Transport through molecular devices with strong coupling to a single vibrational mode is considered in the case where the vibration is damped by coupling to the environment. We focus on the weak tunneling limit, for which a rate equation approach is valid. The role of the environment can be characterized by a frictional damping term $S(\omega)$ and corresponding frequency shift. We consider a molecule that is attached to a substrate, leading to frequency-dependent frictional damping of the single oscillator mode of the molecule, and compare it to a reference model with frequency-independent damping featuring a constant quality factor $Q$. For large values of $Q$, the transport is governed by tunneling between displaced oscillator states giving rise to the well-known series of the Frank-Condon steps, while at small $Q$, there is a crossover to the classical regime with an energy gap given by the classical displacement energy. Using realistic values for the elastic properties of the substrate and the size of the molecule, we calculate $I-V$ curves and find qualitative agreement between our theory and recent experiments on $C_{60}$ single-molecule devices.

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I. INTRODUCTION

In the emerging field of single-molecule electronics there is a large interest in transport through mesoscopic systems with strong electron-phonon coupling. There has been a number of experiments in which transport through a single molecule has been reported. One example is the series of experiments by Park et al.\cite{1} where it was shown that the current through a single $C_{60}$ molecule was strongly coupled to a single vibrational mode. The single phonon mode was associated with the motion of the molecule in the confining potential created by the van-der-Waals interaction with the electrodes. Later, similar devices with more complicated molecules were investigated\cite{2} and they also showed excitation spectra which may be associated with emission of vibrational quanta.

Theoretically, there has been a large amount of work on the problem of tunneling through a single level with coupling to phonon modes. In many experimental realizations the tunnel coupling to the leads is rather weak, and the transport is dominated by the well-known Coulomb blockade effect. In this regime, where the transport is sequential, the use of a rate equation approach is appropriate rather than a coherent scattering approach. Motivated by the above mentioned single-molecule experiments, the rate equation approach has been used in a number of recent papers.\cite{2,3,4,5,6} Some of these studies dealt with the issue of non-equilibrium phonon states, and the possibility of having negative differential conductance in such molecular systems.\cite{2,3,4,5,6} Physically, it is an essential question how the excited vibrational levels are allowed to relax, either through coupling to the environment, for example the phonons or plasmons of the metal substrate, or by virtue of the tunneling electrons.\cite{2,3,4,5,6} In the case where the relaxation of the vibrational mode is faster than the tunneling rate one can assume an equilibrium phonon distribution.

The coupling between the vibrational mode and the environment depends strongly on which vibrational mode is considered. For intra-molecular vibrations the lifetime can be very long.\cite{7,8} However, for the experiments of Ref.\cite{2}, it was suggested that the vibrational motion was associated with a center of mass motion, which is coupled to the environment more strongly as we discuss in this paper. A sketch of the physical setup that we consider is shown in Fig. 1.

In this paper, we assume that the tunneling rate is much smaller than the rate of relaxation to other degrees

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**FIG. 1:** Illustration of the system considered in this paper. The molecule is attached to substrates, e.g., by van-der-Waals interactions, and the movement in this potential is modelled by springs with spring constants $k_{M,1}$ and $k_{M,2}$. When an electron hops onto the molecule, the force created by image charges or local electric fields causes a shift of the equilibrium position of the oscillator and consequently emissions of quanta. The weights of the different final states are given by the well-known Frank-Condon overlap factors. The main objective of this paper is to consider the influence of damping of the molecular motion by emission of phonons into the substrates.
of freedom. Hence, the usual rate equation approach is applicable, and we can assume that the phonons relax between each tunneling event according to a thermal boson distribution. We study a model of one single molecular orbital with strong Coulomb repulsion coupled to a dissipative environment. The dissipation is caused by coupling to phonon modes of the electrodes as well as electromagnetic modes and it is represented by a bath of harmonic oscillators. The description is thus similar to the well-known theory of Coulomb blockade in an electromagnetic environment.\textsuperscript{13,14,15,16} However, there is a difference in how the coupling to the environment appears. In the electromagnetic environment case, the tunneling of an electron results in a sudden displacement of the position of the charge, while here the tunneling results in a sudden appearance of a force on the oscillator. For this reason, we go through the derivations in some detail and derive a general formula for the $I$-$V$ curves. This general result does not depend on the nature of the environment but we then specialize to two cases. We consider a molecule attached to a substrate, using a continuum model for the substrate, and compare our result to a reference model featuring frequency-independent damping and quality factor. The $I$-$V$ curves, as a function of the elastic parameters of the substrate and the size of the molecule, feature quite different line shapes as compared to the assumption of constant friction.

To get a simple estimate of the importance of the coupling to the substrate, consider a model where the molecule position $x$ is coupled to a one-dimensional substrate through a spring with spring constant $k_M$. For small substrate displacements, force balance gives that

$$-k_M x \approx v_s^2 \rho_{1D} \left( \frac{\partial u(z)}{\partial z} \right)_{z=0}, \quad (1)$$

where $u(z)$ is the substrate displacement, $\rho_{1D}$ is the 1D mass density, and $v_s$ is the sound velocity. At a given frequency $\omega$, the outgoing soundwaves are $u(z, \omega) = a e^{i k z / v_s}$, where $a$ is a constant. Finding $a$ from (1), we can insert it into the equation of motion for $x$ to obtain the quality factor $Q$ at the resonance frequency $\omega_0$:

$$Q = \frac{m_0 \rho_{1D} v_s \omega_0^3}{k_M^2} = \frac{\rho_{1D} v_s}{m_0 \omega_0} = \frac{m}{m_0}, \quad (2)$$

where $m_0$ is the molecule mass with $\omega_0^2 = k_M / m_0$, and $m = \rho_{1D} v_s / \omega_0$ is the mass of a wavelength long piece of the substrate. With realistic parameters for a C$_{60}$ molecule on a gold substrate, as was used in the experiments of Ref.\textsuperscript{2}, the quality factor is between 1 and 10, and therefore we expect the broadening to be substantial. This furthermore confirms the assumption that, for this type of molecular device, relaxation through the environment is much faster than through tunneling.

The paper is organized as follows. The model Hamiltonian is defined in Section II, and in Section III we derive an expression for the current from rate equations. The function that describes the tunneling density of states is then solved in absence of the dissipative environment in Section IV and with coupling to the environment in Section V. We discuss different models for the dissipative coupling in Section VI where we also discuss the physical implications. Section VII contains examples of $I$-$V$ curves, and finally, a summary as well as a comparison with the experiments of Ref.\textsuperscript{2} can be found in Section VIII.

## II. MODEL HAMILTONIAN

We consider a model of one single spin-degenerate molecular level coupled to two leads (generalization to more molecular levels is straightforward). The single level is coupled to the vibrational mode of the molecule through the charge on the dot. The coupling between the oscillator and the environment is included as a linear coupling to a bath of harmonic oscillators in the spirit of the theory by Caldeira and Leggett.\textsuperscript{17} The model Hamiltonian then reads

$$H = H_{LR} + H_D + H_B + H_{DB} + H_{bath} + H_{Bbath} + H_T, \quad (3)$$

with

$$H_{LR} = \sum_{k\sigma, \alpha=L,R} \xi_{k\sigma} c_{k\sigma, \alpha}^\dagger c_{k\sigma, \alpha} \quad (4a)$$

$$H_D = \sum_{\sigma} \xi_0 d_{\sigma}^\dagger d_{\sigma} + U n_{d\uparrow} n_{d\downarrow}, \quad (4b)$$

$$H_B = \frac{p_0^2}{2m_0} + \frac{1}{2} m_0 \omega_0^2 x_0^2, \quad (4c)$$

$$H_{DB} = \lambda x_0 \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma}, \quad (4d)$$

$$H_{bath} = \sum_j \left( \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 x_j^2 \right), \quad (4e)$$

$$H_{Bbath} = \sum_j \beta_j x_j x_0, \quad (4f)$$

where the $c_{k\sigma, \alpha}^\dagger$, $c_{k\sigma, \alpha}$ and the $d_{\sigma}^\dagger$, $d_{\sigma}$ are creation and annihilation operators for the leads and the dot, respectively, $x_0$ is the oscillator degree of freedom, $\{x_j\}$ describes the set of environment degrees of freedom and $m_j$, $\omega_j$ their respective masses and frequencies, $\xi_0$ is the onsite energy, and $U$ is the Coulomb interaction on the molecule. The coupling constants between electron-oscillator and oscillator-bath are $\lambda$ and $\{\beta_j\}$, respectively. The lead electron energies are given by

$$\xi_{k\sigma} = \varepsilon_{k\sigma} - \mu_\sigma, \quad (5)$$

where $\mu_\sigma$ is the chemical potential of lead $\sigma$. Finally, the tunnel Hamiltonian is

$$H_T = \sum_{k\sigma, \alpha=L,R} t_{k\sigma} (c_{k\sigma, \alpha}^\dagger d_{\alpha} + d_{\sigma}^\dagger c_{k\sigma, \alpha}). \quad (6)$$
The tunneling amplitudes could in principle also depend on the oscillator position. In the experimental realizations in Refs. 2,3,4, this is probably a small effect since the oscillator length is of order a few pm whereas the tunneling matrix element changes on the scale of nm. For simplicity, we do not take any such non-linear effects into account, but we note that a position dependence of the tunneling amplitudes, for example of the form \( \exp(-x_0/\ell) \), could easily be included in the present formalism.

The force acting on the charged molecule, represented by the term \( \dot{H}_{DB} \), is caused by electric fields originating from either static impurity charges or image charges. Since this force on the molecule is counteracted by a force on these charges and, hence, on the environment, we should in principle also include the interaction between the environment coordinates and the charge on the molecule. This would in fact lead to a qualitatively different behavior since Ohmic dissipation is cut off at frequencies smaller than the inverse size of the total system, i.e., the inverse range of the interaction between the charges on the molecule and the charges in the environment. This interesting subtlety was pointed out in Ref. 18. However, since the van-der-Waals interaction between molecule and the substrate is short range compared to the electrostatic forces, we will consider the force acting on the molecule as an external quantity, which is thus not coupled to the dissipative environment. We do note, however, that including such a coupling would in fact lead to a small discontinuity at the beginning of each step in the \( I-V \) curve. The experimental data of, e.g., Ref. 2 does not seem to suggest such a discontinuity, and we therefore specialize to the case where the environment coordinates are unaffected by the charge on the molecule.

We now want to relate the coupling constants in the boson-bath coupling to the finite damping of the vibrational mode, which can be accomplished by studying the classical equations of motion. After removing the bath degrees of freedom, thereby neglecting the term \( \dot{H}_{DB} \) that will be removed by a unitary transformation below, we end up with the following equation of motion in the frequency domain:

\[
[\omega^2 - \omega_0^2 - S(\omega)] \dot{x}_0 + \sum_j \frac{\beta_j^2}{m_j} \frac{1}{(\omega + i\eta)^2 - \omega_j^2} = 0,
\]

where we have defined

\[
S(\omega) = \frac{1}{m_0} \sum_j \frac{\beta_j^2}{m_j} \frac{1}{(\omega + i\eta)^2 - \omega_j^2}.
\]

which is complex in general and gives rise to frictional damping and a frequency shift of the bare frequency \( \omega_0 \).

In Section VII.B we will explicitly calculate \( S(\omega) \) for the case of a molecule attached to a semi-infinite substrate.

We eliminate the coupling term \( \dot{H}_{DB} \) of the Hamiltonian by a unitary transformation similar to the one used in the independent boson model at the cost of introducing displacement operators in the tunneling term. However, since we are dealing with a somewhat more complicated system due to the coupling to the bosonic bath, the unitary transformation in Ref. 14 has to be generalized. We define the transformation

\[
\hat{H} = \hat{S} \hat{H} \hat{S}^\dagger, \quad \hat{S} = e^{-iA_n}, \quad A = p_0 \ell + \sum_j p_j \ell_j,
\]

where \( n_d = \sum_\sigma d_\sigma^\dagger d_\sigma \). Using that

\[
\dot{x}_0 = x_0 - \lambda n_d, \quad \dot{x}_j = x_j - \ell_j n_d,
\]

it is a matter of simple algebra to show that the linear coupling term \( \dot{H}_{DB} \) cancels if we set

\[
\ell = \frac{\lambda}{m_0 [\omega_0^2 + S(0)]}, \quad \ell_j = \frac{-\ell \beta_j}{m_j \omega_j^2},
\]

and the Hamiltonian then transforms into

\[
\hat{H} = \hat{H}_{LR} + \hat{H}_D + \hat{H}_B + \hat{H}_{bath} + \hat{H}_{Bbath} + \hat{H}_T,
\]

where

\[
\hat{H}_T = \sum_{k\sigma, \alpha = L,R} t_{k\sigma, \alpha} \left( c_{k\sigma, \alpha}^\dagger A_{\sigma} + d_\sigma^\dagger e^{-iA_{\sigma}} c_{k\sigma, \alpha} \right)
\]

and

\[
\hat{H}_D = \varepsilon_0 \sum_\sigma d_\sigma^\dagger d_\sigma + \hat{U} n_d n_d^\dagger, \quad \varepsilon_0 = \varepsilon_0 - \frac{1}{2} \lambda^2.
\]

Here, \( \hat{U} = U - \lambda \ell \) is the Coulomb repulsion modified by the phonon mediated interaction. For a weak Coulomb interaction, this can result in a negative effective \( U \), which was discussed in Ref. 20.

**III. RATE EQUATIONS AND CURRENT FORMULA**

We derive an expression for the current in the weak tunneling limit using the usual kinetic equation approach. As mentioned in the Introduction, the most important assumption here is that the tunneling rate is much smaller than all other time scales, which means that we can assume the vibrational degrees of freedom and the Fermi seas in the two electrodes to be in equilibrium at all times. For simplicity, we consider only two charge states and therefore let \( U = \infty \), which leaves us with only three states: empty, and occupied by either spin up or down. The probabilities for the three states are denoted \( P_0 \), \( P_\uparrow \), and \( P_\downarrow \), respectively. The rate equations are

\[
\begin{pmatrix}
-2\Gamma_{10} & \Gamma_{01} & \Gamma_{01} \\
\Gamma_{10} & -\Gamma_{01} & 0 \\
\Gamma_{10} & 0 & -\Gamma_{01}
\end{pmatrix}
\begin{pmatrix}
P_0 \\
P_\uparrow \\
P_\downarrow
\end{pmatrix} = 0,
\]

which combined with the condition \( P_0 + P_\uparrow + P_\downarrow = 1 \) has the solution

\[
P_0 = \frac{\Gamma_{01}}{\Gamma_{01} + 2\Gamma_{10}}, \quad P_\uparrow = P_\downarrow = \frac{\Gamma_{10}}{\Gamma_{01} + 2\Gamma_{10}}.
\]
where \( \gamma_{10} \) is the tunneling rate for tunneling from the empty state to a singly occupied state, and \( \gamma_{01} \) is the rate for the reverse process. Since the electron can tunnel out of both left and right leads, both rates have left and right contributions: \( \gamma_{ij} = \gamma_{ji}^L + \gamma_{ji}^R \). The tunneling rates are calculated using Fermi’s Golden Rule, thereby treating \( H_T \) of Eq. (13) as the perturbation and assuming a thermal equilibrium distribution of the lead electrons and the phonon bath. Following standard derivations, we obtain

\[
\begin{align*}
\gamma_{10}^\alpha &= \gamma_{\alpha} \int \frac{d\omega}{2\pi} \mathcal{F}(\omega) n_{\alpha}(\epsilon_0 + \omega), \\
\gamma_{01}^\alpha &= \gamma_{\alpha} \int \frac{d\omega}{2\pi} \mathcal{F}(-\omega)(1 - n_{\alpha}(\epsilon_0 + \omega)),
\end{align*}
\]  

where we have defined the function

\[
\mathcal{F}(\omega) = F(-\omega) e^{\beta_\omega}, \quad \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \mathcal{F}(\omega) = 1.
\]

We can use Eq. (14) to show that the rates in Eq. (17) can be written as

\[
\gamma_{10}^\alpha = \gamma_{\alpha} n_{\alpha}, \quad \gamma_{01}^\alpha = \gamma_{10}^\alpha e^{\beta(\epsilon_0 - \epsilon_{\alpha})},
\]

where we defined

\[
\bar{n}_{\alpha} = \int \frac{d\omega}{2\pi} \mathcal{F}(\omega) n_{\alpha}(\omega + \epsilon_0).
\]

The current through the molecule is now given by

\[
I = -e(2P_0 \gamma_{10}^L - (P_+ + P_-) \gamma_{01}^L) = 2e \frac{\Gamma_R^L \Gamma_0^L}{\Gamma_1^L} (1 + \frac{\Gamma_0^L}{\Gamma_1^L}).
\]

Using Eq. (20), this can also be written as

\[
I = -2e \frac{\Gamma_L \Gamma_R \tilde{n}_R \tilde{n}_L}{\Gamma_L \tilde{n}_L + \Gamma_R \tilde{n}_R} (e^{\beta(\epsilon_0 - \epsilon_{\alpha})} - e^{\beta(\epsilon_0 - \epsilon_{\alpha})}).
\]

**IV. WITHOUT COUPLING TO THE ENVIRONMENT**

We start by discussing the limit when the oscillator is not coupled to the environment, which means that thermal smearing dominates over dissipative broadening. However, we still assume that the coupling is stronger than the tunnel coupling so that the molecule equilibrates between each tunneling event. This section is thus equivalent to the results in other rate equation calculations, but for completeness and later comparison we write down this limiting case.

The phonon average is performed assuming thermal equilibrium, and we have

\[
F_0(t) = \exp\{ g (e^{-i\omega_0 t} - 1) (1 + N) + g (e^{i\omega_0 t} - 1) N \},
\]

where

\[
g = \frac{1}{2} \left( \frac{\ell}{\ell_0} \right)^2, \quad \ell_0^2 = \frac{1}{m_0 \omega_0}, \quad N = n_B(\omega_0),
\]

Here, \( g \) is an important parameter determined by the ratio of the classical displacement length and the quantum mechanical oscillator length. The evaluation of \( F_0(\omega) \) from Eq. (24) is equivalent to the independent boson model and using the result from there we get

\[
F_0(\omega) = 2\pi \sum_{n=\infty}^{\infty} P_n(g) \delta(\omega - n\omega_0),
\]

where

\[
P_n(g) = \exp(-g \coth(b)) e^{nb} I_n \left( \frac{g}{\sinh(b)} \right), \quad b = \frac{\beta \omega_0}{2},
\]

and \( I_n \) is the modified Bessel function of the first kind. The finite-temperature result involves both positive and negative values of \( I_n \) for the even and odd cases, respectively.
negative values of \( n \), corresponding to emission and absorption of phonons, respectively. At zero temperature, this reduces to having only positive values of \( n \) because of the factor \( e^{\alpha_0 \omega} / 2 \), and hence only emission processes are possible. In the limit \( T \to 0 \), we thus have a series of emission peaks at \( \omega = n \omega_0 \) for positive \( n \) and with weights given by the Poisson distribution \( P_n \to e^{-g}\gamma^n/n! \).

The current can now be found from Eq. (23). In Fig. 4 we show examples of current-voltage characteristics using Eq. (23) for symmetric and asymmetric junctions. In the following, we study how the physics gets modified by the coupling to the environment.

\[ \text{V. WITH COUPLING TO THE ENVIRONMENT} \]

In presence of coupling to the environment, the evaluation of the function \( F(t) \) in Eq. (13) is in principle straightforward since the Hamiltonian is quadratic in the oscillator and bath degrees of freedom. We obtain

\[ F(t) = \exp \left( B(t) - B(0) \right), \quad B(t) = \langle A(t) A(0) \rangle_0, \quad (28) \]

where the operator \( A \) is defined in Eqs. (9) and (11). The expectation value \( \langle \ldots \rangle_0 \) is to be evaluated with respect to \( \hat{H} \) without the tunneling term. At this point, it is convenient to use the fluctuation-dissipation theorem,

\[ B(\omega) = -2 \text{Im} [B^R(\omega)](1 + n_B(\omega)), \quad (29) \]

to express \( B(t) \) in terms of the corresponding retarded Green’s function

\[ B^R(t) = -i \theta(t) [\langle A(t), A(0) \rangle_0]_0. \quad (30) \]

Here, \( n_B(\omega) = (e^{\beta_0 \omega} - 1)^{-1} \) is the usual Bose function. In order to find this retarded correlation function, we define the following auxiliary Green’s functions:

\[ G^K_0(t) = -i \theta(t) \frac{1}{\ell} \langle [O(t), A(0)]_0 \rangle, \quad (31) \]

from which we obtain \( B^R \) as

\[ B^R = (\ell G^R_0 + \sum_j \ell_j G^R_{p_j}) \ell \]

\[ = \ell^2 (G^R_0 - \sum_j \frac{\beta_j}{m_j \omega_j^2} G^R_{p_j}). \quad (32) \]

The equations of motion for these functions are in frequency domain given by

\[ \begin{pmatrix} \omega & \frac{-i m_0 \omega^2}{\omega} & \omega \\ \frac{-i m_0 \omega}{\omega} & \frac{G^R_0}{G^R_{p_0}} & \frac{G^R}{G^R_{p_0}} \\ \omega & \frac{-i m_0 \omega}{\omega} & \frac{G^R}{G^R_{p_0}} \end{pmatrix} \begin{pmatrix} i \beta_0 G^R_{x_0} + \frac{i \beta_0 G^R_{x_0}}{m_0 \omega_0^2} \frac{G^R_{x_0}}{G^R_{p_0}} - \frac{i \beta_0 G^R_{x_0}}{m_0 \omega_0^2} \frac{G^R_{x_0}}{G^R_{p_0}} \end{pmatrix}, \quad (33) \]

\[ \begin{pmatrix} \omega + i \eta & \frac{-i m_j \omega}{\omega} & \omega - i \eta \\ \frac{-i m_j \omega}{\omega} & \frac{G^R_{x_j}}{G^R_{p_j}} & \frac{G^R_{x_j}}{G^R_{p_j}} \\ \omega - i \eta & \frac{-i m_j \omega}{\omega} & \frac{G^R_{x_j}}{G^R_{p_j}} \end{pmatrix} \begin{pmatrix} i \beta_j G^R_{x_j} + \frac{i \beta_j G^R_{x_j}}{m_j \omega^2} \frac{G^R_{x_j}}{G^R_{p_j}} - \frac{i \beta_j G^R_{x_j}}{m_j \omega^2} \frac{G^R_{x_j}}{G^R_{p_j}} \end{pmatrix}. \quad (34) \]

Solving this linear set of equations for the Green’s functions and inserting the results into Eq. (22), we obtain

\[ B^R(\omega) = \frac{2 g \bar{\omega}_0}{\omega^2 - \bar{\omega}_0^2} - \bar{S}(\omega) \left( 1 - \frac{\bar{S}(\omega)}{\omega^2} \right), \quad (35) \]

where we have defined \( \bar{S}(\omega) = \bar{S}(\omega) - S(0) \) and the experimentally observable renormalized frequency \( \bar{\omega}_0 = \omega_0 + S(0) \). Using (29), the function \( B(\omega) \) thus follows as

\[ B(\omega) = -4 g \frac{1 + n_B(\omega)}{\omega^2} \text{Im} \left[ \frac{\bar{\omega}_0^2}{\omega^2 - \bar{\omega}_0^2 - \bar{S}(\omega)} \right], \quad (36) \]

where now \( g = e^2 / 2 \ell_0^2 \) is defined with respect to the renormalized frequency \( \bar{\omega}_0 \), i.e. \( \ell_0 = 1 / m_0 \omega_0 \). This result can then be used to find

\[ F(t) = \exp \left( \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \left( e^{-i \omega t} - 1 \right) B(\omega) \right). \quad (37) \]

Eq. (37) is equivalent to the result for the Coulomb blockade of a single tunnel junction with coupling to the electromagnetic environment. In the Coulomb blockade problem, the tunneling density of states was related to the impedance as seen from the junction, here the \( I-V \) characteristic is in a similar way related to the frictional damping of the oscillator mode. In both cases, the low energy form of the spectrum is a power law at low temperatures. At small frequencies \( \omega \ll \omega_0 \) and zero temperature, we get the following power law behavior:

\[ F(\omega) \propto \omega^{\alpha - 1}, \quad \alpha = \frac{2 g}{\omega_0 \pi} \lim_{\omega \to 0} \left( \text{Im} \bar{S}(\omega) / \omega \right). \quad (38) \]

Furthermore, we use the trick by Minnhagen21 to find the \( F \)-function as the solution of the integral equation

\[ F(\omega) = \frac{1}{\omega} \int_0^\infty \frac{d\zeta}{2\pi} F(\zeta) B(\zeta - \omega)(\zeta - \omega), \quad (39) \]

which is useful for the numerical evaluation of \( F \).

\[ \text{VI. MODELS FOR S(\omega)} \]

\[ \text{A. Frequency-independent quality factor Q} \]

As a first attempt, we can assume \( S \) to be of the form

\[ S(\omega) = S(0) + i \frac{\bar{\omega}_0}{Q}, \quad (40) \]

which leads to a frequency-independent quality factor \( Q \) of the single vibrational mode, similar to the Ohmic dissipation model of Caldeira and Leggett in Ref. 17. The model is also similar to the Coulomb blockade problem of an LCR circuit16 which is described by the same formula. The limit \( Q \to \infty \) is seen to coincide with
the results in Section XV since in this limit \( B(\omega) \to 2\pi(1 + n_B(\omega))(\pm)\delta(\omega \pm \omega_0) \), and when this is inserted into Eq. (37), we get (41). We also see that, for a critical value of \( Q_c = 2g/\pi \), the function \( F \) and, hence, the differential conductance change from having a divergence at small energies to vanish at small energies.

In Fig. 3, we plot the function \( F \) and its integral for different values of \( g \) and frequency-independent \( Q \). The curves have been calculated from Eq. (39) at zero temperature. We take \( Q = 20, 10, 5, 2.5, 2g/\pi, 0.1, 0.01 \), where \( g = 0.5 \) in (a) and (b), \( g = 1 \) in (c) and (d), and \( g = 2 \) in (e) and (f). The curves have been displaced for clarity by multiples of \( (1,0) \) in (a), (c), and (e), and by multiples of \( (0.25,1) \) in (b), (d), and (f) (largest \( Q \) to the left). For large \( Q \), the integrated function goes to the dissipationless results, where the step heights are given by the Poisson distribution (leftmost staircase in (a), (c), and (e)), whereas for small \( Q \) it goes to a step function at \( \varepsilon = g\omega_0 \) (vertical line). Note also that the differential conductance at the first step remains sharp while the higher order steps are smeared when \( Q > Q_c \).

In Fig. 4, we plot the integral of the function \( F \) for \( g = 4 \) and different \( Q \) at zero temperature. We take \( Q = \infty \) (dashed line), 20, 8/\pi, 0.1. At \( Q \lesssim Q_c \) the steps disappear, while for \( Q \gtrsim Q_c \) the curves approach the classical limit, which is a step function at \( \varepsilon = 4\omega_0 \). The inset shows the \( F \)-function itself for the same parameters.

The disappearance of the steps, which happens at \( Q_c \), is therefore different from the crossover to the classical regime. This is shown in Fig. 4, where we plot the integral of \( F \) for \( g = 4 \) for different values of \( Q \). For \( Q = 20 \), the steps are only slightly broadened, while for \( Q = Q_c \), the steps are almost fully broadened but the line still follows the quantum behavior. Only for smaller \( Q \) do we approach the classical result, which is a step function at \( g\omega_0 \).

### B. Coupling to a substrate

We consider a molecule of mass \( m_0 \) attached to a substrate that extends over the semi-infinite half-space \( z \geq 0 \). The case of two substrates, as is shown in Fig. 1, is a straightforward generalization and will be discussed at the end of the calculation. The 3D Lagrangian density for the substrate is given by

\[
\mathcal{L}(\vec{r}, t) = \frac{1}{2} \rho \left[ \left( \frac{\partial \vec{u}}{\partial t} \right)^2 - (v_x^2 - 2v_y^2) \left( \nabla \times \vec{u} \right)^2 - v_z^2 \left( \nabla \times \vec{u} \right)^2 \right] - 2v_y^2 \frac{\partial \vec{u}}{\partial x} \frac{\partial \vec{u}}{\partial x} .
\]
where \( v_l \) and \( v_t \) are the longitudinal and transverse sound velocities, and \( \rho \) is the mass density. This Lagrangian leads to the following equation of motion:

\[
\partial_t^2 \vec{\upsilon} - v_t^2 \nabla^2 (\nabla \cdot \vec{\upsilon}) + v_t^2 \nabla \times \nabla \times \vec{\upsilon} = 0
\]  

(44)

Having in mind a small molecule attached to the origin, the assumption of cylindrical symmetry around the \( z \)-axis seems reasonable. We define \( u_r \) and \( u_z \) as the displacements in radial direction and parallel to the \( z \)-axis, respectively.

We consider the case that the molecule only exerts a total force \( F \) perpendicular to the substrate surface:

\[
F = k_M \left[ x - \int_0^\infty 2\pi rf(r)u^0_z(r)dr \right],
\]

(45)

where \( u^0_z(r) \) is the parallel displacement at the surface defined by \( z = 0 \), and \( f(r) \) is a normalized distribution function, i.e. \( \int 2\pi rf(r)dr = 1 \). This imposes the following boundary conditions on the stress tensor \( T^{23} \)

\[
T_{xr}|_{z=0} = 0, \quad T_{zz}|_{z=0} = -F f(r),
\]

(46)

where the components \( T_{xr} \) and \( T_{zz} \) can be written as functions of the displacements \( u_r \) and \( u_z \) (see, e.g., Refs. [24, 25]). The solution is then a straightforward generalization of the procedure for a point source with \( f(r) \propto \delta(r)/r \) outlined by Lamb in Ref. [26]. We obtain in frequency space

\[
u^2 (r) = F \frac{2\pi}{v_l^2} \int_0^\infty \frac{kv_l f_k}{G(k, \omega)} J_0(kr)dk, \]

(47)

where we have defined the following quantities:

\[
\nu_{l,t} = \begin{cases} \sqrt{\frac{k^2 - \frac{\omega^2}{v_l^2}}{\nu_{l,t}}} & \text{if } k^2 > \frac{\omega^2}{v_l^2}, \\ -i \sqrt{\frac{k^2 - \frac{\omega^2}{v_l^2}}{\nu_{l,t}}} & \text{if } k^2 < \frac{\omega^2}{v_l^2}, \end{cases}
\]

(48)

\[
G(k, \omega) = 4\mu_L \nu_{l,t} k^2 - (\lambda_L + 2\mu_L)(\nu_t^2 + k^2) \nu_t^2 + \lambda_L k^2 \nu_t^2 + \lambda_L k^4,
\]

(49)

where \( \mu_L \) and \( \lambda_L \) are the Lamé coefficients, which are related to the sound velocities as

\[
\nu_t = \sqrt{\frac{\lambda_L + 2\mu_L}{\rho}}, \quad \nu_l = \sqrt{\frac{\mu_L}{\rho}},
\]

(50)

and \( f_k \) is the Fourier-Bessel transform of the force distribution \( f(r) \),

\[
f_k = \int_0^{\infty} f(r)J_0(kr)rdk.
\]

(51)

The \((-\)\)-sign in the definition of \( \nu_{l,t} \) in Eq. [48] is necessary for selecting the retarded response \( \omega \rightarrow \omega + i\eta \) corresponding to outgoing waves since the square-root function has a branch cut on the negative real axis.

The total force \( F \) involves \( u^0_z(r) \) and vice versa, see Eqs. [45, 47], so that we obtain:

\[
\int_0^{\infty} 2\pi r f(r)\nu^0_z(r)dr = \frac{R(\omega)}{1 + R(\omega)},
\]

(52)

where

\[
R(\omega) = k_M \frac{2\pi \omega^2}{v_t^2} \int_0^{\infty} \frac{kn f^2_k}{G(k, \omega)} dk.
\]

(53)

The function of interest, \( S(\omega) \), can then be deduced from the equation of motion for the molecule in frequency space:

\[
-M \omega^2 x_0(\omega) = -k_M \left[ x_0(\omega) - \int_0^{\infty} 2\pi r f(r)\nu^0_z(r)dr \right],
\]

(54)

Identifying \( k_M/\omega_M \) with the bare frequency \( \omega_M^2 \), we obtain

\[
\left[ \omega^2 - \omega_M^2 + \frac{R(\omega)}{1 + R(\omega)} \right] x_0(\omega) = 0,
\]

(55)

which implies upon comparison with Eq. [47]

\[
S(\omega) = -\omega_M^2 \frac{R(\omega)}{1 + R(\omega)}.
\]

(56)

For the situation where the molecule is attached to two substrates it is simple to see that the function \( S(\omega) \) becomes instead

\[
S(\omega) = \frac{k_{M,1}}{M_1} R_1(\omega) - \frac{k_{M,2}}{M} R_2(\omega),
\]

(57)

where \( R_{1,2} \) is given by Eq. [49] but with \( k_M \) replaced by \( k_{M,1,2} \) and, if the two substrates are different, with substrate parameters changed accordingly. However, because of the lack of detailed knowledge about the actual geometry of the device, and since the coupling to the two sides of the junction is very likely to be asymmetric, we will in the following make the simplifying assumption that the molecule only couples to one substrate.

Our results for \( R(\omega) \) in Eq. [53] imply that the imaginary part of \( S(\omega) \) (which will eventually be responsible for the frictional damping) has contributions not only from extended waves in the substrate but also from waves that are confined to the surface, the so-called Rayleigh waves. Mathematically, this contribution arises from \( G(k, \omega) \) being zero for a specific value of \( k \). This value falls into the regime where both \( \nu_t \) and \( \nu_l \) are real, i.e., where wavevectors \( k \) are larger than allowed for transversal and longitudinal waves, see Eq. [48, 26].

In order to compare our result [49] to experimental data, we need to choose a specific model for the force distribution function \( f(r) \). The most realistic model would involve a distribution in accord with the van-der-Waals potential, however, as a result of that \( f_k \) is a rather involved function of \( k \). For simplicity, we therefore choose

\[
f(r) = \frac{1}{2\pi D^2} e^{-r/D}, \quad \text{i.e., } f_k = \frac{1}{2\pi \sqrt{1 + k^2 D^2}}.
\]

(58)
The parameter $D$ is on the order of the width $D_0$ of the molecule, e.g., $D_0 = 10.4\,\text{Å}$ for a $C_{60}$ molecule. For this model, we can explicitly extract $S(0)$, since then
\[ R(0) = \frac{3}{64} \frac{\omega_0^2 M a^2}{(\alpha^2 - 1) \mu_0^2 D}. \]  
where $\alpha \equiv \nu_t/\nu_s$. Note that $R(0)$ the squared bare frequency $\omega_0^2 = \langle \omega^2 \rangle - \langle \omega \rangle^2$ so that we end up with
\[ S(0) = -\omega_0^2 \frac{\omega_0^2 R(0)/\omega_0^2}{1 + \omega_0^2 R(0)/\omega_0^2}. \]

This result has the particular effect on the damping coefficient $\text{Im} S(\omega)/\omega$ that it is independent of $D/D_0$ at zero frequency. We show plots of the real and imaginary parts of $S(\omega)$ in Fig. 5. The real part, and thus the renormalization of the bare frequency as a function of energy, goes to zero rather quickly, whereas the imaginary part remains nonzero over a large frequency range. The latter is important for the damping since the quantity $\omega \omega_0/\text{Im} S(\omega)$ takes the place of the quality factor. The fact that this quantity tends towards a constant at zero frequency illustrates that the imaginary part of $S(\omega)$ rises linearly with $\omega$ for small $\omega$.

We plot the results for $F$ and its integral in Fig. 6. First we note that the shape of the staircases is markedly different from the constant $Q$-factor model: they are asymmetric and more steep on the rising side with a rather sharp transition to the next step. The asymmetry is even more obvious in the peaks of $F$ itself. We also note that a larger spread of the coupling over the surface, i.e., larger $D/D_0$, makes the peaks in $F$ and the steps in its integral sharper and less asymmetric. For large $D/D_0$, the staircase tends towards the large constant $Q$ limit of before since then $\omega/\text{Im} S(\omega)$ grows rapidly with $\omega$ and at the same time $S(0) \to 0$.

![FIG. 5: Real part (dotted line) and imaginary part (solid line) of $S(\omega)$ as a function of frequency for a $C_{60}$ molecule on a gold substrate and the particular choice $D/D_0 = 1$. The imaginary part tends towards zero linearly which is illustrated in the inset: the “quality factor” $\omega \omega_0/\text{Im} S(\omega)$ tends towards a constant at zero frequency.](image)

![FIG. 6: The function $F(\xi)$ and its integral for different values of $g$, making use of (59) for $S(\omega)$. The curves have been calculated from Eq. (39) at zero temperature, assuming a $C_{60}$ molecule attached to a gold substrate. We take $D/D_0 = 0.5$, $0.75$, $1$, $2$, where $g = 0.5$ in (a) and (b), $g = 1$ in (c) and (d), and $g = 2$ in (e) and (f). The curves have been displaced for clarity by multiples of $(1,0)$ in (a), (c), and (e) (largest $D/D_0$ to the right), and by multiples of $(1.5,1.5)$ in (b), (d), and (f) (largest $D/D_0$ at the bottom). The staircases in (a), (c), and (e) feature sharper and less asymmetric steps for larger $D/D_0$ but are clearly visible in any case. The asymmetry is even more apparent in the plots of $F$ in (b), (d), and (f). In contrast to the constant $Q$-factor results in Fig. 5 even the first step in the staircase gets smeared for smaller $D/D_0$. However, we recover the large constant-$Q$ limit for large $D/D_0$.](image)

### VII. I-V CURVES

In this Section, we show a number of I-V curves using the expression in Eq. (24) at zero temperature based on the $F$-function, both for the case of frequency-independent quality factor and for the substrate model (60) for $S(\omega)$ discussed in the previous section.

In Fig. 7 we show current-voltage characteristics for constant $Q = 5$ and $g = 0.5$, $1$, $2$. For this value of $Q$, the Frank-Condon steps are still visible. If we took even smaller values of $Q$ (not shown) such that the steps disappear, the characteristics are still strongly modified by the electron-vibron coupling in the sense that a gap develops in the I-V curve. Such an effect was recently claimed to be observed in a different type of device.22

We also show I-V curves corresponding to a $C_{60}$ molecule coupled to a gold substrate, using the substrate model of Sec. VII B see Fig. 8. We display the I-V curves for $g = 0.5$, $1$, $2$, both for symmetric and for asym-
metric tunneling contacts, however, we restrict ourselves to \( D/D_0 = 1 \) since the general features are very similar for other choices of \( D/D_0 \). Upon comparison with the frequency-independent \( Q \)-factor model, we note that the \( I-V \) staircases are in general less steep and smoother but still clearly exhibit the expected Frank-Condon steps.

### VIII. SUMMARY AND DISCUSSION

#### A. Summary

We have included broadening of the phonon sidebands due to frictional coupling of the oscillator mode within a kinetic equation approach. Since we have worked in the limit where the tunneling time is much smaller than the lifetime of the oscillator, we have assumed that the oscillator and the environment are in thermal equilibrium and in this case an analytical result for the current is obtained.

In the reference model featuring the frequency independent oscillator quality factor \( Q \), we recover the usual Frank-Condon physics for large values of \( Q \). The transition between the two different charge states is then given by the usual overlap of two displaced oscillator wavefunctions, the governing parameter being the ratio of the displacement length \( \ell \) and the oscillator length \( \ell_0 \), or \( g = \ell^2 / 2 \ell_0^2 \). For moderate quality factors \( Q > Q_c = 2g/\pi \), the steps are smeared but still visible. For even smaller values of the quality factor, the decay time of the oscillations becomes shorter than the quantum mechanical uncertainty time, which happens when \( Q < 1/g \). In this strongly damped case the tunneling process crosses over to a regime with a gap given by the classical displacement energy.

We were also able to calculate \( S(\omega) \) for a molecule that is attached to a substrate and showed how the molecule loses energy to the substrate. The model features similar general results as the constant \( Q \)-factor model, however, it is different in that the steps in the \( I-V \) curves rise more smoothly but feature a rather sharp transition to the next step, which then again rises up smoothly. The underlying reason is the peak structure of \( F \), which exhibits asymmetric peaks due to the frequency dependent damping coefficient. We also note the dependence on the spread of the coupling over the substrate surface, parameterized by \( D/D_0 \), where our results tend towards the large constant \( Q \) limit for large \( D/D_0 \).

#### B. Comparison with experiments

We have also tried to fit the present theoretical results to the experiments in Ref. 2 for which the theory
molecules were attached to two leads, it therefore seems likely that the broadening is dominated by coupling to the environment.

A rough qualitative agreement, except for the steepness on the rising side of the steps, can be achieved for the frequency-independent quality factor if we assume $g \approx 1 - 2$ and $Q \approx 2 - 6$. However, in order to obtain quantitative agreement, it is necessary to assume different values for $g$ and $Q$ for different values of the gate and source-drain voltages. Our model for $S(\omega)$ that corresponds to a molecule attached to a substrate, see Sec. VI B, features qualitative agreement with experiment if we assume $g$ and $D/D_0$ to be on the order of unity. The asymmetry in the peak structure of $F$ actually provides for a better quantitative fit to the experimental data than is possible for the constant $Q$-factor model. This is illustrated in Fig. 9.

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