

Vibrational instabilities in charge transport through molecular nanojunctions: The role of anharmonic nuclear potentials

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The current-induced vibrational dynamics is a key factor determining the mechanical stability of molecular nanojunctions. Beyond conventional Joule heating, a different mechanism leading to vibrational instability, which is induced by nonconservative current-induced forces, has been reported at low bias voltage. Given reports that this mechanism can induce extremely large vibrational excitation in models in which the unperturbed vibrational potentials are harmonic, a natural question is whether it can also be a source of current-induced bond rupture and dissociation in anharmonic systems. Consequently, in this work, we extend previous investigations of two-level, two-mode molecular nanojunctions to various anharmonic unperturbed vibrational potentials. Using a mixed quantum-classical approach based on electronic friction and Langevin dynamics, we first explore the impact of nonconservative forces on dissociation dynamics in Morse-type potentials. Furthermore, using quartic vibrational potentials, we use steady-state vibrational excitation and electric current to explore the impact of anharmonicity on this mechanism of vibrational instability, investigating whether it survives beyond the purely harmonic limit in this system.

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I. INTRODUCTION

The continuous aim to further miniaturize electronic circuits has led to the idea of building electronic devices from single molecules [1–8]. The simplest building blocks of such molecular devices, molecular nanojunctions, are constructed by attaching single molecules to two metallic leads. Beyond potential technological applications, such devices offer fascinating insight into nonequilibrium physics and can be used to explore intriguing novel physical effects that originate from the quantum mechanical nature of such systems.

One of the most fundamental obstacles regarding the investigation of molecular nanojunctions, both in technological applications and experiments, is their stability under nonequilibrium charge transport when applying a finite bias voltage. The interaction between the vibrational and electronic degrees of freedom (DOFs) within the molecule causes current-induced or Joule heating, which can lead to vibrational instabilities [9–18] and current-induced rupture of parts of the junction [19–29].

While Joule heating may significantly influence the stability of the nanojunction at high bias voltages, there have been reports of a different mechanism of vibrational instability already at low bias voltage in systems with multiple active vibrational modes [30–33]. Generally, this mechanism can be

understood in a mixed quantum-classical framework of the vibrational dynamics, in which the nuclear vibrational DOFs are treated classically, and the quantum electronic DOFs are integrated out, appearing as effective electronic forces. Under further assumptions of Markovianity and weak nonadiabaticity, this yields the Markovian electronic friction and Langevin dynamics approach, in which the electronic forces explicitly separate into an adiabatic mean force, electronic friction, and a stochastic force.

At equilibrium, these electronic forces possess certain properties. For example, at zero bias voltage, the electronic friction tensor is positive semi-definite; the second fluctuation-dissipation theorem (FDT) is satisfied; and the adiabatic mean force is conservative. However, in nonequilibrium scenarios, such as at finite bias voltage, these properties are not guaranteed, potentially leading to negative electronic friction, breaking of FDT through Joule heating, and a non-conservative adiabatic mean force [34–40]. It is exactly this last effect that provides the basis for the multimode mechanism of vibrational instability under investigation in this work. Specifically, if two or more vibrational frequencies in a multimode system are degenerate, the nuclear trajectory follows a path with fixed rotational direction and, hence, gains energy in each cycle from the nonconservative force field [34], eventually leading to an instability.

Although this mechanism is well understood for degenerate vibrational modes, there have been differing reports about whether it survives in nondegenerate multimode systems. For example, in Refs. [30,32], the authors used an eigenmode analysis to predict that the Berry force, which corresponds to the antisymmetric component of the electronic friction tensor, can pull the vibrational trajectories into elliptical shapes, therefore allowing vibrational instability even for

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nondegenerate vibrational modes [30,32,41,42]. In contrast, we recently used a fully coordinate-dependent Markovian Langevin equation to simulate the dynamics of the same system as in Ref. [32], and only observed instabilities for truly degenerate vibrational modes [33]. For nondegenerate modes, the dynamics remained stable, and the Berry force had a negligible impact on the dynamics.

Given that the mechanism is highly sensitive to detuning of the frequencies of the unperturbed vibrational potentials, a natural question is whether it is also highly sensitive to anharmonicity in the unperturbed nuclear potentials. Moreover, if this mechanism of vibrational instability can be observed in systems with anharmonic, unbound potentials, would it then have a measurable impact on bond rupture and the corresponding dissociation dynamics? These questions are highly relevant for more realistic systems, in which vibrational frequencies may indeed be close to degenerate, but are unlikely to be purely harmonic, and may give an important hint as to why experimental evidence of this mechanism is scarce [43].

Motivated by these questions, in this work, we explore the vibrational dynamics of various degenerate and nondegenerate anharmonic multimode systems. As in Ref. [33], we treat the vibrational dynamics with a Markovian Langevin equation [32,44–59] and calculate the electronic forces via nonequilibrium Green's functions (NEGFs) [46,47,49,54,60,61], which form the combined (NEGF-LD) approach. Specifically, we explore a two-level, two-mode dissociative model containing Morse potentials instead of harmonic oscillators, as well as a simpler quartic model that allows for rigorous investigation of the anharmonic effects. Via dissociation rates and steady-state vibrational energies, we show that the mechanism of vibrational instability arising from nonconservative electronic forces disappears when the unperturbed vibrational potential is even slightly anharmonic.

The paper is structured as follows. In Sec. II, we introduce a general two-level, two-mode model of a molecule interacting with metallic leads. In Sec. III, we give an overview of the nonequilibrium transport theory in this work, first demonstrating how to obtain electronic forces from NEGFs and then describing the vibrational dynamics with a Markovian Langevin equation. In Sec. IV, we apply the approach to various model systems for which we simulate the vibrational dynamics, thereby analyzing the effect of anharmonic nuclear potentials on their stability and steady-state observables.

Since we have to differentiate between classically and quantum mechanically treated coordinates and momenta, we will explicitly denote the vectors of position and momentum operators as $\hat{\mathbf{x}}$ and $\hat{\mathbf{p}}$, while their classical counterparts will be denoted by $\mathbf{x}$ and $\mathbf{p}$. Moreover, we use units where $e = \hbar = 1$.

II. MODEL

In this section, we introduce the general model of a molecular nanojunction and specify it for the particular models considered within this work, thereby expanding the model considered in Ref. [33] to anharmonic potentials. The total Hamiltonian of the setup is

$$H = H_{\text{mol}} + H_{\text{leads}} + H_{\text{mol-leads}}, \quad (1)$$

where H_{mol} is the molecular Hamiltonian, H_{leads} is the Hamiltonian of the leads, and $H_{\text{mol-leads}}$ describes the interaction between the two.

In our model, the molecular Hamiltonian consists of a vibrational component, $H_{\text{mol}}^{\text{vib}}$, and a term accounting for both the purely electronic contribution and the electronic–vibrational interactions, $H_{\text{mol}}^{\text{el}}$:

$$H_{\text{mol}} = \underbrace{\sum_{mn} h_{mn}(\hat{\mathbf{x}}) d_m^\dagger d_n}_{=H_{\text{mol}}^{\text{el}}} + \underbrace{\sum_i \left(U_{u,i}(\hat{x}_i) + \frac{\hat{p}_i^2}{2m_i} \right)}_{=H_{\text{mol}}^{\text{vib}}}. \quad (2)$$

The operators $d_m^\dagger$ and d_m create and annihilate an electron at the m th energy level with energy $h_{mm}(\hat{\mathbf{x}})$, respectively. The off-diagonal elements $h_{mn}(\hat{\mathbf{x}})$ refer to the electron hopping between the electronic levels. Moreover, $U_{u,i}(\hat{x}_i)$ denotes the potential of the uncharged state of the molecule along vibrational mode i . The i th vibrational DOF has coordinate $\hat{x}_i$, and momentum $\hat{p}_i$. Since we will consider exclusively models with two vibrational modes, we collect them into vectors $\hat{\mathbf{x}} = (\hat{x}_1, \hat{x}_2)$ and $\hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2)$, respectively.

The energies of the electronic DOFs are contained in the matrix of single-particle energies and interactions, $h(\hat{\mathbf{x}})$, which in this work will always have the form

$$h(\hat{\mathbf{x}}) = \begin{pmatrix} U_c^{(1)}(\hat{x}_2) - U_{u,2}(\hat{x}_2) & t(\hat{x}_1) \\ t(\hat{x}_1) & U_c^{(2)}(\hat{x}_2) - U_{u,2}(\hat{x}_2) \end{pmatrix}. \quad (3)$$

Here, $U_c^{(1)}(\hat{x}_2)$ and $U_c^{(2)}(\hat{x}_2)$ denote the potentials of the charged states (1) and (2). The off-diagonal terms, $t(\hat{x}_1)$, describe vibrationally assisted hopping between the electronic levels. The specific form of the introduced potentials used in this work will be given in Sec. IV. Note that, in general, both vibrational modes may couple diagonally and off-diagonally to both electronic levels. In principle, such systems can also be explored in the NEGF-LD framework introduced in Sec. III. In this work, however, we have chosen the explicit form of Eq. (3) as it represents the simplest anharmonic extension of previous investigations into instabilities arising from current-induced forces in multimode systems [30–33,39].

To this end, throughout this work we further restrict the anharmonicity to mode 2, such that the potential of mode 1 has the form

$$U_{u,1}(\hat{x}_1) = \frac{1}{2} m_1 \omega_1^2 \hat{x}_1^2. \quad (4)$$

Moreover, the hopping between the electronic levels is assumed to always couple linearly to coordinate $\hat{x}_1$, such that

$$t(\hat{x}_1) = t_0 + \lambda_1 \hat{x}_1. \quad (5)$$

Furthermore, to compare our results to previous work [33], we will also consider the corresponding harmonic version of Eq. (3), which we obtain by performing a Taylor expansion of $U_{u,2}(\hat{x}_2)$, $U_c^{(1)}(\hat{x}_2)$, and $U_c^{(2)}(\hat{x}_2)$ up to second order around their respective minima. For example, the corresponding

harmonic potential of $U_{u,2}(\hat{x}_2)$ is

$$U_{u,2}^{\text{harm}}(\hat{x}_2) = U_{u,2}(\hat{x}_2)|_{\hat{x}_2^0} + \frac{\partial}{\partial \hat{x}_2} U_{u,2}(\hat{x}_2)|_{\hat{x}_2^0} (\hat{x}_2 - \hat{x}_2^0) + \frac{1}{2} \frac{\partial^2}{\partial \hat{x}_2^2} U_{u,2}(\hat{x}_2)|_{\hat{x}_2^0} (\hat{x}_2 - \hat{x}_2^0)^2. \quad (6)$$

Throughout this work, we choose the potential $U_{u,2}^{\text{harm}}(\hat{x}_2)$ such that the minimum of the potential is at $\hat{x}_2^0 = 0$. Using a similar procedure, we obtain the corresponding harmonic versions of $U_c^{(1)}(\hat{x}_2)$ and $U_c^{(2)}(\hat{x}_2)$.

Finally, the harmonic analog of Eq. (3) is given by

$$h^{\text{harm}}(\hat{\mathbf{x}}) = \begin{pmatrix} \varepsilon_0 + \lambda_2 \hat{x}_2 & t_0 + \lambda_1 \hat{x}_1 \\ t_0 + \lambda_1 \hat{x}_1 & -\varepsilon_0 - \lambda_2 \hat{x}_2 \end{pmatrix}, \quad (7)$$

where $\lambda_i = \tilde{\lambda}_i \sqrt{m_i \omega_i}$, and the potentials of both coordinates in the uncharged state are now harmonic,

$$U_{u,i}^{\text{harm}}(\hat{x}_i) = \frac{1}{2} m_i \omega_i^2 \hat{x}_i^2. \quad (8)$$

The parameters $\tilde{\lambda}_i$, ω_i , ε_0 and t_0 are determined by the Taylor expansion of $U_{u,i}(\hat{x}_i)$, $U_c^{(1)}(\hat{x}_2)$, and $U_c^{(2)}(\hat{x}_2)$.

The left (L) and right (R) leads are modeled as reservoirs of noninteracting electrons,

$$H_{\text{leads}} = \sum_{\alpha \in \{L, R\}} \sum_k \varepsilon_{k\alpha} c_{k\alpha}^\dagger c_{k\alpha}. \quad (9)$$

The energy of state k in lead α is given by $\varepsilon_{k\alpha}$, while $c_{k\alpha}^\dagger$ and $c_{k\alpha}$ denote the corresponding creation and annihilation operators, respectively. Both leads are held at local equilibrium, such that they have a well-defined chemical potential, μ_α , and temperature, T . By applying a bias voltage to the junction, $\Phi = \mu_L - \mu_R$ with $\mu_L = -\mu_R = e\Phi/2$, the system is driven out of equilibrium.

The interaction between the molecule and the leads is given by

$$H_{\text{mol-leads}} = \sum_{k,\alpha} \sum_m V_{k\alpha,m} (c_{k\alpha}^\dagger d_m + d_m^\dagger c_{k\alpha}), \quad (10)$$

where $V_{k\alpha,m}$ describes the coupling strength between state m in the molecule and state k in lead α . For noninteracting reservoirs and a molecule-lead coupling linear in the respective creation and annihilation operators, the influence of the leads on the molecular dynamics is completely described by two-time correlation functions, which are in turn characterized in terms of the spectral density of each lead,

$$\Gamma_{\alpha,mm'}(\epsilon) = 2\pi \sum_k V_{k\alpha,m} V_{k\alpha,m'}^* \delta(\epsilon - \varepsilon_{k\alpha}). \quad (11)$$

We will work in the wideband limit, such that the spectral density is a constant: $\Gamma_{\alpha,mm'}(\epsilon) = \Gamma_{\alpha,mm'}$. Moreover, we exclusively consider models where only level (1) couples to the left lead and level (2) to the right lead, such that $\Gamma_{L,22} = \Gamma_{R,11} = \Gamma_{\alpha,21} = \Gamma_{\alpha,12} = 0$. Moreover, we assume that the remaining coupling strengths are the same: $\Gamma_{L,11} = \Gamma_{R,22} = \Gamma$, and will refer to Γ as the molecule-lead coupling strength.

III. NONEQUILIBRIUM TRANSPORT THEORY

In this section, we briefly introduce and discuss the approaches we use to investigate the influence of anharmonic potentials on vibrational instabilities in molecular nanojunctions. More detailed overviews can be found in Refs. [32,33,52–54,57,60,61].

First, in Sec. III A, we introduce the classical approximation to the vibrational dynamics, before introducing the further timescale separation approximation in Sec. III B that leads to a Markovian Langevin equation. Finally, in Secs. III C and III D, we provide expressions for the resulting electronic forces in terms of NEGFs and discuss the numerical details and observables, respectively.

A. Classical vibrational dynamics

As shown in Refs. [52] and [32], the time evolution of the fully quantum mechanically vibrational DOFs, $\hat{\mathbf{x}}(t)$, can be exactly expressed in terms of the Feynman-Vernon influence functional, which incorporates the effect of the electronic DOFs in the molecule and leads via an effective action. From this starting point, a classical equation of motion for the vibrational DOFs is obtained by introducing Wigner coordinates and expanding the influence functional up to second order in electronic influence and in the quantum difference to the classical path, denoted by $\delta\mathbf{x}(t) = \hat{\mathbf{x}}(t) - \mathbf{x}(t)$:

$$m_i \ddot{x}_i = - \frac{\partial U_{u,i}}{\partial x_i} - \underbrace{\text{Tr}_{\text{el}} \left\{ \frac{\partial H_{\text{mol}}^{\text{el}}(\mathbf{x}(t))}{\partial x_i} \rho_{\text{el}}[\mathbf{x}(t)] \right\}}_{=F_i[\mathbf{x}(t)]} + f_i(t), \quad (12)$$

where $x_i(t)$ is the i th vibrational coordinate of the classical path.

In this limit, molecular vibrations experience a classical force from the unperturbed vibrational potential, $U_{u,i}(x_i)$, an average electronic force, $F_i[\mathbf{x}(t)]$, and a Gaussian electronic stochastic force, $f_i(t)$. Since in this limit the electronic influence has been expanded only up to second order, $f_i(t)$ is completely characterized by its mean, $\langle f_i(t) \rangle = 0$, and colored correlation function,

$$\langle f_i(t) f_j(t') \rangle = \text{Tr}_{\text{el}} \{ f_i(t) f_j(t') \rho_{\text{el}}(t_0) \} = D_{ij}(t, t'). \quad (13)$$

In general, the exact electronic influence contains higher-order forces and non-Gaussian noise terms, which would appear when continuing the expansion. This also applies to the expansion in $\delta\mathbf{x}(t)$, which would add quantum corrections to both the classical vibrational force and the electronic force terms if taken to higher order. We note that for models containing harmonic vibrational potentials and electronic-vibrational couplings that are linear in the vibrational coordinates, the expansion in $\delta\mathbf{x}(t)$ naturally terminates at the classical limit, but that it is an approximation for the anharmonic models treated in this work. This can also be seen in other approaches to obtaining the LD method, such as applying a partial Wigner transform to the Liouville-von Neumann equation and expanding up to the classical limit [50,57,59].

For noninteracting models as in Sec. II, one can write the average electronic force in terms of Keldysh NEGFs

[45,49,60],

$$F_i[\mathbf{x}(t)] = i\text{Tr}\left\{\frac{\partial h(\mathbf{x})}{\partial x_i}G^<(t, t)\right\}, \quad (14)$$

where the $\text{Tr}\{\dots\}$ indicates a trace over the single-particle Hilbert of $h(\mathbf{x})$. The lesser Green's function is defined as

$$G_{mn}^<(t, t') = i\text{Tr}_{\text{el}}\{d_n^\dagger(t')d_m(t)\rho_{\text{el}}(t_0)\}, \quad (15)$$

where the molecular electronic creation and annihilation operators have been written in the Heisenberg picture,

$$O_{\text{el}}(t) = U_{\text{el}}^\dagger(t, t_0)O_{\text{el}}U_{\text{el}}(t, t_0). \quad (16)$$

Here, the time-evolution operator is given by the time-ordered exponent,

$$U_{\text{el}}(t, t_0) = \mathcal{T}e^{-i\int_{t_0}^t d\tau H_{\text{el}}(\mathbf{x}(\tau))}, \quad (17)$$

where $H_{\text{el}}(\mathbf{x}) = H_{\text{mol}}^{\text{el}}(\mathbf{x}) + H_{\text{leads}} + H_{\text{mol-leads}}$.

The correlation function of the stochastic force can similarly be expressed as [50,61]

$$D_{ij}(t, t') = \text{Tr}_{\text{el}}\{f_i(t)f_j(t')\rho_{\text{el}}(t_0)\} \quad (18)$$

$$= \text{Tr}\left\{\frac{\partial h(\mathbf{x}(t))}{\partial x_i}G^>(t, t')\frac{\partial h(\mathbf{x}(t'))}{\partial x_j}G^<(t', t)\right\}, \quad (19)$$

where the greater Green's function is defined as

$$G_{mn}^>(t, t') = -i\text{Tr}_{\text{el}}\{d_m(t)d_n^\dagger(t')\rho_{\text{el}}(t_0)\}. \quad (20)$$

We explicitly assume that for $t_0 \rightarrow -\infty$ the density matrix for the electronic subsystem is factorized into

$$\rho_{\text{el}}(t_0) = \rho_{\text{mol,el}}(t_0)\rho_{\text{leads}}(t_0), \quad (21)$$

where $\rho_{\text{mol,el}}(t_0)$ is the initial electronic state of the molecule and $\rho_{\text{leads}}(t_0)$ is the initial state of the leads. The latter is a product of Gibbs' states,

$$\rho_{\text{leads}}(t_0) = \prod_{\alpha} \frac{e^{-(H_{\text{leads},\alpha} - \mu_{\alpha})/k_B T}}{\text{Tr}_{\text{leads},\alpha}[e^{-(H_{\text{leads},\alpha} - \mu_{\alpha})/k_B T}]}. \quad (22)$$

B. Timescale separation and Langevin dynamics

In principle, Eq. (12) could be solved directly using the NEGF expressions in Eqs. (14)–(20). In practice, however, it is challenging to sample the colored noise of the stochastic force, which is itself a functional of the vibrational path, and also to self-consistently propagate the electronic and vibrational DOFs. Consequently, most practical mixed quantum-classical treatments introduce further approximations. For example, a deterministic but non-Markovian equation of motion is obtained by neglecting the stochastic force, which leads to the Ehrenfest approach [19,62], while near-adiabatic approximations lead to Langevin-type equations that are much easier to propagate, which is the route taken in this work.

Specifically, we introduce an additional separation of electronic and vibrational timescales, which enables a systematic reduction of memory effects. The electronic relaxation timescale is mostly determined by the molecule-lead coupling strength Γ , while the intrinsic vibrational timescale is determined by the characteristic frequencies ω_i . In the regime

$\epsilon = \omega_i/\Gamma \ll 1$, the electrons relax rapidly compared to vibrational motion, allowing the electronic influence to be expressed as a function of slowly varying vibrational variables.

Within this regime, the dynamics can be reformulated in terms of the central time of the electronic correlation functions, which tracks the slow nuclear evolution, while the relative time encodes fast electronic relaxation. Consequently, the Green's functions appearing in Eq. (14) and Eq. (19) can be expanded in powers of the central-time derivatives, yielding a hierarchy of effective equations of motion for the vibrations. Truncation at leading order in ϵ yields a Markovian Langevin equation, in which the electronic force depends only on the instantaneous nuclear configuration and the noise becomes Gaussian and white. This procedure is shown in detail in Refs. [45] and [60], for example, and yields

$$m_i\ddot{x}_i = -\frac{\partial U_{\text{u},i}}{\partial x_i} + F_i^{\text{ad}}(\mathbf{x}) - \sum_j \gamma_{ij}(\mathbf{x})\dot{x}_j + f_i(t). \quad (23)$$

While the force arising from the unperturbed vibrational potential remains unchanged, the average electronic force has now been expanded:

$$F_i[\mathbf{x}(t)] \approx F_i^{\text{ad}}(\mathbf{x}) - \sum_j \gamma_{ij}(\mathbf{x})\dot{x}_j. \quad (24)$$

Here, $F_i^{\text{ad}}(\mathbf{x})$ represents the zeroth-order, purely adiabatic contribution to the mean electronic force, corresponding to the limit of infinitely fast electronic relaxation at a frozen vibrational frame, $\mathbf{x}$. In contrast, the electronic friction force is proportional to the vibrational velocity and represents the first-order nonadiabatic correction to $F_i^{\text{ad}}(\mathbf{x})$, and is characterized by the electronic friction coefficient, $\gamma_{ij}(\mathbf{x})$. Furthermore, in this limit the correlation function of the stochastic force reduces to

$$\langle f_i(t)f_j(t') \rangle = D_{ij}(\mathbf{x})\delta(t - t'). \quad (25)$$

Before discussing the properties and explicit forms of these electronic forces in terms of NEGFs, we note that Eq. (23) is a Markovian equation of motion, in that the electronic forces do not depend on the vibrational path and the stochastic contribution is now described by white noise. The Markovian limit arises naturally when including terms only to first order in the gradient expansion with respect to the central time. It can be shown that continuing the gradient expansion would yield not only higher-order corrections to the electronic forces but also non-Markovian terms describing colored noise. This has not only been demonstrated with the NEGF treatment used in this work [61], but also in the quantum-classical Liouville equation (QCLE) approach to obtaining electronic friction and Langevin dynamics [49].

We also note that similar systems have previously been analyzed with a different type of Langevin equation, derived under the assumption of weak-electronic vibrational couplings or, equivalently, small-amplitude vibrational motion [30–32]. In this approach, a generalized Langevin equation is derived by expanding the electronic forces around the equilibrium geometry. This represents a fundamentally different approximation from the Markovian Langevin equation used in this work, as the resulting electronic forces are indeed

non-Markovian, but do not retain the full nonlinear dependence on the vibrational coordinates.

We end this section with a brief discussion of the physical interpretation of the electronic forces in Eq. (23) and some relevant equilibrium properties. First, it can be shown that the adiabatic contribution to the mean force is conservative in equilibrium [49],

$$\nabla \times \mathbf{F}^{\text{ad}}(\mathbf{x}) = 0. \quad (26)$$

Critically for the multimode models considered in this work, this property is not guaranteed out of equilibrium: that is, at finite bias voltage $\Phi \neq 0$.

In contrast to $\mathbf{F}^{\text{ad}}(\mathbf{x})$, the electronic friction force captures nonadiabatic energy transfer between the vibrational degrees of freedom and electron-hole pair (EHP) formation in the leads. Indeed, previous investigations into electronic friction have shown that it can explicitly be written as an EHP-weighted density of states [30,32,49]. Similarly to $\mathbf{F}^{\text{ad}}(\mathbf{x})$, the Markovian electronic friction tensor $\gamma_{ij}(\mathbf{x})$ has specific properties in equilibrium, namely that it is symmetric and positive-definite,

$$\sum_{ij} \dot{x}_i \gamma_{ij}(\mathbf{x}) \dot{x}_j \geq 0. \quad (27)$$

Consequently, the equilibrium electronic friction force captures the effect of vibrational relaxation via coupling to EHP creation in a single lead. However, at finite bias voltage, $\gamma_{ij}(\mathbf{x})$ is not guaranteed to be positive semi-definite and, depending on the specific form of the electronic-vibrational coupling, it can contain additional contributions from EHP creation across the junction that can have a driving rather than dissipative effect.

Furthermore, since the electronic friction tensor is not guaranteed to be symmetric out of equilibrium, it can be split into symmetric and antisymmetric contributions,

$$\boldsymbol{\gamma} = \underbrace{\frac{\boldsymbol{\gamma} + \boldsymbol{\gamma}^T}{2}}_{\boldsymbol{\gamma}^S} + \underbrace{\frac{\boldsymbol{\gamma} - \boldsymbol{\gamma}^T}{2}}_{\boldsymbol{\gamma}^A}. \quad (28)$$

Here, $\boldsymbol{\gamma}^A$ represents a Berry force that, although it does not directly contribute to the dissipative or driving nature of the dynamics, can be critical in pulling trajectories in specific directions in the nonconservative adiabatic force field. We note that the notation used in this work differs from some investigations that explicitly separate the symmetric and antisymmetric components, calling $\boldsymbol{\gamma}^S$ the electronic friction and $\boldsymbol{\gamma}^A$ the Berry force [30,32,41,42].

Finally, it can be shown that the equilibrium process of vibrational relaxation due to coupling to EHP formation in the leads, which is described by the electronic friction, is balanced by the reverse process of vibrational excitation due to EHP decay. This effect is captured by the stochastic force, and it further manifests in the classical fluctuation-dissipation theorem,

$$D_{ij}(\mathbf{x}) = k_B T \gamma_{ij}(\mathbf{x}), \quad (29)$$

which, again, is only satisfied in equilibrium. A unique feature of molecular nanojunctions is that so-called stochastic or Joule heating can occur in nonequilibrium, where finite bias

voltage can cause $D_{ij}(\mathbf{x}) \geq k_B T \gamma_{ij}(\mathbf{x})$ for a significant range of the vibrational landscape and induce an overall energy transfer to the molecular vibrations.

Note that the classical limit is generally justified in the limit of $\omega \gg k_B T$, compared to the regime explored in this work, where $\omega \sim k_B T$. However, we specifically consider the nonequilibrium situation in which the molecule is subject to an electric current, where the effective temperature of the molecule is primarily determined by the current-induced forces acting on the vibrational DOFs and can greatly exceed the temperature of the leads. Therefore, in the nonequilibrium steady state, the vibrational DOFs are expected to equilibrate to temperatures well above $k_B T$, such that a classical treatment is justified.

C. NEGF expressions for the electronic forces

The electronic forces can be calculated in the Keldysh NEGFs framework via

$$F_i^{\text{ad}}(\mathbf{x}) = i \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi} \text{Tr} \left\{ \frac{\partial h(\mathbf{x})}{\partial x_i} \tilde{G}_{(0)}^<(\varepsilon, \mathbf{x}) \right\}, \quad (30)$$

$$\gamma_{ij}(\mathbf{x}) = -i \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi} \text{Tr} \left\{ \frac{\partial h(\mathbf{x})}{\partial x_i} \tilde{G}_{(1),x_j}^<(\varepsilon, \mathbf{x}) \right\}, \quad (31)$$

and

$$D_{ij}(\mathbf{x}) = \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi} \text{Tr} \left\{ \frac{\partial h(\mathbf{x})}{\partial x_i} \tilde{G}_{(0)}^>(\varepsilon, \mathbf{x}) \frac{\partial h(\mathbf{x})}{\partial x_j} \tilde{G}_{(0)}^<(\varepsilon, \mathbf{x}) \right\}, \quad (32)$$

and are equivalent to the ones in Refs. [45,60,61]. Note that the Green's functions with the index (0) correspond to the zeroth-order expansion of Eq. (14) and Eq. (18), while the ones with the index (1) come from the first-order expansion. The adiabatic lesser/greater Green's function in Eq. (30) and Eq. (32), $\tilde{G}_{(0)}^{</>}$, is given by

$$\tilde{G}_{(0)}^{</>} = \tilde{G}_{(0)}^R \tilde{\Sigma}^{</>} \tilde{G}_{(0)}^A, \quad (33)$$

where the retarded/advanced Green's functions take the standard form,

$$\tilde{G}_{(0)}^{R/A} = (\varepsilon \hat{I} - h - \tilde{\Sigma}^{R/A})^{-1}. \quad (34)$$

By taking the wideband limit for the leads, the self-energies for lead α take the form

$$\tilde{\Sigma}_{\alpha}^R = -\frac{i}{2} \Gamma_{\alpha}, \quad \tilde{\Sigma}_{\alpha}^A = \frac{i}{2} \Gamma_{\alpha}, \quad (35)$$

$$\tilde{\Sigma}_{\alpha}^<(\varepsilon) = i f_{\alpha}(\varepsilon) \Gamma_{\alpha}, \quad \tilde{\Sigma}_{\alpha}^>(\varepsilon) = -i [1 - f_{\alpha}(\varepsilon)] \Gamma_{\alpha}, \quad (36)$$

with the Fermi-Dirac function given by

$$f_{\alpha}(\varepsilon) = \frac{1}{1 + e^{(\varepsilon - \mu_{\alpha})/k_B T}}. \quad (37)$$

The total self-energy, which is a sum of the self-energy contributions from each lead, is written without a lead subscript, $\tilde{\Sigma}^R = \sum_{\alpha} \tilde{\Sigma}_{\alpha}^R$. The wideband limit in Eq. (35) can be justified for typical metals used in molecular nanojunctions, which generally have bandwidths on the order of 5 – 10 eV [63,64].

Moreover, the first nonadiabatic correction to the adiabatic lesser Green's function in Eq. (31), $\tilde{G}_{(1),x_j}^<$, corresponds to the

Green's functions in Eq. (15) expanded to first order and is given by [54]

$$\tilde{G}_{(1),x_j}^< = \frac{1}{2i} \tilde{G}_{(0)}^R \left(\tilde{\Sigma}^< \tilde{G}_{(0)}^A \left[\tilde{G}_{(0)}^A, \frac{\partial h}{\partial x_j} \right]_- + \frac{\partial h}{\partial x_j} \tilde{G}_{(0)}^R \frac{\partial \tilde{\Sigma}^<}{\partial \varepsilon} + \tilde{G}_{(0)}^< \frac{\partial h}{\partial x_j} + \text{H.c.} \right) \tilde{G}_{(0)}^A. \quad (38)$$

In the same way, we define the first-order correction to the retarded Green's function as

$$\tilde{G}_{(1),x_j}^R = \frac{1}{2i} \tilde{G}_{(0)}^R \left[\tilde{G}_{(0)}^R, \frac{\partial h}{\partial x_j} \right]_- \tilde{G}_{(0)}^R. \quad (39)$$

We end this part with a discussion of the validity of the Markovian NEGF-LD used in this work. Generally, a classical description of the vibrational DOFs is assumed to be justified in regimes where $k_B T \gg \omega_i$ and nuclear quantum effects can be neglected. However, when simulating steady-state transport observables, this can extend even to $k_B T \sim \omega_i$, which corresponds to the parameter regime explored in this work [58]. This is rationalized by considering the electronic-vibrational coupling, and by extension the molecule-lead coupling, which leads to a broadening of the quantized vibrational energy levels, and the fact that quantum vibrational coherences decay in the nonequilibrium steady state. Furthermore, given that we only investigate small anharmonic perturbations to the vibrational potentials, we expect the corresponding quantum corrections to also be small. Consequently, we do not expect quantum effects to significantly influence the main conclusions of this investigation.

Furthermore, the electronic friction approach is justified for systems with a clear timescale separation between the electronic and vibrational DOFs. While the electronic timescales are mostly determined by the molecule-lead coupling, Γ , the vibrational timescales are determined by the effective harmonic frequencies of the vibrational DOFs, ω_i . Since all results in our investigation are obtained in the limit $\Gamma \gg \omega_i$, this condition is fulfilled and we can expect the electronic friction approach to be valid.

D. Langevin simulations and observables

All observables of interest are obtained by simulating the vibrational dynamics of our model systems by solving the Langevin equation in Eq. (23). In this work, we use the ABOBA algorithm, an efficient method for integrating stochastic differential equations. The approach splits the generator of the Langevin equation into three components (A, B, O) using a Trotter decomposition and applies them in a specific sequence. For a more comprehensive outline of the method, see Ref. [65]. In the context of charge transport in molecular nanojunctions, this algorithm has previously also been applied in Refs. [33,58].

Since the Langevin equation describes a stochastic process, we need to average over many trajectories to calculate meaningful averages of the observables of interest. Assuming that the molecule is initially in its vibrational ground state, we sample N_{traj} initial conditions from the Wigner distribution of

the ground state of a two-dimensional harmonic oscillator,

$$\rho_W(\mathbf{x}, \mathbf{p}) = \prod_i \frac{1}{\pi} e^{-m_i \omega_i (x_i - x_i^0)^2 - \frac{1}{m_i \omega_i} p_i^2}. \quad (40)$$

For the anharmonic potentials considered here, the frequency ω_i is obtained by the harmonic approximation to the uncharged potentials $U_{u,2}(x_2)$ at the respective minima of their potential wells, x_2^0 , as given in Eq. (6). With initial conditions generated from this sampling procedure, the trajectories are then propagated in time using the ABOBA algorithm mentioned above.

For the dissociative models in this paper, we define a certain threshold position $\mathbf{x}^{\text{diss}}$. Each time a trajectory exceeds this position, the molecular junction is assumed to be dissociated. Based on this definition of $\mathbf{x}^{\text{diss}}$, we calculate time-dependent dissociation probabilities via an ensemble average over the trajectories,

$$P_{\text{diss}}(t) = \frac{1}{N_{\text{traj}}} \sum_{n \in N_{\text{traj}}} \Theta(\mathbf{x}_n(t) - \mathbf{x}^{\text{diss}}). \quad (41)$$

In contrast, in the non-dissociative models, we use the average vibrational energy of each mode as a measure of instability, $\langle E_i \rangle(t)$. At time t , this is obtained by

$$\langle E_i \rangle(t) = \frac{1}{N_{\text{traj}}} \sum_{j=1}^{N_{\text{traj}}} E_i(\mathbf{x}_j(t), \mathbf{p}_j(t)) \quad (42)$$

$$E_i(\mathbf{x}_j(t), \mathbf{p}_j(t)) = U_{u,i}(x_{i,j}(t)) + \frac{p_{i,j}(t)^2}{2m_i}, \quad (43)$$

where $(x_{i,j}(t), p_{i,j}(t))$ refers to the phase-space position of vibrational mode i in trajectory j at time t . Note that this expression only considers the potential of the unperturbed nuclear potentials and does not include the energy originating from the electronic-vibrational interaction.

We also investigate steady-state quantities, which we obtain by propagating N_{traj} initial conditions to a time t_{ss} at which both $\langle E_i \rangle(t)$ are constant. Upon reaching the steady state, we propagate the trajectories further and sample N_{sample} equally spaced points, yielding a total of $N_{\text{tot}} = N_{\text{traj}} \times N_{\text{sample}}$ points from which the expectation values of observables are computed. Following this procedure, we evaluate steady-state expectation values of the vibrational kinetic energies as

$$\langle E_i \rangle^{\text{ss}} = \frac{1}{N_{\text{tot}}} \sum_{j=1}^{N_{\text{tot}}} E_i(\mathbf{x}_j, \mathbf{p}_j). \quad (44)$$

Similarly, the steady-state expectation values of an electronic observable O can be obtained by replacing the kinetic energy variable with the corresponding phase-space-dependent quantum expectation value, $\langle O \rangle_{\text{el}}(\mathbf{x}_j, \mathbf{p}_j)$:

$$\langle O \rangle^{\text{ss}} = \frac{1}{N_{\text{tot}}} \sum_{j=1}^{N_{\text{tot}}} \langle O \rangle_{\text{el}}(\mathbf{x}_j, \mathbf{p}_j). \quad (45)$$

We are specifically interested in the electric current from lead α ,

$$\langle I_\alpha \rangle_{\text{el}} = - \left\langle \frac{dN_\alpha}{dt} \right\rangle_{\text{el}}, \quad (46)$$

which can be expressed in the Heisenberg picture as

$$\langle I_\alpha \rangle_{\text{el}}(t) = -i\langle [H(t), N_\alpha(t)] \rangle_{\text{el}}, \quad (47)$$

where N_α is the occupation number operator of lead α .

Similarly to the electronic forces in Sec. III B, the full semiclassical electric current operator can be expanded to first order in gradients of the central time. This allows one to express $\langle I_\alpha \rangle_{\text{el}}(t)$ in terms of an adiabatic contribution, $\langle I_\alpha^{\text{ad}}(\mathbf{x}) \rangle$, which depends instantaneously on the molecular coordinates, and a first-order nonadiabatic correction, $\langle I_\alpha^{\text{na}}(\mathbf{x}, \mathbf{p}) \rangle$, which additionally accounts for the non-zero momenta of the molecule:

$$\langle I_\alpha \rangle_{\text{el}}(\mathbf{x}, \mathbf{p}) \approx \langle I_\alpha^{\text{ad}} \rangle_{\text{el}}(\mathbf{x}) + \langle I_\alpha^{\text{na}} \rangle_{\text{el}}(\mathbf{x}, \mathbf{p}). \quad (48)$$

The adiabatic term is given by [66],

$$\langle I_\alpha^{\text{ad}} \rangle_{\text{el}}(\mathbf{x}) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\varepsilon \text{Re}(\text{Tr}\{\tilde{G}_{(0)}^< \tilde{\Sigma}_\alpha^A + \tilde{G}_{(0)}^R \tilde{\Sigma}_\alpha^<\}), \quad (49)$$

while the nonadiabatic correction is [41,60]

$$\langle I_\alpha^{\text{na}} \rangle_{\text{el}}(\mathbf{x}, \mathbf{p}) = \sum_j I_{\alpha,j}^{\text{na}}(\mathbf{x}) \frac{p_j}{m_j} \quad (50)$$

$$I_{\alpha,j}^{\text{na}}(\mathbf{x}) = \int_{-\infty}^{\infty} \frac{d\varepsilon}{\pi} \text{Re}(\text{Tr}\{\tilde{G}_{(1),x_j}^< \tilde{\Sigma}_\alpha^A + \tilde{G}_{(1),x_j}^R \tilde{\Sigma}_\alpha^<\}). \quad (51)$$

IV. RESULTS

In this section, we will explore the influence of anharmonic nuclear potentials on nanojunction stability by performing Langevin simulations of the vibrational dynamics. First, we will investigate the vibrational dynamics and the dissociation dynamics of the two-level, two-mode system introduced in Sec. II with Morse potentials for the uncharged and charged states. By expanding the Morse potentials up to second order, we directly compare the vibrational dynamics of the anharmonic model with the corresponding harmonic case. Next, in order to obtain a quantitative understanding of the effect of anharmonicities on vibrational instability, we consider quartic potentials, which can be easily tuned. Note that our aim is to investigate effects of anharmonic potentials on the stability and dissociation dynamics of nanojunctions in general, and not of a specific molecule.

A. Vibrational dynamics in a dissociative model

We start by specifying the parameters and potentials of the general model introduced in Sec. II. The two electronic levels (1) and (2) describe two sites of a molecular bridge, such as in a diatomic molecule, and each couples only to the closest lead. In this scenario, the vibrational coordinate x_2 describes the center-of-mass motion of the entire molecule, while the vibrational coordinate x_1 describes the bond-stretching motion between both parts of the molecule. The raw nuclear potential of vibrational coordinate x_2 is given by

$$U_{u,2}(x_2) = D_u(1 - e^{-a_u(x_2 - x_2^0)})^2 \quad (52)$$

$$(53)$$

while the potential of charged state m is

$$U_c^{(m)}(x_2) = D_c^{(m)}(1 - e^{-a_c^{(m)}(x_2 - x_c^{(m)})})^2 + V_c^{(m)}. \quad (54)$$

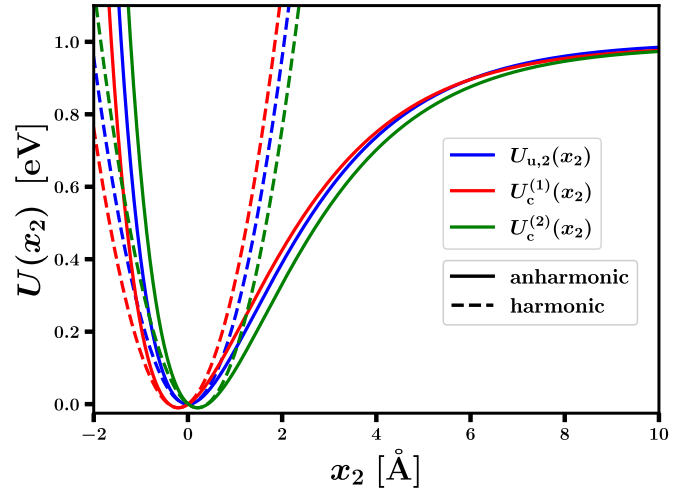


FIG. 1. Potentials $U_{u,2}(x_2)$, $U_c^{(1)}(x_2)$, and $U_c^{(2)}(x_2)$ of the uncharged state and the charged states (1) and (2), as well as their harmonic approximations. The parameters are the same as in Set (1) in Table I, with $\omega_2 = 20$ meV.

Here, $x_c^{(m)}$ describes the shift in the equilibrium geometry of the molecule upon state (m) becoming occupied. For large displacements from the equilibrium geometry, the molecule can dissociate along the x_2 coordinate, with the dissociation threshold taken as $x_2^{\text{diss}} = 10$ Å. These potentials are illustrated in Fig. 1. The functional dependence of the potential $U_{u,1}(x_1)$ and the hopping between the electronic levels has already been given in Sec. II.

The parameters of $U_{u,2}(x_2)$, $U_c^{(1)}(x_2)$, and $U_c^{(2)}(x_2)$ are determined by their respective harmonic approximations, as outlined in Sec. II, and are given by

$$a_u = \omega_2 \sqrt{\frac{m_2}{2D_u}}, \quad a_c^{(m)} = \omega_2 \sqrt{\frac{m_2}{2D_c^{(m)}}}, \quad (55)$$

$$x_2^0 = 0, \quad x_c^{(m)} = -\tilde{\lambda}_m / \sqrt{m_2 \omega_2^2}, \quad (56)$$

and

$$V_c^{(m)} = \varepsilon_0 - (\tilde{\lambda}_m)^2 / (2\omega_2). \quad (57)$$

The parameters $\tilde{\lambda}_m$, ω_i , ε_0 , and t_0 are chosen such that the harmonic approximation to the Morse potentials yields a

TABLE I. Two sets of parameters used for the analysis in this work. The only difference between the two sets is the electronic-vibrational coupling, $\tilde{\lambda}_i$.

Parameters	Set (1)	Set (2)
ω_1	20 meV	20 meV
ω_2	20 meV, 22.5 meV	20 meV, 22.5 meV
$\tilde{\lambda}_i$	20 meV	4 meV
ε_0	0	0
t_0	-0.2 eV	-0.2 eV
$D_u, D_c^{(1)}, D_c^{(2)}$	1 eV	1 eV
m_i	5 amu	5 amu
$k_B T$	25.8 meV	25.8 meV
Γ_α	1 eV	1 eV

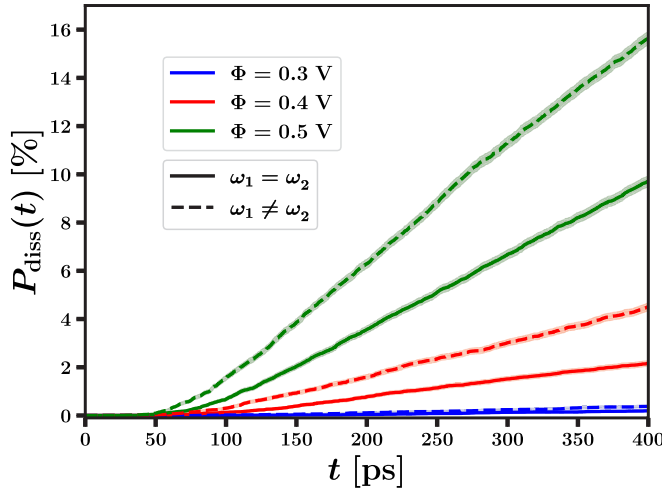


FIG. 2. Dissociation probability P_{diss} over time for different voltages and the two cases $\omega_1 = \omega_2$ and $\omega_1 \neq \omega_2$. For the case of $\omega_1 \neq \omega_2$, we set $\omega_1 = 20$ meV and $\omega_2 = 22.5$ meV. Other parameters are listed in Set (1) in Table I. The dissociation threshold is $x_2^{\text{diss}} = 10$ Å. The number of initial trajectories for each curve is $N_{\text{traj}} = 20000$. The standard deviation is marked by the shaded area around each curve.

harmonic system with similar parameters as in Refs. [32,33], where the mechanism for vibrational instability has been thoroughly studied. The explicit parameters used are given in Table I. Note that we use two parameter sets, which differ only in the electronic-vibrational couplings, $\tilde{\lambda}_i$.

Previous studies of purely harmonic models with similar parameters have predicted strong vibrational instabilities in the case of degenerate vibrational modes. For example, in Ref. [33], a large vibrational excitation was observed at relatively low bias voltages of $\Phi = 0.3$ V. Consequently, we are particularly interested in whether a similar effect can also occur in a dissociative model. Specifically, we examine the case where the effective frequency of mode 2 is degenerate with the frequency of the harmonic potential of mode 1: $\omega_2 = \omega_1$. If the mechanism of vibrational instability had a significant effect on the dynamics, then it could increase the dissociation probability beyond that of normal Joule heating.

To this end, in Fig. 2, we show the dissociation probability as a function of time for various voltages and the degenerate, $\omega_1 = \omega_2$, and nondegenerate, $\omega_1 \neq \omega_2$, cases. Parameters have been taken from set (1). Fig. 2 demonstrates that the dissociation probability at time t increases with increasing voltage. Counterintuitively, for all voltages considered here, it appears that the dissociation probability in the degenerate case is consistently smaller than in the nondegenerate case. We discuss this in further detail below.

Although not shown here, the dissociation probability for Set (2) remains below 1% over the timescale considered in Fig. 2, even at large bias voltages, $\Phi = 2$ V. This indicates that the junction is more stable for smaller electronic-vibrational couplings. Furthermore, for Set (2), the dissociation probabilities do not differ significantly between the cases of degenerate and nondegenerate modes.

The behavior shown in Fig. 2 is in clear contrast to the mechanism of vibrational instability in multimode degenerate

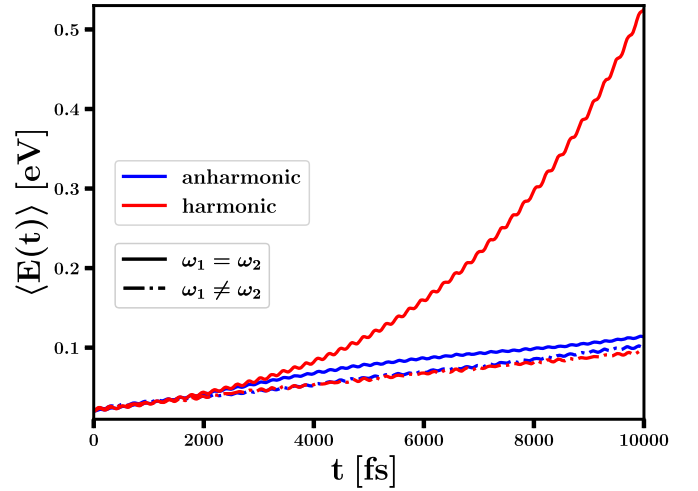


FIG. 3. Total vibrational energy $\langle E \rangle = \langle E_1 \rangle + \langle E_2 \rangle$ over time for the anharmonic and harmonic system and the two respective cases $\omega_1 = \omega_2$ and $\omega_1 \neq \omega_2$. For the case of $\omega_1 \neq \omega_2$, we set $\omega_1 = 20$ meV and $\omega_2 = 22.5$ meV. Other parameters are the same as in parameter set (1) in Table I. The voltage is $\Phi = 0.5$ V.

harmonic systems [30–33], such as in Eqs. (8) and (7). While in the harmonic case, vibrational dynamics is highly unstable for $\omega_1 = \omega_2$, it appears that higher excitation and hence higher dissociation occur for nondegenerate modes in this anharmonic system. Consequently, it appears that the original effect leading to a vibrational instability for harmonic systems vanishes when at least one of the nuclear potentials is a Morse potential.

To investigate the harmonic and anharmonic differences in more detail, in Fig. 3 we compare the total vibrational energy of this anharmonic system to the total vibrational energy obtained in the harmonic limit. In the harmonic limit, the vibrational dynamics differ significantly between the degenerate and nondegenerate cases. In the degenerate case, the energy of both modes increases rapidly over time, eventually leading to a vibrational instability. Conversely, in the nondegenerate case, the vibrational energy increases substantially more slowly than in the degenerate case, in agreement with Refs. [30–33]. In the anharmonic limit, however, the degeneracy of ω_1 and ω_2 only leads to a marginal difference in the vibrational dynamics of both systems. Furthermore, the growth of $\langle E \rangle(t)$ in the degenerate and nondegenerate cases is significantly slower than in the degenerate harmonic system, closely resembling the behavior of the nondegenerate harmonic case. The insensitivity of the vibrational dynamics to mode degeneracy in the anharmonic system implies that the dissociation probability of the junction is also not enhanced by ω_1 and ω_2 being degenerate, as shown in Fig. 2.

Next, we discuss why the vibrational dynamics of the anharmonic model is largely unaffected by mode degeneracy. The harmonic approximation to the anharmonic potentials, $U_{u,2}(x_2)$ and $U_c^{(m)}(x_2)$, is obtained via a Taylor expansion around the expansion point x_2^0 . In the vicinity of this point, the harmonic approximation is accurate, $U_{u,2}^{\text{harm}}(x_2) \approx U_{u,2}(x_2)$, and the vibrational dynamics essentially experiences two harmonic potentials with frequencies ω_1 and ω_2 . However, once

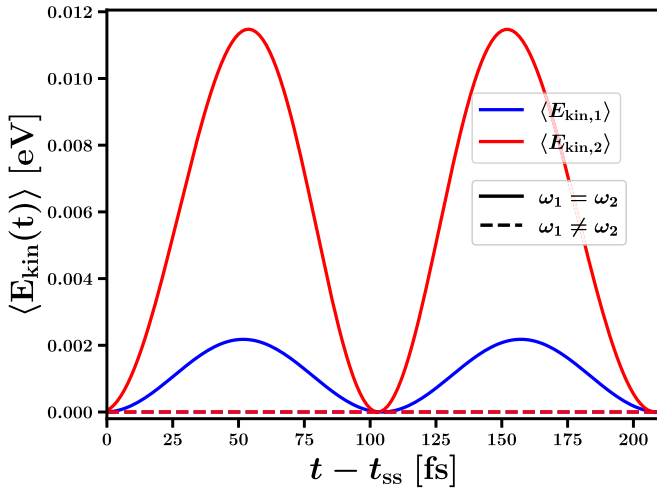


FIG. 4. Kinetic energies $\langle E_{\text{kin},1} \rangle$ and $\langle E_{\text{kin},2} \rangle$ of the individual vibrational modes over time for the anharmonic system. At the time t_{ss} , the system has reached a limit cycle and the average kinetic energy stops changing over time. Shown are the two cases $\omega_1 = \omega_2$ and $\omega_1 \neq \omega_2$. The trajectory has been initialized with the initial conditions $(x_1, x_2) = (0, 0)$ and $(p_1, p_2) = (0, 0)$. The parameters are the same as for Fig. 2; however, the stochastic force is removed: $\mathbf{f}(t) = \mathbf{0}$. The voltage is $\Phi = 0.5$ V.

the molecular trajectory moves away from x_2^0 , the harmonic approximation becomes less accurate and the effective frequency ω_2 does not reflect the true restoring force of the Morse potential. Indeed, one observes in Fig. 1 that the effective frequency ω_2 of the Morse potential in the direction of dissociation will be smaller than the bottom of the well, effectively detuning the oscillators away from x_2^0 .

Since the mechanism leading to vibrational instabilities is highly sensitive to frequency detuning between the modes, the effect vanishes once the vibrational dynamics leaves the vicinity of x_2^0 . Consequently, there is no effect on the dissociation dynamics, because, although the vibrational motion can be excited around the bottom of the well, the dominant contribution once it nears x_2^{diss} is still Joule heating, which does not differ significantly between the degenerate and nondegenerate cases.

This is also observable in Fig. 4, where remnants of the effect are visible. Here, the time evolution of the kinetic energy of a single trajectory for both $\omega_1 = \omega_2$ and $\omega_1 \neq \omega_2$ for the full anharmonic Morse potential is shown. To remove the perturbative influence of the stochastic force, we have also set the stochastic force to zero: $\mathbf{f}(t) = \mathbf{0}$. Since the trajectories do not equilibrate without a stochastic force, we plot the part of the trajectory once it reaches a limit cycle after time t_{ss} . If $\omega_1 = \omega_2$, the molecular trajectory in the vicinity of x_2^0 follows an ellipse with fixed rotational direction in the (x_1, x_2) plane, as shown in Fig. 5. Here, one also observes that the adiabatic electronic force field is nonconservative: $\nabla \times \mathbf{F}^{\text{ad}}(\mathbf{x}) < 0$.

Consequently, in this region, the trajectory gains energy from $\mathbf{F}^{\text{ad}}(\mathbf{x})$ that can compensate energy loss due to the electronic friction force. Although it is not shown here, the electronic friction tensor is positive semi-definite for the entire vibrational coordinate range, such that it has a purely dissipative effect. Therefore, for degenerate vibrational modes, the vibrational kinetic energy does not decay to zero, as

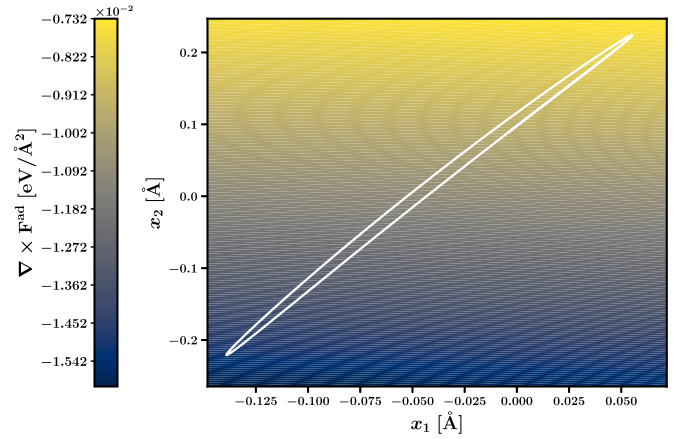


FIG. 5. Trajectory in the (x_1, x_2) plane after reaching a limit cycle in white for the anharmonic model and the case $\omega_1 = \omega_2$. The random force has been removed, $\mathbf{f}(t) = \mathbf{0}$. The bias voltage is $\Phi = 0.5$ V. The background shows the curl of the force field.

can be seen in Fig. 4. Note the oscillatory behavior of the trajectory in the degenerate case in Fig. 4, which originates from the approximately harmonic dynamics near the bottom of the unperturbed vibrational potential of coordinate x_2 . Thus the vibrational trajectory moves under the influence of the harmonic potentials in the x_1 and x_2 directions. Moreover, since the stochastic force is turned off, there is also no noise observable in the trajectories. Despite these persistent oscillations, the overall vibrational excitation without the stochastic force is still small, as the effect vanishes when the trajectory moves too far away from x_2^0 , such that electronic friction dominates and effectively caps the maximum kinetic and potential energy.

In contrast, in the nondegenerate case, the molecular trajectory does not follow a fixed rotational direction and will, in total, not gain energy from the force field. For clarity, this has not been shown in Fig. 5, as it obscures the elliptical trajectory for $\omega_1 = \omega_2$. Furthermore, because the random force has been artificially turned off, there is no compensation for dissipation due to the electronic frictional force and the kinetic energy decays to zero over time, as shown in Fig. 4.

B. Influence of quartic anharmonicity on the vibrational dynamics

In the previous section, it was shown that the mechanism of vibrational instability present for degenerate vibrational frequencies and harmonic vibrational modes largely disappears when one mode is replaced by a Morse potential and has no effect on the dissociative dynamics. However, as shown in Fig. 4, remnants of the mechanism are still present near the bottom of the potential wells. Given that realistic molecular potentials are generally anharmonic, this raises an important question. Namely, did the signature of vibrational instability in Sec. IV A vanish due to the specific nature of the Morse potentials used, or will other, simple forms of anharmonic perturbations to the unperturbed vibrational potentials also destroy this mechanism?

To explore this question, we now investigate the degree of anharmonicity a system is allowed to exhibit before the

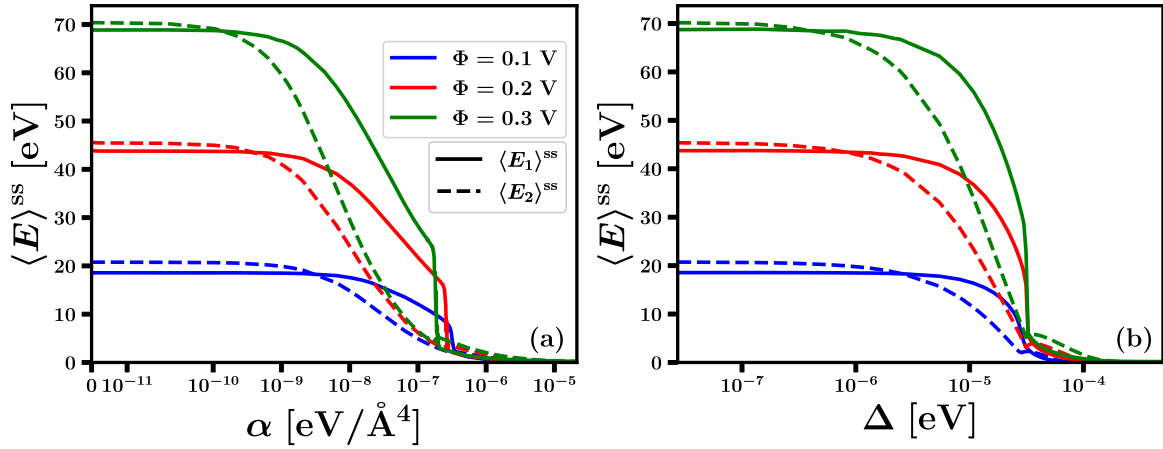


FIG. 6. (a) Steady-state vibrational energy $\langle E_1 \rangle^{ss}$ and $\langle E_2 \rangle^{ss}$ of the individual modes in the quartic system for different values of the anharmonicity parameter α and different bias voltages. The frequencies are $\omega_1 = \omega_2 = 20$ meV, all other parameters are the same as in parameter set (1) listed in Table I. (b) Steady-state vibrational energy of the individual modes for the harmonic system for different values of frequency difference Δ . The frequencies are $\omega_1 = 20$ meV and $\omega_2 = \omega_1 + \Delta$. For all frequencies, the electronic vibrational couplings are chosen such that $\lambda_{1/2} = \tilde{\lambda}_1 \sqrt{m_1 \omega_1}$. All other parameters are the same as for the quartic system.

signature of the vibrational instability vanishes. In order to simplify the effect of the anharmonicity, we will not use a Morse potential, instead taking the harmonic system introduced in Eqs. (7) and (8) and adding a quartic contribution to $U_{u,2}(x_2)$,

$$U_{u,2}(x_2) = \frac{1}{2} m_2 \omega_2^2 x_2^2 + \alpha x_2^4. \quad (58)$$

This allows us to rigorously control the strength of the anharmonicity via a single parameter, α .

In Fig. 6(a), we show the vibrational energy for different values of the anharmonicity parameter α and different bias voltages for the quartic system introduced above. Note that we show the steady-state vibrational energy, as this can be reached for the bound quartic potentials. Based on Fig. 6(a), we can distinguish three regimes in the vibrational dynamics for all voltages considered. In the first regime, where $0 < \alpha < 10^{-9} \frac{\text{eV}}{\text{\AA}^4}$, we observe a clear vibrational instability. Here, the vibrational energy in the steady state reaches unrealistically high values already at very low bias voltages. Note that a realistic junction would already break before reaching such high vibrational energies. The fact that we are able to observe such high energies is due to the non-dissociative potentials of our model.

The second regime, where $10^{-9} \frac{\text{eV}}{\text{\AA}^4} < \alpha < 10^{-6} \frac{\text{eV}}{\text{\AA}^4}$, marks the suppression of this instability. While the vibrational energy in this regime is still substantial, the energy distribution among both vibrational modes changes significantly and the energy difference between both modes becomes larger. The energy of vibrational mode $\langle E_1 \rangle^{ss}$ only starts decreasing for slightly larger α than $\langle E_2 \rangle^{ss}$, as the latter contains the quartic contribution.

We note that in this regime, the system does not exhibit a unique steady state for certain values of α . For the latter mentioned points, the stochastic force pushes individual trajectories to one of two steady states, which differ significantly in their vibrational energy. This is also connected to the steep decrease in vibrational energy between $10^{-7} \frac{\text{eV}}{\text{\AA}^4} <$

$\alpha < 10^{-6} \frac{\text{eV}}{\text{\AA}^4}$. As this finding does not further impact the following analysis, we defer a detailed analysis of the vibrational dynamics in this regime to the end of this section.

The third regime, where $\alpha > 10^{-6} \frac{\text{eV}}{\text{\AA}^4}$ marks the stable regime where the signature of the instability vanishes. Here, the vibrational energy is significantly smaller than in the other two regimes and the junction is essentially stable.

The results shown here indicate that adding even a small anharmonicity to one of the harmonic potentials destroys the mechanism leading to a vibrational instability observed in degenerate harmonic models. This observation is similar to our findings in Ref. [33], in which it was shown that the instability also vanishes in harmonic systems upon slightly detuning the vibrational frequencies: $\Delta = \omega_2 - \omega_1 \neq 0$. To connect to these ideas, in Fig. 6(b), we also show the vibrational kinetic energy of the harmonic approximation to the quartic model as a function of the manual detuning parameter Δ .

Here, we observe a similar dependence of $\langle E_i \rangle^{ss}$ on Δ as it had to the anharmonicity parameter α in the quartic system. Specifically, for the harmonic system with manual detuning, we can also distinguish three different regimes of the vibrational dynamics: the regime of instability ($\Delta < 10^{-6}$ eV), the transition regime in which the instability is suppressed, (10^{-6} eV $< \Delta < 10^{-4}$ eV) and the regime where the dynamics become stable ($\Delta > 10^{-4}$ eV).

As we observe in Fig. 6, increasing the anharmonicity parameter α for the quartic system and increasing the frequency difference in the harmonic system have a similar impact on the vibrational dynamics of the respective system. However, while the results show a qualitative similarity, it seems like the signature of the instability is even more sensitive to anharmonicity than to the frequency difference in the harmonic system. In the following, we explore this behavior in further detail.

First, we observe the values of α_c and Δ_c that mark the onset of the instability in Fig. 6(a) and Fig. 6(b), respectively. The values of α_c and Δ_c are determined by considering the

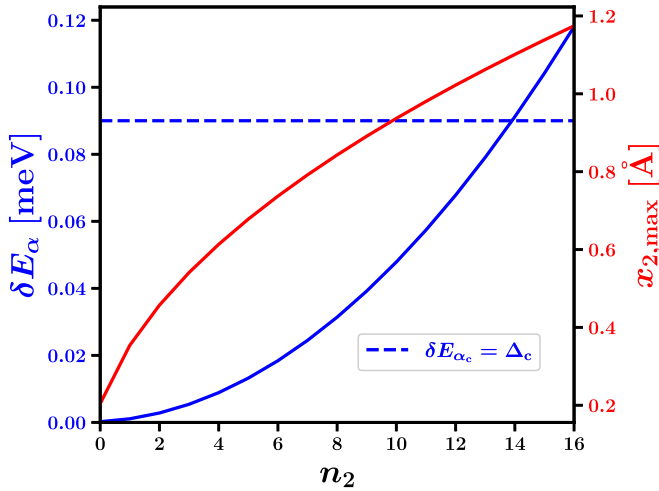


FIG. 7. Energy difference δE_α between the vibrational modes caused by the quartic term, and the classical turning point $x_{2,\max}$ as a function of the occupation number n_2 .

smallest values of α and Δ where the vibrational energy in one of the modes exceeds $E_c = 2$ eV at a voltage of $\Phi = 0.3$ V, which corresponds to values of $\alpha_c = 1 \times 10^{-6} \frac{\text{eV}}{\text{\AA}^4}$ and $\Delta_c = 9 \times 10^{-5}$ eV. Once the vibrational energy in one of the modes exceeds E_c , we assume the junction to exhibit a vibrational instability. Note that, although the exact choice of the vibrational energy marking the onset of an instability is somewhat arbitrary, different choices would not qualitatively impact the following analysis.

Next, we calculate the energy detuning between the vibrational modes induced by the anharmonicity via first-order perturbation theory, in which α is treated as a small parameter:

$$\delta E_\alpha = \frac{3\alpha}{4m_2^2\omega_2^2}(2n_2 + 2n_2^2 + 1), \quad (59)$$

where n_2 is the occupation number of the vibrational mode corresponding to coordinate x_2 . Note that, although we treat the vibrational modes classically, one can still define a classical harmonic analog to the occupation number via $n_i = \langle E_i \rangle / \omega_i$.

For the harmonic system, the energy difference between both oscillators is simply

$$\delta E_\Delta = \Delta. \quad (60)$$

By setting $\delta E_{\alpha_c} = \delta E_{\Delta_c}$ and using the values of α_c and Δ_c marking the onset of instability, it is possible to determine the occupation number for which the anharmonicity and the frequency detuning lead to the same energy difference between both modes.

Moreover, by considering the classical turning point of the harmonic oscillator,

$$x_{2,\max} = \pm \sqrt{\frac{2(n_2 + \frac{1}{2})}{m_2\omega_2}}, \quad (61)$$

we can determine the position at which the energy difference caused by the quartic term becomes larger than the energy difference caused by the frequency detuning. In Fig. 7, we show δE_{α_c} and $x_{2,\max}$ for different values of n_2 . The point at

which $\delta E_{\alpha_c} = \delta E_{\Delta_c}$ is at a relatively low vibrational occupation, $n_2 \approx 14$, which corresponds to $x_{2,\max} \approx \pm 1.1$ Å.

Consequently, we observe that even for relatively small deviations from the bottom of the potential well, $|x_2| > 1.1$ Å, the quartic anharmonicity induces a larger energy deviation of both modes than the manual detuning Δ that has already been shown to destroy the mechanism of vibrational instability [33]. As a result, for $\alpha > \alpha_c$, the mechanism leading to the instability is suppressed for such small-amplitude motion that it has no influence on the steady-state vibrational excitation.

The results presented in this section show that even a small anharmonicity in one of the nuclear potentials destroys the effect leading to a vibrational instability in degenerate harmonic systems. Given that the anharmonicity in this section was a simple quartic term with relatively small anharmonicity parameter, it is unclear whether this mechanism of vibrational instability would be observable in more realistic molecular nanojunction systems, as even molecules containing degenerate vibrational modes are rarely purely harmonic. Indeed, in Sec. IV A, where we included more realistic Morse potentials, the dissociation dynamics showed no evidence of the instability.

In the last part of this section, we present a more detailed analysis of the vibrational dynamics shown in Fig. 6(a) in Sec. IV B. In particular, we discuss the occurrence of the steep decrease of the vibrational energy in Fig. 6(a). We start by showing the expectation values of the vibrational energy over time for two different values of α in Fig. 8. The first value of $\alpha = 1 \times 10^{-7} \frac{\text{eV}}{\text{\AA}^4}$ lies distant from the kink in Fig. 6(a), while the second value of $\alpha = 1.8 \times 10^{-7} \frac{\text{eV}}{\text{\AA}^4}$ lies within the region of the kink.

While Fig. 8(a) shows that within the timescale considered here both modes have reached the vibrational steady state, Fig. 8(b) shows that the average vibrational energy is still changing over time. While Fig. 8(b) suggests that the vibrational steady state is not yet reached, we demonstrate in the following that the system exhibits no unique steady state.

In Fig. 9, we show the vibrational energy of individual trajectories for mode (1) for $\alpha = 1.8 \times 10^{-7} \frac{\text{eV}}{\text{\AA}^4}$. To remove any dependence of the steady state on the initial condition, all trajectories have been initialized with the same initial condition, $(x_1, x_2) = (0, 0)$ and $(p_1, p_2) = (0, 0)$, in contrast to all previous calculations. The energy of the individual trajectories oscillates around two different mean values, indicating that the system exhibits two steady states. Moreover, when setting $\mathbf{f}(t) = 0$, only one steady state is found with similar energy as in one of the beforehand mentioned steady states when simulating the full vibrational dynamics. We therefore conclude that in the vicinity of the kink in Fig. 6(a), the stochastic force drives individual trajectories to one of two different steady states.

Since we do not observe a unique steady state for certain values of α , we have to adjust the procedure outlined in Sec. III D to obtain the steady-state observables. In particular, we decide to calculate our observables by averaging over both steady states, weighted by the number of trajectories in each of them. Therefore, depending on the value of α , the number of trajectories in each steady state may change abruptly, which leads to the observed kink in Fig. 6(a). Note that, as already

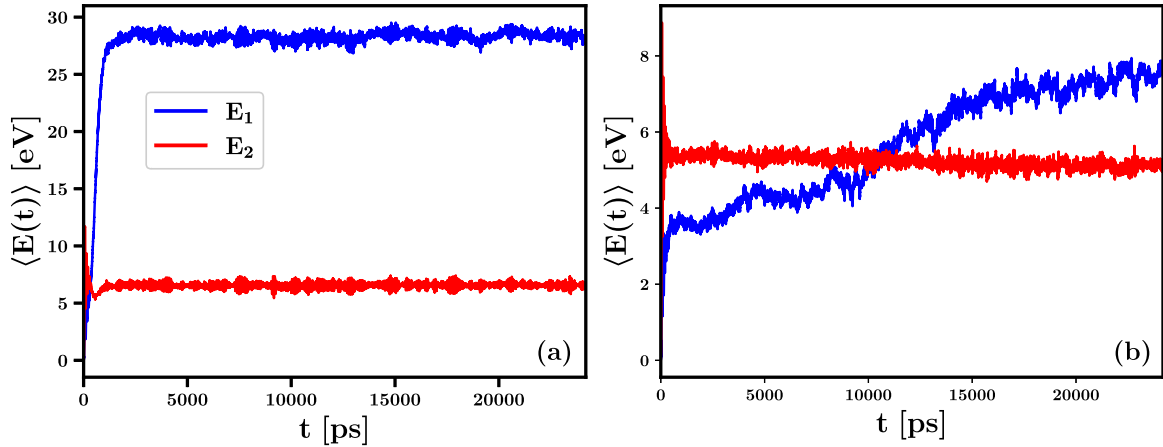


FIG. 8. (a) Average vibrational energy of the two vibrational modes over time for the system from Sec. IV B and a value of $\alpha = 1 \times 10^{-7} \frac{\text{eV}}{\text{\AA}^4}$. (b) Average vibrational energy over time for $\alpha = 1.8 \times 10^{-7} \frac{\text{eV}}{\text{\AA}^4}$. The initial conditions for all trajectories are $(x_1, x_2) = (0, 0)$ and $(p_1, p_2) = (0, 0)$, in contrast to all previous calculations.

mentioned earlier, this concerns only values of α near the kink in Fig. 6(a), and does not impact the main message in this section.

C. Influence of anharmonicity on steady-state electric current

So far, the discussion was centered on the impact of anharmonicity on the vibrational dynamics. We now turn to its effect on the steady-state electric current. We consider the same model with the same parameters as in Sec. IV B.

Figure 10 shows the adiabatic current through the left lead, $\langle I_L^{\text{ad}} \rangle^{\text{ss}}$, and its first-order nonadiabatic correction $\langle I_L^{\text{ad}} \rangle^{\text{ss}} + \langle I_L^{\text{na}} \rangle^{\text{ss}}$ for the same range of the anharmonicity parameter α as in Fig. 6(a) and different bias voltages. For all voltages shown here, the adiabatic contribution to the current shows a strong signature for $10^{-9} \frac{\text{eV}}{\text{\AA}^4} < \alpha < 10^{-6} \frac{\text{eV}}{\text{\AA}^4}$, which is the same range of α for which the vibrational energy drops significantly

in Fig. 6(a). For increasing α , $\langle I_L^{\text{ad}} \rangle^{\text{ss}}$ first increases, reaching its maximum around $2 \times 10^{-7} \frac{\text{eV}}{\text{\AA}^4}$, before it decreases over a small range of α and starts increasing again.

This signature in the adiabatic current can be attributed to the fact that, between $10^{-9} \frac{\text{eV}}{\text{\AA}^4} < \alpha < 10^{-6} \frac{\text{eV}}{\text{\AA}^4}$, the vibrational dynamics change significantly, redistributing the vibrational energy among both modes, as we showed in Fig. 6(a). Therefore, within this range of α , the molecular trajectory also changes considerably. To illustrate this, we show the molecular trajectory in the (x_1, x_2) plane in Fig. 11 exemplarily for two values of α . For $\alpha = 10^{-8} \frac{\text{eV}}{\text{\AA}^4}$, the radius of curvature is larger than for $\alpha = 10^{-7} \frac{\text{eV}}{\text{\AA}^4}$, since the system possesses more vibrational energy, as shown in Fig. 6(a). Moreover, considering the magnitude of the adiabatic current, $\langle I_L^{\text{ad}} \rangle_{\text{el}}(\mathbf{x})$, we see that for $\alpha = 10^{-7} \frac{\text{eV}}{\text{\AA}^4}$, on average, the trajectory intersects the areas of the coordinate grid where $\langle I_L^{\text{ad}} \rangle_{\text{el}}(\mathbf{x})$ has a larger

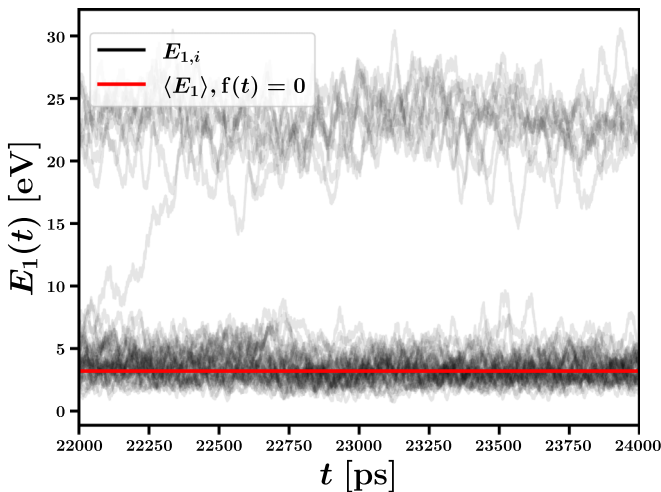


FIG. 9. Vibrational energy of individual trajectories over time for mode (1) and $\alpha = 1.8 \times 10^{-7} \frac{\text{eV}}{\text{\AA}^4}$. The red curve shows the average vibrational energy for mode (1) within the time considered here obtained by setting $\mathbf{f}(t) = 0$. All trajectories have the same initial condition, $(x_1, x_2) = (0, 0)$ and $(p_1, p_2) = (0, 0)$.

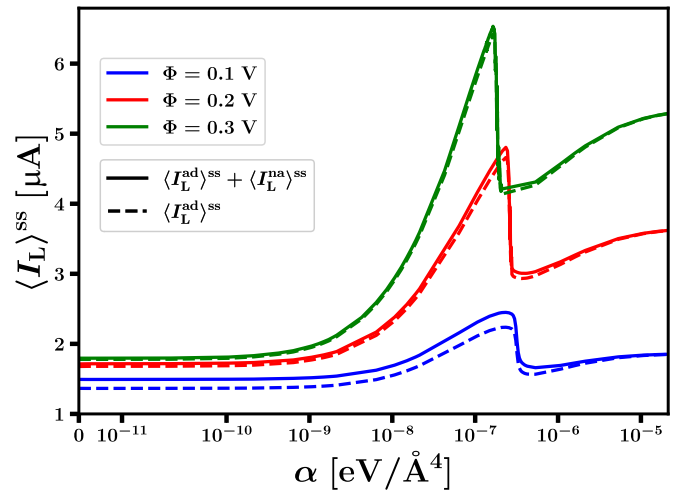


FIG. 10. Adiabatic current and its first-order nonadiabatic correction $\langle I_L^{\text{ad}} \rangle^{\text{ss}} + \langle I_L^{\text{na}} \rangle^{\text{ss}}$ and the purely adiabatic current $\langle I_L^{\text{ad}} \rangle^{\text{ss}}$ for different values of the anharmonicity parameter α and different bias voltages.

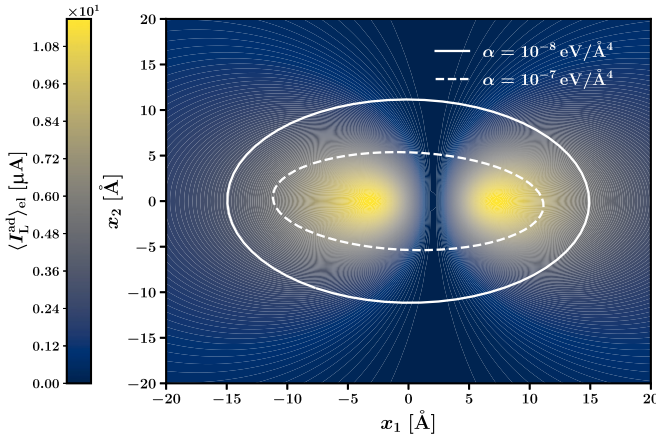


FIG. 11. Trajectories in the (x_1, x_2) plane after reaching a limit cycle for different values of α . The random force has been removed, $\mathbf{f}(t) = \mathbf{0}$. The bias voltage is $\Phi = 0.3$ V. The background shows the adiabatic current, $(I_L^{\text{ad}})_{\text{el}}(\mathbf{x})$, as given in Eq.(49).

magnitude more often than for $\alpha = 10^{-8} \frac{\text{eV}}{\text{\AA}^4}$. This change in the radius of curvature and the shape of the trajectory in the steady-state leads to the observed non-monotonous behavior in the current for different values of α .

Adding the first-order nonadiabatic correction to the current increases the overall current slightly for all voltages considered. This increase in magnitude can be explained considering the formula for the nonadiabatic contribution to the current in Eq. (51). Because the nuclear momenta are substantially large in regimes of vibrational instability and the nonadiabatic correction is proportional to the individual momenta, the nonadiabatic correction to the current becomes relevant.

For increasing bias voltage, on the other hand, the nonadiabatic correction becomes less relevant. This can be attributed to the fact that the radius of curvature of the molecular trajectory increases for increasing bias, since the trajectory gains more energy from the force field [see Fig. 6(a)]. Once the radius becomes sufficiently large, the trajectory no longer intersects the areas of the coordinate grid where the $I_{L,j}^{\text{na}}(\mathbf{x})$ have a significant magnitude, similar to what we showed for the adiabatic current in Fig. 11. Thus, for increasing voltage, the nonadiabatic correction to the current decreases. Moreover, since for larger α , the instability is suppressed, and the nuclear momenta become substantially smaller, the nonadiabatic current becomes less relevant in this regime.

V. CONCLUSION

In this work, we investigated the influence of anharmonic nuclear potentials on the vibrational dynamics and the corresponding mechanical stability of multimode molecular nanojunctions. This extends previous harmonic investigations of vibrational instabilities originating from nonconservative electronic forces in two-level, two-mode systems. To simulate the vibrational dynamics in our model systems, we used a mixed quantum-classical approach based on electronic friction and Langevin dynamics.

First, we investigated the vibrational dynamics in a dissociative model containing one harmonic and one Morse oscillator. We showed that the dissociation dynamics of this model was almost completely unaffected by the degeneracy of the effective frequencies, although remnants of the effect were visible for small regions around the bottom of the potential well. Based on our simulations, we would not expect this mechanism to show a significant effect when measuring dissociation rates in an experiment.

Next, we investigated whether the specific form and strength of the anharmonicity affects the mechanism of vibrational instability. To this end, we additionally considered a model containing one harmonic and one quartic oscillator. We found that adding even a small quartic term to a harmonic potential destroys this mechanism. Furthermore, we connected these findings to previous work on purely harmonic oscillators, where it was found that the instability vanishes even for small detunings of the two oscillators. Our analysis showed that the effective detuning induced by even very small anharmonicities is much larger than what is needed to break the mechanism and stabilize the junction. Finally, we investigated the influence of the anharmonicity on the steady-state current, showing that the steady-state current exhibits a strong signature near the onset of the instability.

While the analysis in this paper has been restricted to generic models of molecular nanojunctions with anharmonic nuclear potentials, our results indicate that anharmonicity destroys the original effect that leads to vibrational instabilities in harmonic models. Based on our results, it is therefore questionable whether instabilities specifically originating from current-induced nonconservative forces could be observed in a molecular junction. Since our results are obtained using a mixed quantum-classical method, benchmark calculations of the full quantum dynamics, for example using the hierarchical equations of motion (HEOM) approach [67–72], could provide a validation of our simulations. Moreover, this approach could be used to study the effect of electron-electron interactions on the mechanism leading to vibrational instabilities, both in a mixed quantum-classical framework and a full quantum description of the dynamics.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX: EQUIVALENCE OF DIFFERENT FRICTION TENSOR EXPRESSIONS

In the literature, there exist different expressions of the friction tensor which are formally equivalent. Here, we show explicitly the equivalence of the expression in Ref. [45] and Eq. (31) in this work. In order to do so, we show that the expression for the first-order nonadiabatic correction to the lesser Green's function entering the friction tensor in Eq. (31), $\tilde{G}_{(1),x_j}^<$, is identical to the expression in Ref. [45]. From this, it immediately follows that the two expressions for the friction tensor in this work and in Ref. [45] are also the same.

For better readability, in this Appendix, we use the notation $\partial_{x_j} \equiv \frac{\partial}{\partial x_j}$, $\partial_\varepsilon \equiv \frac{\partial}{\partial \varepsilon}$. We start by considering the first-order nonadiabatic correction to the lesser Green's function in Ref. [45], which, in our notation, is given by

$$G_{(1),x_j}^< = \frac{i}{2} (\partial_\varepsilon G_{(0)}^< \partial_{x_j} h G_{(0)}^A - G_{(0)}^R \partial_{x_j} h \partial_\varepsilon G_{(0)}^< + (\partial_\varepsilon G_{(0)}^R) \partial_{x_j} h G_{(0)}^< - G_{(0)}^< \partial_{x_j} h \partial_\varepsilon G_{(0)}^A). \quad (\text{A1})$$

Expressing the lesser adiabatic Green's function via

$$G_{(0)}^< = G_{(0)}^R \Sigma^< G_{(0)}^A. \quad (\text{A2})$$

and using the identity $\partial_\varepsilon G_{(0)}^R = -G_{(0)}^R G_{(0)}^R$, we obtain

$$\begin{aligned} \partial_\varepsilon G_{(0)}^< &= -G_{(0)}^R G_{(0)}^R \Sigma^< G_{(0)}^A + G_{(0)}^R (\partial_\varepsilon \Sigma^<) G_{(0)}^A \\ &\quad - G_{(0)}^R \Sigma^< G_{(0)}^A G_{(0)}^A. \end{aligned} \quad (\text{A3})$$

Entering Eq. (A3) into Eq. (A1) results in

$$\begin{aligned} G_{(1),x_j}^< &= \frac{i}{2} ((-G_{(0)}^R G_{(0)}^R \Sigma^< G_{(0)}^A + G_{(0)}^R (\partial_\varepsilon \Sigma^<) G_{(0)}^A \\ &\quad - G_{(0)}^R \Sigma^< G_{(0)}^A G_{(0)}^A) \partial_{x_j} h G_{(0)}^A \\ &\quad - G_{(0)}^R \partial_{x_j} h (-G_{(0)}^R G_{(0)}^R \Sigma^< + G_{(0)}^R (\partial_\varepsilon \Sigma^<) G_{(0)}^A \\ &\quad - G_{(0)}^R \Sigma^< G_{(0)}^A G_{(0)}^A) \\ &\quad + (\partial_\varepsilon G_{(0)}^R) \partial_{x_j} h G_{(0)}^< - G_{(0)}^< \partial_{x_j} h \partial_\varepsilon G_{(0)}^A). \end{aligned} \quad (\text{A4})$$

Expressing $\partial_\varepsilon G_{(0)}^{R/A}$ in the last two terms via $\partial_\varepsilon G_{(0)}^{R/A} = -G_{(0)}^{R/A} G_{(0)}^{R/A}$ and factoring out $G_{(0)}^R$ to the left and $G_{(0)}^A$ to the right, this can be written as

$$\begin{aligned} G_{(1),x_j}^< &= \frac{i}{2} G_{(0)}^R (-\Sigma^< G_{(0)}^A [G_{(0)}^A, \partial_{x_j} h] - \partial_{x_j} h G_{(0)}^R \partial_\varepsilon \Sigma^< \\ &\quad - G_{(0)}^< \partial_{x_j} h + (\partial_\varepsilon \Sigma^<) G_{(0)}^A \partial_{x_j} h + \partial_{x_j} h G_{(0)}^R G_{(0)}^R \Sigma^< \\ &\quad + \partial_{x_j} h G_{(0)}^< - G_{(0)}^R \partial_{x_j} h G_{(0)}^R \Sigma^<) G_{(0)}^A. \end{aligned} \quad (\text{A5})$$

The first three terms in this equation are the same as the first three terms on the right-hand side of Eq. (38). What is left to show is that the other terms correspond to their Hermitian conjugates. We start with the fourth term in Eq. (A5),

$$\begin{aligned} ((\partial_\varepsilon \Sigma^<) G_{(0)}^A \partial_{x_j} h)^\dagger &= \partial_{x_j} h (G_{(0)}^A)^\dagger (\partial_\varepsilon \Sigma^<)^\dagger \\ &= -\partial_{x_j} h G_{(0)}^R \partial_\varepsilon \Sigma^<. \end{aligned} \quad (\text{A6})$$

This is exactly the second term in Eq. (A5). Next, we combine the fifth and seventh term in Eq. (A5) via a commutator and calculate the Hermitian conjugate

$$\begin{aligned} (\partial_{x_j} h G_{(0)}^R G_{(0)}^R \Sigma^< - G_{(0)}^R \partial_{x_j} h G_{(0)}^R \Sigma^<)^\dagger &= ([\partial_{x_j} h, G_{(0)}^R] G_{(0)}^R \Sigma^<)^\dagger \\ &= -\Sigma^< G_{(0)}^A [G_{(0)}^A, \partial_{x_j} h]. \end{aligned} \quad (\text{A7})$$

This corresponds to the first term in Eq. (A5). Finally, the Hermitian conjugate of the sixth term in Eq. (A5) is

$$(\partial_{x_j} h G_{(0)}^<)^\dagger = -G_{(0)}^< \partial_{x_j} h, \quad (\text{A8})$$

corresponding to the third term in Eq. (A5). Thus we can write Eq. (A5) as in Eq. (38) in the main text, from which the equivalence between the expressions for the friction tensor in Ref. [45] and our work follows.

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