaisional Science Foundation.

[1] K. Schwab, E. A. Henriksen, J. M. Worlock, M. L. Roukes, Nature 404, 974 (2000).
[2] L. G. C. Rego and G. Kirczenow, Phys. Rev. Lett. 81, 232 (1998).
[3] Z. Rieder, J. L. Lebowitz, E. Lieb, J. Math. Phys. 8, 1073 (1967).
[4] U. Züürcher, P. Talkner, Phys. Rev. A 42, 3278 (1990).
[5] A. Casher, J. L. Lebowitz, J. Math. Phys. 12, 1701 (1971).
[6] S. Lepri, R. Livi, A. Politi, Phys. Rev. Lett. 78, 1896 (1997).
[7] F. Mokross, H. Buttner, J. Phys. C 16, 4539 (1983).
[8] B. Hu, B. Li, H. Zhao, Phys. Rev. E 57, 2992 (1998).
[9] D. G. Cahill, K. Goodson, A. Majumdar, J. Heat Transfer 124, 223 (2002).
[10] L. Shi, A. Majumdar, J. Heat Transfer 124, 329 (2002).
[11] D. Cahill et al., J. Appl. Phys. 93, 793 (2003).
[12] S. Lepri, R. Livi, A. Politi, Phys. Rep. 377, 1 (2003).
[13] A. Ozpineci, S. Ciraci, Phys. Rev. B 63, 125415/1 (2001).
[14] D. Segal, A. Nitzan, P. Hänggi, J. Chem. Phys. 119, 6840 (2003).
[15] M. Terraneo, M. Peyrard, G. Casati, Phys. Rev. Lett. 88, 094302/1 (2002).
[16] S. Lifson, P. S. Stern, J. Chem. Phys. 77, 4542 (1982).
[17] A. J. Leggett et al., Rev. Mod. Phys. 59, 1 (1987).
[18] A. G. Redfield, IBM J. Res. Develop. 1, 19 (1957).
[19] Eq. (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)).
[20] The heat flux can be equivalently calculated at the left contact.
[21] The general formulation of Ref. 14 yields \( T(\omega) = \frac{2}{\pi} \omega L \Gamma R \left[ \left( \omega^2 - \omega_0^2 \right)^2 + (\Gamma L + \Gamma R)^2 \omega^2 \right]^{-1} \).
[22] G. D. Mahan, Many-particle physics (Plenum press, New York, 2000).
[23] R. A. Marcus, J. Chem. Phys. 24, 966 (1956).
[24] D. M. Leitner, Phys. Rev. Lett. 87, 188102 (2001).