We examine the robustness of single-molecule tunneling diodes to thermal-environmental effects. The diode comprises three fragments: two different conjugated chemical groups at the boundaries, and a saturated moiety in between, breaking conjugation. In this setup, molecular electronic levels localized on the conjugated groups independently shift with applied bias. While in the forward polarity a resonance condition is met, enhancing conductance, in the reversed direction molecular electronic states shift away from each other, resulting in small tunneling currents. In the absence of interactions with a thermal environment (consisting e.g. internal vibrations, solvent), rectification ratios reach three orders of magnitude. We introduce decoherence and inelastic-dissipative effects phenomenologically, by using the “voltage probe” approach. We find that when $\gamma_d \lesssim v$, with $\gamma_d$ the interaction energy of electrons with the environment and $v$ the tunneling energy across the saturated link, the diode is still highly effective, though rectification ratios are cut down by a factor of 2-4 compared to the coherent limit. To further enhance rectification ratios in molecular diodes we suggest a refined design involving four orbitals, with a pair of closely spaced states at each conjugated moiety.

I. INTRODUCTION

One of the simplest building blocks in ordinary semiconductor circuitry, essential for realizing molecular-based electronics, is the rectifier (diode). In fact, the Aviram-Ratner proposal for an organic molecular rectifier largely initiated the field of molecular electronics in 1974. Since then, molecular rectifiers have been fabricated from thin films, self-assembled monolayers (SAMs), and single molecules. However, in general reported rectification ratios were rather low. Only recently have SAMs and single molecule junctions provided robust molecular rectifiers with high conductance, and rectification ratios of two and even three orders of magnitude.

What is the mechanism of electron current rectification in molecular junctions? The literature includes several constructions based on molecules with an asymmetric backbone, different molecule-metal linkers at the two ends, or electrodes of different materials. Fundamentally, from the principles of quantum transport, it is apparent that coherent conduction of noninteracting electrons, as described in scattering theory by the Landauer formula, cannot materialize rectification when energy levels are fixed, independent of applied bias. Two necessary conditions should be simultaneously met for achieving the diode effect: many body interactions should play a role, and a spatial asymmetry should be built into the junction, see e.g. Refs. 15,16, exemplifying charge and heat rectification.

In many proposals, however, the role of many body effects is not spelled out, and it is only included at the level of mean-field, by assuming a screening interaction which creates a voltage drop across the molecular bridge. In particular, theoretical and computational investigations of tunneling diodes employ molecules that are asymmetrically coupled to the electrodes. Using model calculations or first-principle simulations, it is assumed or demonstrated that the junction develops an asymmetric potential profile under bias in the forward and backward direction, see e.g. Refs. 15,21-23. This in turn results in an asymmetric IV characteristics. The development of a voltage drop inside the molecule, however, can be only justified when many body effects (essentially electron-electron interactions) play a role in the junction.

In this paper, we are concerned with single molecule rectifiers made of three fragments, e.g., donor-σ-acceptor junctions. While in their original proposal Aviram and Ratner had assumed vibrationally-assisted intramolecular electron transfer, a related diode can be realized based on quantum tunneling, as presented in Figure 1 and discussed in the next section. Tunneling diodes were investigated for example in Ref. 24, where a DFT + NEGF approach was employed for the study of coherent transport in a three-fragment 1,2-bis(4-(phenylethynyl)phenyl), showing a rectification ratio of $R \sim 1000$. A similar approach (with a different backbone) was adopted in Ref. 25, manifesting $R \sim 100$. These studies and similar proposals employ the Landauer formula for coherent conduction, with the additional assumption of level shift under bias.

The objective of the present work is to examine the robustness of tunneling diodes against environmental effects, when electrons on the junction suffer from decoherence, inelastic effects, and energy dissipation due to their interaction with an “environment”, consisting of degrees of freedom such as molecular vibrations, the solvent, and other electrons. Naturally, since the rectification mechanism in tunneling diodes, depicted in Fig. 1 relies on the sharp contrast between resonant transmission and deep tunneling, rectification ratios should deteriorate when incoherent processes play a role. However, an estimate of this effect for realistic molecular diodes has not yet been provided.
FIG. 1. Illustration of the examined tunneling diode. Displayed are levels (a) at zero bias, (b) forward bias, providing a resonant situation beneficial for conductance, and (c) under reverse bias when levels are shifted away from each other resulting in small tunneling currents.

II. MODEL AND METHOD

We focus on recent proposals for highly rectifying tunneling diodes built from three-fragment molecular backbones such as 1,2-bis(4-(phenylethynyl)phenyl)ethane junctions, see Fig. 2. This asymmetric molecule includes conjugated groups at each end of the junction and a weak tunneling link in the form of a saturated carbon bridge, breaking conjugation. IV characteristics of this system, as calculated with a DFT + NEGF approach, were excellently matched with the two-site (HOMO and HOMO-1) model Hamiltonian

\[ \hat{H} = \left[ \begin{array}{cc} \epsilon_1 + \frac{1}{2} \alpha eV & v \\ v & \epsilon_2 - \frac{1}{2} \alpha eV \end{array} \right], \]

with \( \epsilon_{1,2} \) as the conjugated groups’ site energies at zero bias, \( v \) a small tunneling energy between the units, and \( \alpha \) a phenomenological parameter which describes the fraction of the voltage drop within the molecule, the response to the screening interaction. At zero bias, \( \epsilon_1 = 0 \) and \( \epsilon_2 < 0 \). Under forward bias defined as \( V > 0 \), a resonance situation can be met once \( \epsilon_1 + \frac{1}{2} \alpha eV \approx \epsilon_2 - \frac{1}{2} \alpha eV \), with the shifted levels buried within the bias window, resulting in high currents. Under the reversed operation only tunneling currents contribute in coherent scenarios, see Fig. II Coherent transport can be described by the Landauer formalism. We construct the metal-molecule hybridization matrices with coupling strengths \( \gamma_{L,R} \),

\[ \hat{\Gamma}_L = \gamma_L \left[ \begin{array}{cc} 1 & 0 \\ 0 & 0 \end{array} \right], \quad \hat{\Gamma}_R = \gamma_R \left[ \begin{array}{cc} 0 & 0 \\ 0 & 1 \end{array} \right], \]

and organize the transmission function

\[ T_{L,R}(\epsilon) = \text{Tr}[\hat{\Gamma}_L \hat{G}^r(\epsilon) \hat{\Gamma}_R \hat{G}^a(\epsilon)], \]

defined in terms of the retarded and advanced Greens functions, \( \hat{G}^r(\epsilon) = [\epsilon \hat{I} - \hat{H} + \frac{1}{2}(\hat{\Gamma}_L + \hat{\Gamma}_R)]^{-1}, \hat{G}^a(\epsilon) = [\hat{G}^r(\epsilon)]^\dagger, \hat{I} \) is the identity matrix. The current leaving the \( L \) terminal is calculated from

\[ I_L = \frac{2e}{h} \int_{-\infty}^{\infty} d\epsilon T_{L,R}(\epsilon) [f_L(\epsilon) - f_R(\epsilon)], \]

where \( f_\nu(\epsilon) = [e^{\beta(\epsilon - \mu_\nu)} + 1]^{-1} \) is the Fermi function at the \( \nu = L, R \) terminal with the chemical potential \( \mu_\nu \) and temperature \( T = 1/(k_B \beta) \), \( eV = \mu_L - \mu_R \), \( e \) is the electron charge. In Fig. II we display the IV characteristics and the corresponding rectification ratio

\[ R(V) = \frac{|I(V > 0)|}{|I(V < 0)|} \]

for the 1,2-bis(4-(phenylethynyl)phenyl)ethane molecule, reproducing rectification ratios up to \( R \sim 1000 \) in the coherent limit, as discussed in Ref. 32.

We now assess the role of a thermal environment on this predicted excellent rectifying behavior. The coupling of electrons to other degrees of freedom, e.g., internal molecular vibrations, solvent, other electrons, causes phase decoherence of transmitted electrons, inelastic scattering processes, and energy relaxation. A detailed and accurate description of such processes in molecular conduction is a challenging task, thus for the sake of simplicity and generality, we emulate the environment in a phenomenological manner using Büttiker’s probe approach. We mimic elastic and inelastic scattering of electrons on the molecule by coupling them to fictitious reservoirs, termed “probes.” Specifically, the two molecular sites are coupled to independent (fictitious) metals, identified by ‘1’ and ‘2’. These metals can exchange electrons with the junction, and their properties are determined self-consistently to introduce relevant thermal effects. In direct analogy with Eq. II, we construct the molecule-probes hybridization matrices as

\[ \hat{\Gamma}_1 = \gamma_d \left[ \begin{array}{cc} 1 & 0 \\ 0 & 0 \end{array} \right], \quad \hat{\Gamma}_2 = \gamma_d \left[ \begin{array}{cc} 0 & 0 \\ 0 & 1 \end{array} \right], \]

with \( \gamma_d \) the electron-environment coupling strength. The essential convenience of the probe method lies in its direct correspondence to coherent transport: The current crossing the junction is calculated using the Landauer-Büttiker formula, by generalizing Eq. I to the multi-terminal case,

\[ I_L = \frac{2e}{h} \sum_{j=1,2} \int_{-\infty}^{\infty} d\epsilon T_{L,j}(\epsilon) [f_L(\epsilon) - f_j(\epsilon)], \]

with \( T_{L,j}(\epsilon) = \text{Tr}[\hat{\Gamma}_L \hat{G}^r(\epsilon) \hat{\Gamma}_j \hat{G}^a(\epsilon)] \) and the Green’s functions generalized to include the molecule-probe coupling,
The functions \( f_{1,2}(\epsilon) \) assume a Fermi-function form at temperature \( T \) (uniform across the junction), and we search for \( \mu_{1,2} \) solving Eq. (7). Far-from-equilibrium, when the applied bias is large, an exact analytic solution for this problem is generally missing, though uniqueness is guaranteed\(^{22}\). We thus retrace to a fully numerical procedure, recently implemented for electronic conduction\(^{23}\) and phononic heat transport\(^{24,25}\), and employ the Newton-Raphson method by iterating according to

\[
\begin{bmatrix}
\mu_{k+1}^1 \\
\mu_{k+1}^2 \\
\end{bmatrix} = \begin{bmatrix}
\mu_k^1 \\
\mu_k^2 \\
\end{bmatrix} - \begin{bmatrix}
\frac{\partial \Gamma_1}{\partial \mu_1} & \frac{\partial \Gamma_1}{\partial \mu_2} \\
\frac{\partial \Gamma_2}{\partial \mu_1} & \frac{\partial \Gamma_2}{\partial \mu_2} \\
\end{bmatrix}^{-1} \begin{bmatrix}
I_1 \\
I_2 \\
\end{bmatrix} k,
\]

(9)

converging to the unique set of roots for the probes’ chemical potentials. The voltage probe condition (7) allows phase loss processes and energy exchange. Decoherence without relaxation can be implemented as well with “dephasing probes”, by demanding the energy resolved currents at each probe to vanish, \( I_{1,2}(\epsilon) = 0 \). These strict constraints translate into a set of linear equations for \( f_{1,2}(\epsilon) \), which can be readily solved.

The probe approach for decoherence and relaxation has found many applications in mesoscopic physics for understanding the phenomenology of charge\(^{33,36,37}\) and heat\(^{24,25,38,39}\) transfer. More recently, several studies had implemented probes in molecular electronic problems, albeit limited to linear response situations\(^{40-42}\) or to the simpler dephasing probe approach\(^{44}\).

Below we examine the functionality of tunneling diodes under inelastic effects by implementing the voltage probe approach. Setting the applied voltage, we iterate Eq. (9) to convergence, then calculate the current in the junction from Eq. (8). Convergence is determined by ensuring that the probe potentials \( \mu_{1,2} \) are evolving monotonically, \( |\mu_{k+1}^1 - \mu_k^1| \leq |\mu_k^1 - \mu_{k-1}^1| \), and by confirming that the leakage current to each probe is small, \( |I_{1,2}/I_L| < 10^{-6} \). Our procedure generally required tens to hundreds of cycles to converge, with initial conditions at each bias prepared from converged results at lower voltages.

\[
I_{1,2} = 0,
\]

(7)

with e.g. the probe-1 current

\[
I_1 = \frac{2e}{h} \sum_{j=L,R} \int_{-\infty}^{\infty} dc \mathcal{T}_{1,j}(\epsilon)[f_1(\epsilon) - f_j(\epsilon)].
\]

(8)

The functionality of the junction as a diode is demonstrated in Fig. 2. Inelastic-environmental effects deteriorate the rectifying operation, as expected, yet the junction rectifies substantially even when \( \gamma_d \) is order of the tunneling energy \( v \). When inelastic effects are strong, \( \gamma_d \gg v \), the junction supports only \( R \sim 50 \). Naturally, these values reduce when \( \epsilon_2 \) is placed closer to the Fermi energy, when the gap \( \epsilon_1 - \epsilon_2 \) is reduced, and when \( \gamma_{L,R} \) takes larger values, as was demonstrated in Ref.\(^{27}\).

To understand the decline in the diode operation under environmental effects we display in Fig. 3 the energy resolved currents at the two terminals, \( I_L(\epsilon) \) and \( I_R(\epsilon) \). These currents are calculated from the integrand in Eq. (8) and the corresponding equation for the right terminal. We find that at small biases (0.05 V) the resolved current arranges a single peak located close to the Fermi energy. The role of the environment is to broaden this peak, and

---

**III. RESULTS**

**A. Two-state diodes**

The functionality of the junction as a diode is demonstrated in Fig. 2. Inelastic-environmental effects deteriorate the rectifying operation, as expected, yet the junction rectifies substantially even when \( \gamma_d \) is order of the tunneling energy \( v \). When inelastic effects are strong, \( \gamma_d \gg v \), the junction supports only \( R \sim 50 \). Naturally, these values reduce when \( \epsilon_2 \) is placed closer to the Fermi energy, when the gap \( \epsilon_1 - \epsilon_2 \) is reduced, and when \( \gamma_{L,R} \) takes larger values, as was demonstrated in Ref.\(^{27}\).

To understand the decline in the diode operation under environmental effects we display in Fig. 3 the energy resolved currents at the two terminals, \( I_L(\epsilon) \) and \( I_R(\epsilon) \). These currents are calculated from the integrand in Eq. (8) and the corresponding equation for the right terminal. We find that at small biases (0.05 V) the resolved current arranges a single peak located close to the Fermi energy. The role of the environment is to broaden this peak, and
to slightly enhance the current due to the contribution of inelastic terms. The behavior of the resolved currents at the voltage 0.6 V is displayed in Fig. 3(b). This voltage arranges a resonance configuration most beneficial for conductance, see Fig. 3(b). When \( \gamma_d = 0 \), a single-large contribution to the current shows up (clipped here for clarity), located around \( \epsilon = -0.165 \text{ eV} \), corresponding to the energy of the two molecular sites. When we allow energy exchange with the environment, electrons with energies reaching \( \mu_R = 0.3 \text{ eV} \) contribute, see \( |I_R(\epsilon)| \). These electrons dissipate their energy on the junction, and are re-emitted at the other terminal with lower energies, down to \( \mu_L = -0.3 \text{ eV} \), see the behavior of \( |I_L(\epsilon)| \). Under the reversed bias \(-0.6 \text{ V} \), corresponding to the configuration of Fig. 3(c), an analogous behavior takes place, see Fig. 3(c).

We further present in Figs. 3(b)-(c) the resolved current under the dephasing probe condition, when decoherence effects take place without relaxation. In this case, energy conservation is enforced and electrons on the junction do not absorb/dissipate energy from/to the thermal bath, thus \( |I_L(\epsilon)| = |I_R(\epsilon)| \). The effect of the environment is to broaden the coherent current profile, again disturbing the operation of the diode. Interestingly, the microscopic differences between the two probes as reflected in Fig. 3 do not translate to the macroscopic operation of the device in the present model, and the total-integrated currents under either probes are almost identical. This observation however is not general, and deviations between probes (emulating different microscopic processes) may clearly affect functionality, particularly in multi-site chains.

The departure from the strict tunneling picture limits the operation of the junction as a diode since the contrast between resonant transmission and tunneling no longer stringently holds with inelastic electrons contributing to the current. Note that \( \gamma_{LR} \), the coupling of the molecule to the metals, corresponds to levels’ broadening, and it affects the diode in a parallel manner as the tunneling current becomes over-dominated by ballistic electrons. This effect is presented in Fig. 3 displaying contour plots (log scale) of rectification ratios as a function of \( \gamma_{LR} \) and applied voltage bias at different values for \( \gamma_d \).

In Fig. 3 we further present the rectification ratio at peak voltage, \( R(V_p) \), as a function of \( \gamma_d \). Weakly hybridized junctions operate better as tunneling diodes, yet they are more susceptible to inelastic effects. When the levels are largely broadened with \( \gamma_{LR} = 0.1 \text{ eV} \), the junction still rectifies well with \( R \sim 100 \) in the coherent limit, and it is resistant to the environment as long as \( \gamma_d \lesssim 0.1 \text{ eV} \).

### B. Four-state diodes: sites with quasidegenerate states

The rectifying behavior of a tunneling diode could be enhanced significantly if we mange to attenuate the tunneling current under reverse bias, while keeping intact the resonant current in the forward direction. We recall that in an \( N \)-site molecular chain the tunneling conductance decays exponentially with distance, while the resonant-coherent current is independent of chain length (leaving aside decoherence and dissipation effects). We thus suggest to generalize the two-state tunneling diode of Fig. 1 and include four molecular states, two sites within each conjugated unit, see Fig. 3. In the energy representation, each conjugated unit includes two closely spaced orbitals (at zero bias) instead of a single level. This principle was employed in Ref. 13 to experimentally realize highly rectifying junctions, albeit employing only one conjugated unit and a long saturated tail. The Hamiltonian of the...
four-site molecule takes the form

\[
\hat{H} = \begin{bmatrix} \hat{H}_1 & \hat{V}_{12} \\ \hat{V}_{21} & \hat{H}_2 \end{bmatrix},
\]

with \(\hat{H}_{1,2}\) describing the conjugated units and \(\hat{V}_{12}\) and \(\hat{V}_{21}\) comprising the tunneling terms through the \(\sigma\) bridge,

\[
\hat{H}_1 = \begin{pmatrix} \epsilon_1 + \alpha eV/2 & v_1 \\ v_1 & \epsilon_1 + \alpha eV/2 \end{pmatrix}; \quad \hat{V}_{12} = \begin{pmatrix} 0 & 0 \\ 0 & v \end{pmatrix};
\]

\[
\hat{H}_2 = \begin{pmatrix} \epsilon_2 - \alpha eV/2 & v_2 \\ v_2 & \epsilon_2 - \alpha eV/2 \end{pmatrix}; \quad \hat{V}_{21} = \begin{pmatrix} 0 & v \\ v & 0 \end{pmatrix}.
\]

The two orbitals within each conjugated unit are made close in energy; \(v_{1,2}\) determines departure from degeneracy.

To make a meaningful comparison to the two-site junction, we employ here the same parameters as in Fig. 2. The IV characteristic of the model is displayed in Fig. 4, demonstrating a very large rectification ratio in the coherent limit, but a strong decline in operation under environmental effects. The four-site design thus offers an improved diode functionality, yet a greater sensitivity to thermal effects since a minuscule tunneling current is more easily outplayed by inelastic processes.

IV. CONCLUSIONS

We analyzed the operation of molecular tunneling diodes comprising conjugated-saturated-conjugated segments under environmental effects inducing decoherence and energy relaxation. Specifically, we employed a two-site molecular junction with parameters corresponding to the 1,2-bis(4-(phenylethynyl)phenyl)ethane junction. This system operates as a diode since (i) an asymmetry is built into the molecular backbone, and (ii) an internal potential drop develops within the molecule in response to applied bias. For these reasons, we expect our findings are fully general to constructions with different backbones or system energetics, provided they follow these design principles. The contrast between resonant and tunneling conductances is the key to the optimization of the diode, with rectification ratios reaching three orders of magnitude in coherent situations. The diode performs well under environmental effects as long as \(\gamma_d \lesssim v\), providing \(R \sim 100 - 500\). The decline in the operation of the diode under thermal effects ensues from the contribution of incoherent electrons, playing down the contrast between resonant transmission and tunneling conductance. We further proposed the design of an improved rectifier, suggesting a chemical backbone supporting two closely spaced orbitals within each conjugated unit. This structure provides \(R \sim 10^5\) within our parameters when \(\gamma_d = 0\), though this type of diode shows a greater susceptibility to environmental effects.

An inelastic vibration-assisted diode obeying a similar principle of level alignment was recently investigated in Refs. 46, 47, with a weak, phonon-assisted hopping energy instead of the direct tunneling \(v\). Despite the different conduction mechanism (resonant vs. hopping), this setup

![FIG. 4. Map of rectification ratios as a function of applied bias and metal-molecule hybridization. (a) Coherent limit, (b) \(\gamma_d = 10\) meV, and (c) \(\gamma_d = 100\) meV. Parameters are the same as in Fig. 2.](image1)

![FIG. 5. Decline of rectifying behavior due to environmental interactions with the parameters of Fig. 2. Filled symbols at the left boundary mark corresponding rectification ratios in the coherent \(\gamma_d = 0\) limit.](image2)
produced IV characteristics closely resembling the curve in Fig. 2.

The probe technique employed here for mimicking decoherence and inelastic effects can be feasibly implemented within DFT + NEGF calculations to receive first indications on the role of thermal effects on electron transport in nanojunctions. Our work here is significant beyond the specific analysis of tunneling diodes as we demonstrate for the first time the implementation and utility of the voltage probe method to molecular electronic problems under large biases, introducing inelastic effects into far-from-equilibrium molecular conduction. Our approach allows the interrogation of the role of the environment on other elemental molecular electronic functionalities including negative differential conductance, single-molecule transistors, and nonlinear, phonon-assisted, thermoelectric energy conversion.

ACKNOWLEDGMENTS

This work was funded by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada and the Canada Research Chair Program.

1. Aviram, A.; Ratner, M. A. Molecular Rectifiers. Chem. Phys. Lett. 1974, 29 (2), 277-283.
2. Martin, A. S.; Sambles, J. R.; Ashwell, G. J. Molecular Rectifier. Phys. Rev. Lett. 1993, 70, 218-221.
3. Ng, M.-K.; Yu, L. Synthesis of Amphiphilic Conjugated Diblock Oligomers as Molecular Diodes. Angew. Chem. Int. Ed. 2002, 41, 3598-3601.
4. Chabinyc, M. L.; Chen, X.; Holmlin, R. E.; Jacobs, H.; Skulason, H.; Frisbie, C. D.; Mujica, V.; Ratner, M. A.; Rampi, M. A.; Whitesides, G. M. Molecular Rectification in a Metal-Insulator-Metal Junction Based on Self-Assembled Monolayers. J. Am. Chem. Soc. 2002, 124, 11730-11736.
5. Xu, T.; Peterson, I. R.; Lakshminarthan, M. V.; Metzger, R. Rectification by a Monolayer of Hexadecyloquinolinium Tricyanoquinodimethanide between Gold Electrodes. M. Angew. Chem., Int. Ed. 2001, 40, 1749-1752.
6. Shumate, W. J.; Mattern, D. L.; Jaiswal, A.; Dixon, D. A.; White, T. R.; Burgess, J.; Honcicu, A.; Metzger, R. M. Spectroscopy and Rectification of Three DonorSigmaAcceptor Compounds, Consisting of a One-Electron Donor (Pyrene or Ferrrocene), a One-Electron Acceptor (Perylenebisimide), and a C19 Swallowtail. J. Phys. Chem. B 2006, 110, 111461150.
7. Elbing, M.; Ochs, R.; Koentopp, M.; Fischer, M.; von Hänsich, C.; Weigend, F.; Evers, F.; Weber, H. B.; Mayor, M. A Single-Molecule Diode. Proc. Natl. Acad. Sci. U.S.A. 2005, 102, 8815-8820.
8. Diez-Perez, I.; Hihath, J.; Lee, Y.; Yu, L. P.; Adamska, L.; Kozhushner, M. A.; Olenyik, H; Tao, N. J. Rectification and Stability of a Single Molecular Diode with Controlled Orientation. Nat. Chem. 2009, 1, 635-641.
9. Batra, A.; Darancet, P.; Chen, Q.; Meisner, J. S.; Widawsky, J. R.; Neaton, J. B.; Nuckolls, C.; Venkataraman, L. Tuning Rectification in Single-Molecule Diodes. Nano Lett. 2013, 13, 6233-6237.
10. Nijhuis, C. A.; Reus, W. F.; Whitesides, G. M. Molecular Rectification in Metal-SAM-Metal Oxide-Metal Junctions. J. Am. Chem. Soc. 2009, 131, 17814-17827.
11. Nijhuis, C. A.; Reus, W. F.; Siegel, A. C.; Whitesides, G. M. A Molecular Half-Wave Rectifier. J. Am. Chem. Soc. 2011, 133, 15397-15411.
12. Nernghammong, N.; Yuan, L.; Qi, D. C.; Li, J.; Thompson, D.; Nijhuis, C. A. The Role of van der Waals Forces in the Performance of Molecular Diodes. Nat. Nanotechnol. 2013, 8, 113-118.
13. Yuan, L.; Breuer, R.; Jiang, L.; Schmittel, M.; Nijhuis, C. A. A Molecular Diode with a Statistically Robust Rectification Ratio of Three Orders of Magnitude. Nano Lett., 2015, 15, 5506-5512.
14. Capozzi, B.; Xia, J.; Adak, O.; Dell, E. J.; Liu, Z.-F.; Taylor, J. C.; Neaton, J. B.; Campos, L. M.; Venkataraman, L. Single-Molecule Diodes with High Rectification Ratios Through Environmental Control. Nat. Nanotechnol. 2015, 10, 522-527.
15. Sherif, S.; Rubio-Bollinger, G.; Pinilla-Cianfuegos, E.; Coronado, E.; Agrait, N.; Cuevas, J. C. Current Rectification in a Single Molecule Diode: The Role of Electrode Coupling. arXiv:1504.05382v1.
16. Metzger, R. M. Unimolecular Electrical Rectifiers. Chem. Rev. 2003, 103, 3803-3834.
17. Datta, S. Electronic Transport in Mesoscopic Systems; Cambridge University Press: Cambridge, U.K., 1997.
18. Braunkeber, B.; Feldman, D. E.; Marston, J. B. Rectification in One-Dimensional Electronic Systems Phys. Rev. B 2005, 72, 125311.
19. Segal, D.; Nitzan, A. Spin-boson Thermal Rectifier. Phys. Rev. Lett. 2004, 94, 034301.
Asymmetry and many body interactions are necessary but insufficient conditions for demonstrating the diode effect. In some models only specific types of spatial asymmetry resulted in the diode effect, see e.g. 25,26.

Roy, D. Asymmetric and Asymmetric Charge Transport in Interacting Asymmetric Quantum Impurities. Phys. Rev. B 2010, 81, 085330.

Collet, T.; Schmidtteckert, P. A Minimalistic Diode. Euro. Phys. Lett. 2014, 107, 48006.

Perrin, M. L.; Galan, E.; Eelkema, R.; Grozema, F.; Thijsen, J. M.; van der Zant, H. S. J. Single-Molecule Resonant Tunneling Diode. J. Phys. Chem. C 2015, 119, 5697-5702.

Van Dyck, C.; Ratner, M. A. Molecular Rectifiers: A New Design Based on Asymmetric Anchoring Moieties. Nano Lett. 2015, 15, 1577-1584.

Galperin, M.; Ratner, M. A.; Nitzan, A. Molecular Transport Junctions: Vibrational Effects. J. Phys.: Condens. Matter 2007, 19, 103201.

Böttiker, M. Role of Quantum Coherence in Series Resistors. Phys. Rev. B 1986, 33, 3020-3026 (1986).

Damato, J.; Pastawski, H. M. Conductance of a Disordered Linear Chain Including Inelastic Scattering Event. Phys. Rev. B 1990, 41, 7411.

Jacquet, Ph. A.; Pillet, C. A. Temperature and Voltage Probes Far From Equilibrium. Phys. Rev. B 2012, 85, 125120.

Bediako, S.; Bandyopadhyay, M.; Segal, D. The Probe Technique Far-From-Equilibrium: Magnetic Field Symmetries of Nonlinear Transport. Euro. Phys. J. B 2013, 86, 506.

Bandyopadhyay, M.; Segal, D. Quantum Heat Transfer in Harmonic Chains with Self Consistent Reservoirs: Exact Numerical Simulations. Phys. Rev. E 2011, 84, 011151.

Saaksilaiti, K.; Oksanen, J.; Tulkki, J. Thermal Balance and Quantum Heat Transport in Nanostructures Thermally Localized by Local Langevin Heat Baths. Phys. Rev. E 2013, 88, 012128.

Roy, D.; Dhar, A. Electron Transport in a One Dimensional Conductor with Inelastic Scattering by Self-Consistent Reservoirs. Phys. Rev. B 2007, 75, 195110.

Brandner, K.; Seifert, U. Bound on Thermoelectric Power in a Magnetic Field Within Linear Response. Phys. Rev. E 2015, 91, 012121.

Dhar, A.; Roy, D. Heat Transport in Harmonic Lattices. J. Stat. Phys. 2006, 125, 801-820.

Segal, D. Absence of Thermal Rectification in Asymmetric Harmonic Chains with Self-Consistent Reservoirs. Phys. Rev. E 2009, 79, 012103.

Nozaki, D.; Girard, Y.; Yoshizawa, K. Theoretical Study of Long-ranged Electron Transport in Molecular Junctions. J. Phys. Chem. C 2008, 112, 17408.

Nozaki, D.; Gomes da Rocha, C.; Pastawski, H. M.; Cuniberti, G. Disorder and Dephasing Effects on Electron Transport Through Conjugated Molecular Wires in Molecular Junctions. Phys. Rev. B 2012, 85, 155327.

Venkataramani, R.; Wierzbinski, E.; Waldeck, D. H.; Beratan, D. E. Breaking the Simple Proportionality Between Molecular Conductances and Charge Transfer Rates. Farad. Discuss. 2014, 174, 57-78.

Kilgour, M.; Segal, D. Charge Transport in Molecular Junctions: From Tunneling to Hopping with the Probe Technique. J. Chem. Phys. 2015, 143, 024111.

Chen, S. G.; Zhang, Y.; Koo, S. K.; Tian, H.; Yam, C. Y.; Chen, G. H.; Ratner, M. A. Interference and Molecular Transport: A Dynamical View: Time-Dependent Analysis of Disubstituted Benzenes. J. Phys. Chem. Lett. 2014, 5, 2748.

Nitzan, A. Chemical Dynamics in Condensed Phases: Relaxation, Transfer, and Reactions in Condensed Molecular Systems; Oxford, 2006.

Simine, L.; Segal, D. Vibrational Cooling, Heating, and Instability in Molecular Conducting Junctions: Full Counting Statistics Analysis. Phys. Chem. Chem. Phys. 2012, 14, 13820-13834.

Simine, L.; Segal, D. Path-Integral Simulations with Fermionic and Bosonic Reservoirs: Transport and Dissipation in Molecular Electronic Junctions. J. Chem. Phys. 2013, 138, 214111.

Xu, B.; Dubi, Y. Negative Differential Conductance in Molecular Junctions: an Overview of Experiment and Theory. arXiv:1505.07585.

Perrin, M. L.; Zurek, E.; van der Zant, H. S. J. Single-Molecule Transistors. Chem. Soc. Rev. 2015, 44, 902-919.

Jiang, J.-H.; Kulkarni, M.; Segal, D.; Imry, Y. Phonon-Thermoelectric Transistors and Rectifiers. Phys. Rev. B 2015, 92, 045309.