

When can time-dependent currents be reproduced by the Landauer steady-state approximation?

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We establish well-defined limits in which the time-dependent electronic currents across a molecular junction subject to a fluctuating environment can be quantitatively captured via the Landauer steady-state approximation. For this, we calculate the exact time-dependent non-equilibrium Green's function (TD-NEGF) current along a model two-site molecular junction, in which the site energies are subject to correlated noise, and contrast it with that obtained from the Landauer approach. The ability of the steady-state approximation to capture the TD-NEGF behavior at each instant of time is quantified via the same-time correlation function of the currents obtained from the two methods, while their global agreement is quantified by examining differences in the average currents. The Landauer steady-state approach is found to be a useful approximation when (i) the fluctuations do not disrupt the degree of delocalization of the molecular eigenstates responsible for transport and (ii) the characteristic time for charge exchange between the molecule and leads is fast with respect to the molecular correlation time. For resonant transport, when these conditions are satisfied, the Landauer approach is found to accurately describe the current, both on average and at each instant of time. For non-resonant transport, we find that while the steady-state approach fails to capture the time-dependent transport at each instant of time, it still provides a good approximation to the average currents. These criteria can be employed to adopt effective modeling strategies for transport through molecular junctions in interaction with a fluctuating environment, as is necessary to describe experiments. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4981915>]

I. INTRODUCTION

Recent years have seen remarkable progress in the measurement, modeling, and understanding of structure-function relations in single-molecule junctions.^{1–9} Much of this progress has been catalyzed by experimental developments that have allowed for reliable single molecule junction formation and characterization.^{10–20} In particular, the scanning tunneling microscope based break-junction (STM-BJ) technique offers statistically reproducible properties through rapid, sequential measurement of large numbers of nanoscale junctions.¹²

All of these experiments are performed in an explicitly time-dependent fashion. The time-dependence can arise from repeatedly creating, elongating, and eventually breaking the molecular junction. It can also arise from interactions of the molecule with a thermally fluctuating environment, such as the electrodes or the surrounding solvent. Therefore, in principle, to model this class of experiments it is necessary to solve the Liouville von Neumann equation for a molecule in the presence of leads^{21–33} using, for example, the time-dependent non-equilibrium Green's function (TD-NEGF) method.^{28–33}

Nevertheless, for computational convenience, it is often desirable to approximate the time-dependent transport with steady-state techniques such as the Landauer formalism by

supposing that, even in the presence of time-dependent forces, the transport across the junction is in steady-state at each instant of time during the dynamics. In fact, a standard approach when investigating transport in fluctuating molecular junctions is to perform the molecular dynamics simulation of the fluctuating junction, generate a series of snapshots for the junction geometry, and then calculate the steady-state Landauer transport for each snapshot encountered during the dynamics.^{20,34–42} This approach is convenient because it avoids numerically propagating the dynamics of the density matrix to describe experiments.

Recently, the validity of this often-used steady-state strategy has been called into question⁴³ in the context of simulations of transport through DNA in a solvent which indicates that the steady-state approximation can offer a qualitatively wrong description of the dynamics. While the steady-state approach is clearly not expected to be quantitative under all modeling conditions, its practicality makes it desirable to understand the regime in which it can safely be used to model time-dependent transport phenomena. In this work, we determine well-defined limits in which the time-dependent transport characteristics of molecules subject to a fluctuating environment can be quantitatively captured via the Landauer approach.

To do so, we consider electron transport through a two-site tight-binding molecular junction with on-site energies subject to correlated noise and contrast the current that results from an exact TD-NEGF²⁸ method with that generated by

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supposing that the system is at steady-state at each instant of time. We focus on molecular junctions composed of identical subunits in which the molecular energy eigenstates are delocalized across the junction and connect the two contacts. We study the effect of the molecule-lead coupling, the intramolecular coupling, and the energy fluctuations on the agreement between the two formalisms. As detailed below, the Landauer steady-state approach is found to be a useful approximation when (i) the fluctuations do not disrupt the degree of localization of the molecular eigenstates responsible for transport and (ii) the characteristic time for charge exchange between molecule and leads is fast with respect to the molecular correlation time. These criteria can be employed to adopt effective modeling strategies for transport through molecular junctions in interaction with a fluctuating environment, as is necessary to describe state-of-the-art experiments.

This manuscript is organized as follows: Sec. II defines the model fluctuating molecular junction, the computational strategy, and the metrics of agreement employed in this work. Sec. III discusses the computationally observed agreement between Landauer and TD-NEGF currents under a wide variety of modeling conditions and presents an interpretation of the results in terms of noise-induced changes in the degree of localization. Our main conclusions are summarized in Sec. IV.

II. MODEL AND METHODS

A. Fluctuating molecular junction

As a model of a molecular junction that is subject to a fluctuating environment, we consider a two-site tight-binding molecule coupled to macroscopic electrodes in which the on-site energies are subject to correlated noise, see Fig. 1. The Hamiltonian for the composite metal-molecule-metal junction is given by

$$H(t) = H_M(t) + H_L + H_{ML}, \quad (1)$$

where $H_M(t)$ describes the molecule, H_L the leads, and H_{ML} the molecule-lead coupling. Here, the molecular Hamiltonian can be expressed as

$$H_M(t) = \epsilon_1(t)c_1^\dagger c_1 + \epsilon_2(t)c_2^\dagger c_2 - \gamma(c_1^\dagger c_2 + c_2^\dagger c_1), \quad (2)$$

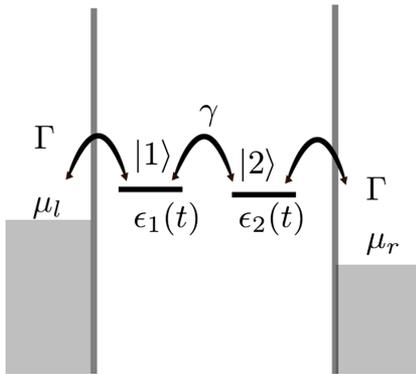


FIG. 1. Two-site tight-binding molecular junction with on-site energies $\epsilon_i(t)$ subject to correlated noise. Here γ is the tight-binding couplings between sites, Γ/\hbar the rate of charge transfer between molecule and contacts, and μ_β the chemical potential of lead $\beta = l, r$.

where the operator c_n^\dagger (or c_n) creates (or annihilates) a fermion in a single site n of energy $\epsilon_n(t)$, i.e., $|n\rangle = c_n^\dagger|0\rangle$, where $|0\rangle$ refers to vacuum. The sites are coupled to one another through the tight-binding coupling γ , and the time-dependence of the on-site energies arises from fluctuations induced by the external environment. As a model of such fluctuations, the time series $\epsilon_i(t)$ is generated using exponentially correlated Gaussian distributed noise of strength σ centered around $\langle\epsilon_i(t)\rangle_T = \lim_{T\rightarrow\infty} \frac{1}{T} \int_0^T \epsilon_i(t)dt$, where $\langle\cdots\rangle_T$ denotes time averages. The initial conditions are sampled from an initial Gaussian distribution of the form^{44,45}

$$P(\epsilon_i(t=0)) = \sqrt{\frac{1}{2\pi\sigma^2}} e^{-(\epsilon_i - \bar{\epsilon}_i)^2/2\sigma^2} \quad (3)$$

centered around $\bar{\epsilon}_i = 0$ and the fluctuations between sites are assumed to be uncorrelated and defined by

$$\langle\epsilon_i(t)\rangle_T = 0; \quad \{\langle\epsilon_i(t)\epsilon_j(s)\rangle_T\} = \delta_{ij}\sigma^2 e^{-(t-s)/\tau_{\text{corr}}} \quad (t > s), \quad (4)$$

where τ_{corr} is the correlation time of the site energies, and where $\langle\cdots\rangle$ denotes average over initial conditions. Throughout this work $\tau_{\text{corr}} = 40$ fs.

In turn, the leads are described by

$$H_L(t) = \sum_{\beta=l,r} \sum_q \epsilon_{\beta q} c_{\beta q}^\dagger c_{\beta q}, \quad (5)$$

where $c_{\beta q}^\dagger$ and $c_{\beta q}$ are the fermionic operators for the lead states and $\beta = l$ or r denotes the left or right lead, respectively. Last, we assume that only site $|1\rangle$ couples to the left lead, while site $|2\rangle$ only couples to the right one, such that the molecule-lead coupling is given by

$$H_{ML} = \sum_q (V_{1q}^l c_{1q}^\dagger c_1 + V_{2q}^r c_{2q}^\dagger c_2 + \text{H.c.}), \quad (6)$$

where V_{nq}^β are the couplings between the molecule and lead β , and H.c. denotes the Hermitian conjugate. The effective molecule-lead coupling is specified by the spectral density $\Gamma_{n,\beta}(\epsilon) = 2\pi \sum_q |V_{nq}^\beta|^2 \delta(\epsilon - \epsilon_{\beta q})$, a quantity that contains information about the characteristic frequencies of the leads and their coupling to the molecule. We focus on the wide-band limit (WBL) where V_{nq}^β and leads' density of states $\zeta^\beta = \sum_q \delta(\epsilon - \epsilon_{\beta q})$ are assumed to be energy independent. In this case, the spectral density is also energy independent and given by

$$\Gamma_{n,\beta} = 2\pi \zeta^\beta |V_n^\beta|^2. \quad (7)$$

In this work, we use $\Gamma_{1,l} = \Gamma_{2,r} = \Gamma$, and zero otherwise. The quantity Γ dictates the characteristic time scale, \hbar/Γ , for charge exchange between the molecule and contacts and generates an effective Lorentzian broadening of the molecular energy levels by 2Γ .

B. Transport computations

For a given trajectory, $\epsilon_i(t)$, the transport was computed using the Landauer formula and the TD-NEGF as developed and implemented by Chen *et al.*²⁸ In the Landauer computations, at each time t , the transmission function, $T(E)$, was computed for all relevant energies and the total current $I_{\text{LD}}(t)$ was numerically evaluated via the Landauer formula. That is,

$I_{LD}(t) = \frac{e}{\pi\hbar} \int dE [f_l(E) - f_r(E)] T(E)$, where e is the elementary charge of an electron, and f_β is the room-temperature (300 K) Fermi function of lead β with chemical potential μ_β . The current was evaluated at equally spaced time intervals every $\tau_{\text{corr}}/2000$.

In turn, in the TD-NEGF the current is obtained by solving the Liouville von Neumann equation for the single-particle electronic reduced density matrix in the presence of leads. In it, the current entering lead β is defined by $I_\beta(t) = -e \frac{d}{dt} \left(\sum_q \langle c_{\beta q}^\dagger c_{\beta q} \rangle \right)$ and the net current passing through the nanojunction is calculated as the average current flowing into the two leads $I_{TD}(t) = (I_l(t) - I_r(t))/2$. The employed method²⁸ combines time dependent density functional theory, NEGF, and the hierarchical equation of motion (HEOM) approach.^{28–31} Specifically, Ref. 28 presents a computational efficient closed set of equations (Eqs. (3), (12), and (14) in Ref. 28) to capture time dependent transport by invoking the wide-band limit and a Padé expansion of the Fermi distribution function. The former allows closing the resulting hierarchy of equations at first tier in the HEOM sense. In turn, the Padé expansion allows for analytically solving the energy integrals that appear in the definition of the self-energies. Here, results were checked for convergence on the number of Padé functions (20) required to represent the leads and on the integration time step ($\tau_{\text{corr}}/2000$) of the Runge Kutta method of order four employed in the numerical integration of the equations of motion.

C. Agreement between methods

The ability of the steady-state approximation to capture the TD-NEGF behavior at each instant of time is quantified via a normalized same-time correlation function of the currents obtained from the two methods,

$$\varrho = \frac{\langle \langle I_{LD}(t) I_{TD}(t) \rangle \rangle_T}{\sqrt{\langle \langle I_{LD}^2(t) \rangle \rangle_T \langle \langle I_{TD}^2(t) \rangle \rangle_T}}. \quad (8)$$

The value of ϱ ranges from 0 to 1, with 1 being perfect correlation and 0 signaling the uncorrelated case. Note that $\varrho = 1$ provided that $I_{LD}(t) = \alpha I_{TD}(t)$ where α is some constant. As such, ϱ measures correlations at each instant of time but is not necessarily indicative of quantitative agreement between the two methods. The global agreement is quantified by examining differences in the average currents

$$\vartheta = \frac{\langle \langle I_{LD}(t) \rangle \rangle_T}{\langle \langle I_{TD}(t) \rangle \rangle_T}. \quad (9)$$

Since the TD-NEGF method captures additional transport mechanisms that are not included in Landauer, typically $\vartheta \leq 1$.

Time and ensemble averages in Eqs. (8) and (9) were obtained by averaging over 1000 individual trajectories each $100\tau_{\text{corr}}$ long. Results were checked for convergence on the number of trajectories and the total propagation time.

III. RESULTS AND DISCUSSION

In order to demonstrate when the Landauer formalism can capture time dependent transport, we quantitatively contrast the Landauer steady-state current with the TD-NEGF current

for a variety of lead-induced broadenings Γ , tight-binding couplings γ , noise strengths σ , and for different bias voltages $eV = \mu_l - \mu_r$. The simulations encompass both resonant and non-resonant transport, circumstances in which the strength of the fluctuations are dominant or perturbative with respect to the tight-binding coupling, and situations in which the time scale for charge transfer between the molecule and leads is either short or long with respect to the molecular correlation time τ_{corr} . Below, we first summarize our basic computational observations (Secs. III A–III D) and then analyze the results in terms of noise-disruption of the degree of delocalization of the levels that dominate transport (Sec. III E).

A. Sample trajectories

Consider first the case in which the molecular orbitals are within the transport window of the leads (between μ_L and μ_R), such that resonant transport is the dominant mechanism for current formation. Figure 2 shows the time dependent site energies, net charge on the molecular bridge, and TD-NEGF and Landauer currents for two particular trajectories under different modeling conditions in which (A) the two methods agree and (B) Landauer offers a poor approximation to the true dynamics (for completeness, additional examples of trajectories comparing TD-NEGF and Landauer currents are included in Fig. S1 of the [supplementary material](#)). Qualitatively, in the case in which Landauer is a good approximation, the steady state transport properties of the junction change mildly during the dynamics (up to an order of magnitude or so) and thus the TD-NEGF current stays close to the steady-state limit. By contrast, in Fig. 2(b) the steady state transport changes by four orders of magnitude when the molecular site energies come in and out of resonance. As a consequence, the current through the system is not near the steady state, and TD-NEGF and Landauer do not coincide.

B. Agreement is determined by γ/σ

Figure 3 shows the degree of local [Eq. (8)] and global [Eq. (9)] agreement between the TD-NEGF and Landauer for 129 modeling conditions. Each point corresponds to an average over 1000 realizations chosen such that the pristine molecule would be under resonant transport conditions. The simulations systematically vary the basic parameters of the model (γ , σ , and Γ) and all results are plotted against a single parameter $\eta = \gamma/\sigma$. The quantity η summarizes the extent to which the strength of the noise σ dominates over the tight-binding coupling γ between sites. The lead induced broadening Γ is color coded and plotted with respect to the energy gap of the pristine molecule 2γ . The exact modeling conditions employed to construct the figure are summarized in the [supplementary material](#).

Remarkably, under a wide range of modelling conditions the agreement between the TD-NEGF and Landauer is mostly determined by a single parameter $\eta = \gamma/\sigma$. When $\eta \gg 1$, the noise is perturbative with respect to the tight-binding coupling and the Landauer steady-state approximation provides an adequate description of the current dynamics. Under these conditions, Landauer adequately describes the TD-NEGF current not only on average (Fig. 3(b)) but at each instant of time (Fig. 3(a)). By contrast, when the noise dominates over

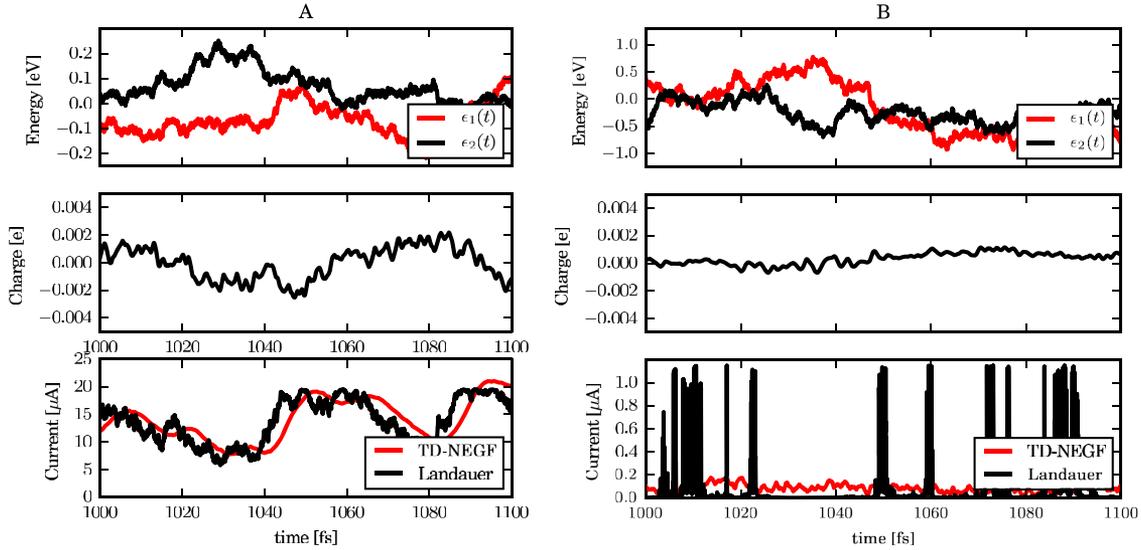


FIG. 2. Resonant transport: Comparison of the TD-NEGF and Landauer time-dependent currents in a situation in which Landauer is (a) a useful ($\rho = 0.9893$ and $\theta = 0.9694$) and (b) poor ($\rho = 0.2114$ and $\theta = 0.2381$) approximation to the dynamics. The plot shows a segment of the dynamics of the site energies $\epsilon_1(t)$ and $\epsilon_2(t)$ (top panel), net charge in the junction (middle panel), and associated currents (bottom panel) for a single trajectory. The chemical potentials $\mu_L = 1.5$ eV and $\mu_R = -1.5$ eV are chosen such that the molecular orbitals are in the transport window at each instant of time, so that resonant transport dominates. (a) $\Gamma = 0.1$ eV, $\gamma = 0.1$ eV, $\sigma = 0.1$ eV. (b) $\Gamma = 0.005$ eV, $\gamma = 0.01$ eV, $\sigma = 0.5$ eV. Note that Landauer fails when the noise induces large changes in the steady-state transport properties.

$\gamma, \eta \ll 1$ and the Landauer strategy to model time-dependent transport fails both locally and globally.

C. Non-resonant transport

Results thus far have focused on the case of resonant transport. Nevertheless, simulations of time-dependent processes using the Landauer strategy often focus on the zero-bias limit where the conductance across the junction is determined by the transmission at the Fermi level $T(E_F)$. This is a practical limit in simulations where a large number (10^5 – 10^9) of molecular snapshots need to be taken into account because it avoids computing the transmission at several energies. It is thus important to determine how the above observations are modified when the molecular energy eigenstates are not in the transport window. Figure 4 shows the local and global agreement for different bias voltages under circumstances in which Landauer is both a good ($\eta = 10$) and a modest ($\eta = 0.5$) approximation to the TD-NEGF resonant transport. As the

voltage is decreased, the transport goes from a resonant to a non-resonant mechanism. The voltage at which this transition approximately happens is signaled by a gray line in the figure. In both cases, as the voltage is decreased Landauer retains its ability to describe the TD-NEGF transport *on average* as quantified by ρ . However, the local agreement becomes poor when transitioning to non-resonant transport. To understand why this is the case, consider Fig. 5 which shows the on-site energies and current for a particular trajectory with $\eta = 10$. While the NEGF currents can be positive or negative due to forward and backward scattering events, the Landauer current is strictly positive. Thus, the two currents are not correlated at each instant of time even when their averages coincide.

D. Dependence on the molecule-lead charge transfer rate

Figure 6 shows the dependence of the local and global agreement on the lead-induced broadening Γ under resonant

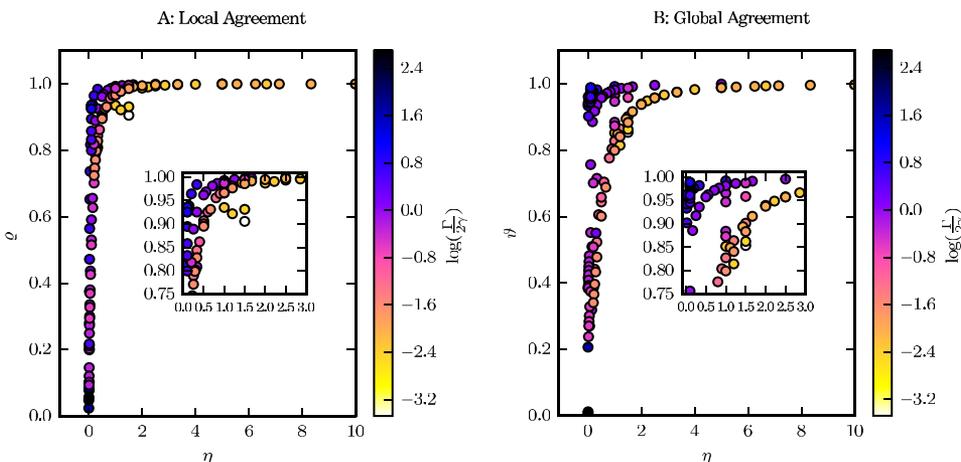


FIG. 3. (a) Local and (b) global agreement between Landauer and TD-NEGF for resonant transport as a function of $\eta = \gamma/\sigma$. The plotted data correspond to simulations with different σ , γ , and Γ . The color code signals the strength of the lead induced broadening Γ with respect to the energy gap of the pristine molecule. For all simulations, we employed a 3 V bias voltage and $T = 300$ K. Note that under a wide range of modeling conditions Landauer and TD-NEGF agree locally and globally when $\eta \gtrsim 1$. The agreement further improves with increasing Γ .

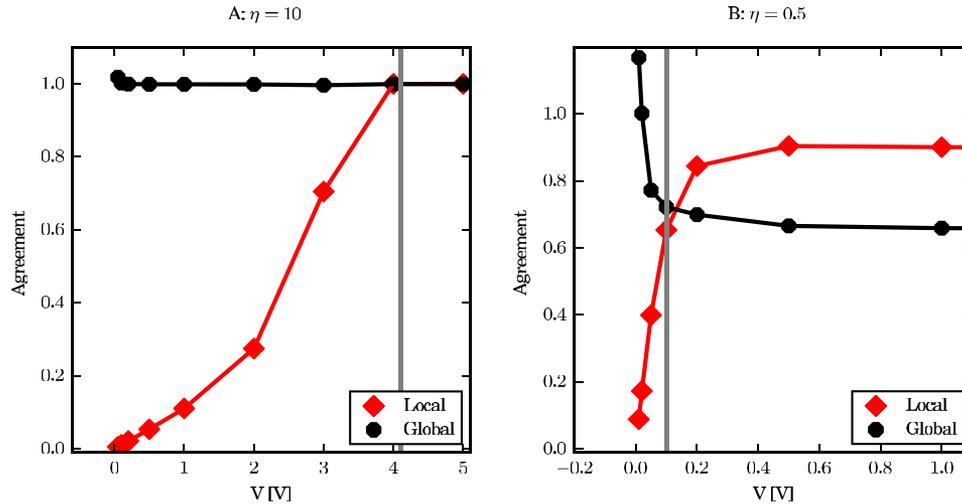


FIG. 4. Agreement between the TD-NEGF and Landauer under non-resonant conditions. The plot shows the local (ϱ) and global (ϑ) agreement as a function of bias voltage for (a) large and (b) moderate η . In (a) $\Gamma = 0.1$ eV, $\gamma = 0.1$ eV, $\sigma = 0.01$ eV, and the Fermi energy $\mu_F = -2$ eV. In (b) $\Gamma = 0.01$ eV, $\gamma = 0.05$ eV, $\sigma = 0.1$ eV, and $\mu_F = 0$ eV. In both cases, the bias voltage is applied symmetrically around μ_F . As the bias increases, the transport transitions from a non-resonant to a resonant mechanism. The gray line indicates the voltage above which transport for the pristine molecule becomes resonant. Note how under the non-resonant condition the TD-NEGF and Landauer can agree on average, even when they do not agree at every instant in time.

(left panel) and non-resonant (right panel) conditions. In circumstances where $\eta \gtrsim 1$, for the Landauer strategy to be a good approximation to the true current across the system the characteristic time scale for charge transfer between the molecule and metallic contacts (\hbar/Γ) must be small with respect to the molecular correlation time τ_{corr} , i.e., $\Gamma \gg \hbar/\tau_{\text{corr}}$. In this way, the leads can resolve any significant changes in the molecule

induced by the noise and the current can stay close to its steady state value.

The inset in Fig. 3 shows how the global and local agreement changes when increasing $\Gamma/2\gamma$ for different fixed values of η . In circumstances when $\eta \lesssim 1$, where the Landauer strategy is not a useful approximation, increasing $\Gamma/2\gamma$ actually improves the agreement between Landauer and TD-NEGF both globally and locally. From a time-dependent perspective, this occurs because by increasing Γ one is reducing the time required for the junction to reestablish steady state transport.

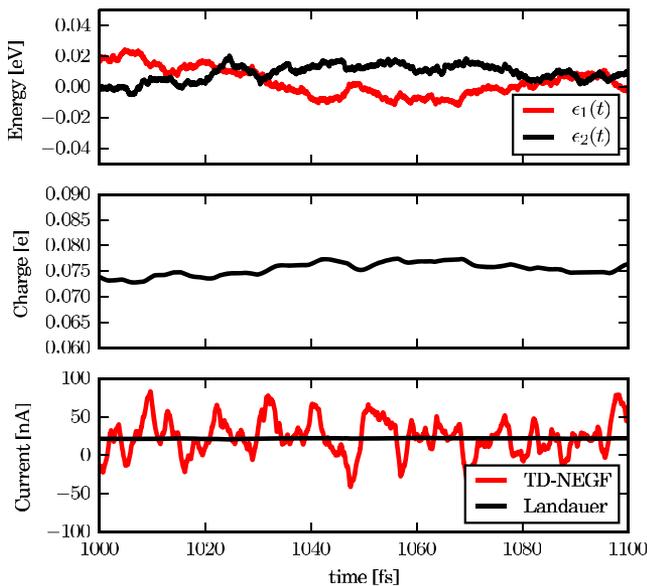


FIG. 5. Non-resonant transport: Comparison of the TD-NEGF and Landauer time-dependent currents for a single trajectory. The plot shows a segment of the dynamics of the site energies $\epsilon_1(t)$ and $\epsilon_2(t)$ (top panel), net charge of the junction (middle panel), and associated current (bottom panel). Here, $\Gamma = 0.1$ eV, $\gamma = 0.1$ eV, $\sigma = 0.01$ eV. The chemical potentials ($\mu_L = -0.5$ eV, $\mu_R = -3.5$ eV) are chosen such that the molecular orbitals are always outside the transport window. Under these conditions, non-resonant transport is dominant. Note that while the TD-NEGF and Landauer currents disagree at each instant of time ($\varrho = 0.7049$), the two quantities agree on average ($\vartheta = 0.9963$).

E. Interpretation in terms of noise-induced changes in localization

The collection of numerical results discussed in Secs. III A–III D indicates that Landauer is a useful approximation to the true TD-NEGF dynamics when (i) the time scale for charge transfer between the molecule and leads is fast with respect to the molecular correlation time $\Gamma \gg \hbar/\tau_{\text{corr}}$ and (ii) the strength of the noise in the site energies is small with respect to the tight-binding coupling between sites, i.e., $\eta = \gamma/\sigma \gg 1$. Remarkably, provided that $\Gamma \gtrsim \hbar/\tau_{\text{corr}}$, the degree of agreement between Landauer and TD-NEGF is well described by a single parameter η over a wide range of simulation conditions. Further, we have observed that when η is suboptimal, increasing Γ actually improves the agreement between the TD-NEGF and Landauer. How to interpret these basic observations?

For the Landauer approach to time-dependent currents to be a useful strategy, transport needs to be close to the steady state during the dynamics. Thus, Landauer becomes a poor approximation when the noise constantly induces large changes to the steady state transport because the NEGF dynamics is kept far from the steady state. Insight into how this can happen is provided by considering the Landauer current in the case in which both molecular levels are in the transport window, as described below.

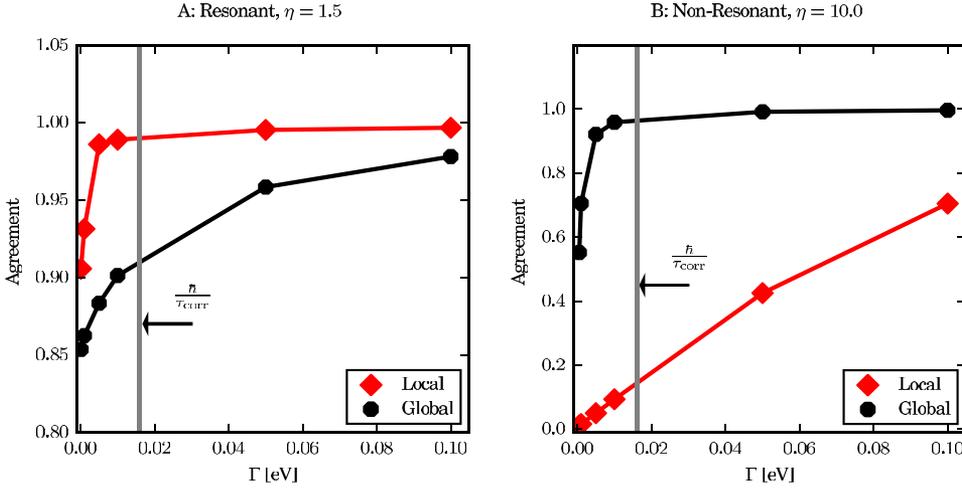


FIG. 6. Agreement between the TD-NEGF and Landauer as a function of lead-induced broadening Γ under (a) resonant and (b) non-resonant conditions. In (a) $\gamma = 0.15$ eV, $\sigma = 0.1$ eV, and $V = 3$ V. In (b) $\gamma = 0.1$ eV, $\sigma = 0.01$ eV, $\mu_F = -2$ eV, and $V = 3$ V. The gray line indicates the value of \hbar/τ_{corr} . When the time scale for charge transfer between molecules and lead $\hbar/\Gamma \gg \tau_{\text{corr}}$, the two methods coincide for $\eta \gtrsim 1$.

1. Resonant steady-state transport through a two-level junction

The Landauer current through a junction with two molecular levels $\alpha = \pm$ is written as

$$I(V) = \frac{e}{\pi\hbar} \sum_{\alpha=\pm} \int_{-\infty}^{\infty} T_{\alpha}(E) (f_l(E + eV/2) - f_r(E - eV/2)) dE, \quad (10)$$

where $f_{\beta}(E)$ is the Fermi function of lead β , and

$$T_{\alpha}(E) = \frac{\Gamma_{\alpha}^l(E)\Gamma_{\alpha}^r(E)}{(E - E_{\alpha})^2 + [(1/2)\Gamma_{\alpha}(E)]^2} \quad (11)$$

is the transmission function at a given energy E associated with level α of energy E_{α} .⁴⁶ Here $\Gamma_{\alpha}(E) = \Gamma_{\alpha}^l(E) + \Gamma_{\alpha}^r(E)$ and $\Gamma_{\alpha}^{\beta}(E) = 2\pi \sum_q |H_{\beta q, E_{\alpha}}|^2 \delta(E - \epsilon_{\beta q})$. The quantity $H_{\beta q, E_{\alpha}}$ is the matrix element of the Hamiltonian between the level q in lead β and the molecular orbital. In the site basis, the molecular orbital $|E_{\alpha}\rangle = \sum_n c_n^{(\alpha)} |n\rangle$ and thus

$$\begin{aligned} \Gamma_{\alpha}^{\beta}(E) &= 2\pi \sum_q |H_{\beta q, E_{\alpha}}|^2 \delta(\mu_F - \epsilon_{\beta q}) \\ &= 2\pi \sum_{q \in \beta} \left| \sum_n c_n^{(\alpha)} V_{q,n}^{\beta} \right|^2 \delta(\mu_F - \epsilon_{\beta q}) \\ &= 2\pi \sum_{q \in \beta} (|c_1^{(\alpha)}|^2 |V_{q,1}^l|^2 \delta_{\beta,l} + |c_2^{(\alpha)}|^2 |V_{q,2}^r|^2 \delta_{\beta,r}) \\ &\quad \times \delta(\mu_F - \epsilon_{\beta q}) \\ &= (|c_1^{(\alpha)}|^2 \delta_{\beta,l} + |c_2^{(\alpha)}|^2 \delta_{\beta,r}) \Gamma, \end{aligned} \quad (12)$$

where we have taken into account that only site 1 (2) couples to the left (right) contact and Eq. (7). In the 0 K approximation for the Fermi functions, and when the molecular orbitals are inside the transport window $[-eV/2, eV/2]$, the Landauer current Eq. (10) simplifies to

$$\begin{aligned} I &\approx \frac{e}{\pi\hbar} \sum_{\alpha} |c_1^{(\alpha)}|^2 |c_2^{(\alpha)}|^2 \int_{-\infty}^{\infty} \frac{\Gamma^2}{(E - E_{\alpha})^2 + \Gamma^2/4} dE, \\ &= \frac{4e\Gamma}{\hbar} |c_1^{(\pm)}|^2 |1 - |c_1^{(\pm)}|^2|, \end{aligned} \quad (13)$$

where we employed Eq. (12). In the last step, we also took into account that for a two-level junction there is a symmetry in the site occupations for the ground and excited states: $|c_1^{(-)}|^2 = |c_2^{(+)}|^2$ and $|c_2^{(-)}|^2 = |c_1^{(+)}|^2$. As shown, the current through

the junction depends on the product of the populations of the molecular orbitals at the contact sites $|c_1^{(\pm)}|^2 |c_2^{(\pm)}|^2$.

Equation (13) can be developed further. Define $\bar{\epsilon} = \frac{\epsilon_1 + \epsilon_2}{2}$ and $\Delta = \epsilon_2 - \epsilon_1$. The energy eigenvalues are $E_{\pm} = \bar{\epsilon} \pm \sqrt{\Delta^2/4 + \gamma^2}$ and the corresponding eigenstates

$$|E_{\pm}\rangle = \frac{\lambda_{\pm}}{\sqrt{\lambda_{\pm}^2 + 1}} |1\rangle + \frac{1}{\sqrt{\lambda_{\pm}^2 + 1}} |2\rangle, \quad (14)$$

where $\lambda_{\pm} = -\frac{1}{\Delta/2\gamma \pm \sqrt{(\Delta/2\gamma)^2 + 1}}$. Substituting $c_1^{(\pm)} = \frac{\lambda_{\pm}}{\sqrt{\lambda_{\pm}^2 + 1}}$ into Eq. (13), yields

$$\begin{aligned} I &= \frac{4e\Gamma}{\hbar} \left| \frac{\lambda_{+}}{\lambda_{+}^2 + 1} \right|^2 \\ &= \frac{e\Gamma}{\hbar} \frac{1}{\Delta^2/4\gamma^2 + 1}. \end{aligned} \quad (15)$$

Therefore the current is reduced when the noise induces a large separation between site energies $|\Delta|$ with respect to 2γ . When this happens, the molecular orbitals localize in one of the sites, reducing the effective coupling between the molecule and the two leads and, thus, reducing the current. The maximum current is achieved when the molecular levels are maximally delocalized such that $|c_1|^2 = 1/2$.

2. Noise-induced changes in the steady-state current

During the stochastic dynamics, the fluctuations of the site energies lead to changes in the steady-state current by changing $|\Delta| = |\epsilon_1 - \epsilon_2|$. The average $|\Delta|$ in a given trajectory is given by

$$\begin{aligned} \langle |\Delta| \rangle_T &= \frac{1}{2\pi\sigma^2} \iint e^{-(\epsilon_1^2 + \epsilon_2^2)/2\sigma^2} |\epsilon_1 - \epsilon_2| d\epsilon_1 d\epsilon_2 \\ &= \frac{1}{2\pi\sigma^2} \int |\Delta| e^{-\Delta^2/4\sigma^2} d\Delta \int e^{-\bar{\epsilon}^2/\sigma^2} d\bar{\epsilon} \\ &= \frac{2\sigma}{\sqrt{\pi}}. \end{aligned} \quad (16)$$

Thus, the figure of merit that controls how much the stochastic fluctuations generate appreciable current fluctuations can be defined as

$$\frac{\gamma}{\langle |\Delta| \rangle_T} \sim \frac{\gamma}{\sigma} = \eta, \quad (17)$$

which is the quantity used to analyze the data.

3. Origin of the observed trends

The key idea in understanding the observed trends is that, provided that $\Gamma \gtrsim \hbar/\tau_{\text{corr}}$, a discrepancy between the TD-NEGF and Landauer occurs when the noise can lead to strong changes in the steady state current. In light of Eq. (13), this happens when the noise completely changes the degree of localization of the molecular orbitals. The extent to which this is possible in a given trajectory is determined by $\eta = \gamma/\sigma$. When η is small, fluctuations in the site energies can strongly change the degree of localization of the molecular orbitals. Such changes keep the TD-NEGF current far from the steady state and make the Landauer estimate of the time-dependent currents of limited applicability. In other words, Landauer is a useful approximation for the TD-NEGF currents only when the noise does not induce changes in the degree of delocalization of the molecular orbitals responsible for transport.

IV. FINAL REMARKS

In conclusion, we have isolated well-defined conditions under which the time-dependent electronic currents across a molecular junction subject to a fluctuating environment can be quantitatively captured via the Landauer steady-state approximation. The Landauer steady-state approach is found to be a useful approximation when (i) the fluctuations do not disrupt the degree of localization of the molecular eigenstates responsible for transport and (ii) the characteristic time for charge exchange between the molecule and leads is fast with respect to the molecular correlation time. In the context of the model investigated here, the first condition requires $\eta = \gamma/\sigma \gg 1$ while the second one requires $\hbar/\Gamma \ll \tau_{\text{corr}}$. In essence, condition (i) guarantees that the magnitude of the steady state current does not vary drastically as a consequence of changes induced by the noise. If that is the case, the TD-NEGF current will stay close to the steady state and Landauer becomes a useful approximation to capture the current dynamics. In turn, condition (ii) guarantees that the rate of charge-transfer between the molecule and contacts is sufficiently fast such that it can resolve any significant dynamical changes in the molecule.

For resonant transport, when these conditions are satisfied, the Landauer approach is found to accurately describe the current, both on average and at each instant of time. For non-resonant transport, we find that while the steady-state approach fails to capture the time-dependent transport at each instant of time, it still provides a good approximation to the average current. This latter observation brings light into the important question of how to interpret the non-resonant current I_{NR} or, equivalently, the low-bias conductance $G = I_{\text{NR}}/V$ computed for individual snapshots encountered in a MD trajectory of the junction of evolution. As observed, the current across (conductance of) each snapshot of the junction has no obvious relation with experimentally measurable values. However, the time-averaged currents that are experimentally recorded do coincide with the Landauer currents averaged over a statistically significant set of molecular conformations.

These conditions for agreement between Landauer and TD-NEGF were isolated based on simulations on a tight-binding molecule coupled by its ends to metallic contacts

described in the wide bandwidth limit. Both the molecule and leads were supposed to be well described by an effective single-particle electronic Hamiltonian. Further, no back action of the molecule to the fluctuating environment was considered. While the isolated conditions are expected to be applicable in a wide variety of situations, additional conditions may emerge for more complex leads and lead-molecule couplings, for systems where Coulomb blockade is important, or in situations in which the current generates significant electron-nuclear dynamics.

At this point, it is useful to connect these results with previous observations on the ability of Landauer to reproduce TD-NEGF currents in fluctuating junctions. The DNA simulations investigated in Ref. 43 are in a situation in which $\sigma \sim 0.1$ eV, $\gamma \sim 0.03$ eV, $\Gamma = 1$ meV, and $\tau_{\text{corr}} \sim 200$ fs. Thus, \hbar/Γ is long with respect to the molecular correlation time and the strength of the noise is large with respect to the tight binding couplings. Thus, the simulations violate both identified conditions and Landauer is a poor approximation to the current dynamics. In Ref. 47, the authors argue that in order to have coherent transport the molecular orbitals responsible for the transport across the junction must be delocalized. In light of the results presented here, it becomes clear that this statement is not entirely precise as, in the absence of fluctuations, transport through a junction with localized states will be well described by the Landauer approach. What leads to the disagreement between Landauer and TD-NEGF in Ref. 47 is that the noise can strongly change the magnitude of the steady-state current by changing the degree of localization of the states involved in the transport.

It is important to stress that the isolated conditions apply to physical circumstances where the effect of the environment can be described as a time-dependent potential term in the Hamiltonian. Deciding which type of quantum environment admits such a time-dependent description ultimately relies on contrasting with the experiment. Nevertheless, theoretical analyses⁴⁸ suggest that this can occur when there is no entanglement between the molecular degrees of freedom of interest (i.e., the levels responsible for transport) and the environmental degrees of freedom and when the environment can be thought of in the classical limit. We thus expect the above considerations to apply to the thermal dynamics induced by poor solvents or torsional motions. By contrast, high frequency molecular vibrations or highly entangled vibronic states are expected to require a full quantum description to be correctly captured in the TD-NEGF.

Under plausible experimental conditions at room temperature and in solution, $\sigma \sim 0.1$ eV and $\Gamma \sim 0.01$ eV.^{47,49} Under such conditions, the Landauer approach is useful for molecules with tight-binding couplings that dominate over the noise and correlation times longer than ~ 60 fs. In this scenario, for instance, the time-dependent current through rigid conjugated molecules can be well described by Landauer as conformational changes are not expected to change the degree of level delocalization. By contrast, systems with tight-binding couplings between constitutive units that are small with respect to noise in the site energies such as DNA, RNA, or molecular dimers will be cases in which the use of Landauer approach can be problematic. These criteria can be employed to adopt

effective modeling strategies for transport through molecular junctions in interaction with a fluctuating environment, as is necessary to describe experiments.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for trajectories comparing TD-NEGF and Landauer currents under representative modeling conditions and simulation conditions employed to produce Fig. 3.

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