Charge-state dynamics in electrostatic force spectroscopy

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Received 25 January 2016, revised 22 April 2016
Accepted for publication 10 May 2016
Published 31 May 2016

Abstract
We present a numerical model that allows us to study the response of an oscillating probe in electrostatic force spectroscopy to charge switching in quantum dots at various time scales. The model provides more insight into the behavior of frequency shift and dissipated energy under different scanning conditions when measuring a temporarily charged quantum dot on a surface. Namely, we analyze the dependence of the frequency shift, the dissipated energy, and their fluctuations on the resonance frequency of the tip and on the electron tunneling rates across the tip–quantum dot and quantum dot–sample junctions. We discuss two complementary approaches to simulating the charge dynamics, a stochastic and a deterministic one. In addition, we derive analytic formulas valid for small amplitudes, describing relations between the frequency shift, dissipated energy, and the characteristic rates driving the charging and discharging processes.

Keywords: atomic force microscopy, electron tunneling, redox nanoswitches, electrostatic force spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

Further development of electronic devices and their performance strongly depends on our ability to characterize and control charge distribution down to the atomic scale. From this perspective, scanning tunneling microscopy (STM) [1] and atomic force microscopy (AFM) [2] are very important tools that allow imaging and manipulation of single atoms on surfaces. In particular, the recent development of dynamic atomic force microscopy (dAFM) [3–5] provides a powerful tool for probing the local structure [6–9] and chemical composition [10, 11] of surfaces with a resolution reaching the atomic scale on semiconductor [12], metallic [13] and insulating [14] surfaces. Kelvin probe force microscopy (KPFM), a technique derived from dAFM, can be used to probe local variations of work functions down to the nanometer scale [15]. It has been demonstrated that KPFM is also able to reach atomic [16–18] and sub-molecular [19] resolution. However, a straightforward interpretation in terms of local contact potential difference is not possible at the atomic scale [20–23].

The recent development of scanning probe techniques (see e.g. [13, 24, 25]) has made simultaneous acquisition of data in both AFM and STM channels possible. This has brought new possibilities, not only for the advanced characterization of surfaces [26, 27], but also for the study of the influence of the tunneling current on detected forces [28]. The latter relies on a proper decoupling of AFM and STM channels [29]. The bias dependence of resonance frequency shift measured in dAFM can be exploited beyond KPFM in so-called electrostatic force spectroscopy (EFS) [30], which consists in sweeping the voltage and measuring $\Delta f(V)$ at a particular position with the height and voltage regulating feedbacks off. KPFM or EFS complemented with an STM channel have the potential to become a convenient tool for studying the dynamics of charging and discharging local structures here referred as ‘quantum dots’ (QDs). These QDs are thought of as objects capable of storing electric charge and thus being able to switch between two or more distinguishable charge states (for instance charged and neutral). They may have the form of nanoclusters (such as InAs clusters on InP [31–33] and Au quantum dots [30]), molecules or even single atoms (such as Au atoms on NaCl [34, 35]).
Such QDs are of considerable interest because of their potential applications in nanoelectronics [36]. The above referenced examples have been successfully probed using EFS in two seminal papers [31, 35], which paved a route towards a new concept of controlling charge on the atomic scale. However, the characteristic time scales of this quantum-dot charge-state dynamics can span many orders of magnitude depending on the details of the studied system as well as on the immediate position of the AFM scanning probe. Consequently, the time scales of the charge dynamics relate in different ways to the characteristic time scales of the measuring instrument, such as the cantilever oscillation frequency $f_0$, bandwidth of the AFM feedback, sampling rate of the $\Delta f(V)$ measurement, etc. The manifestation of phenomena related to the switching will depend on the ratio of the various time constants involved. For instance, the different ionization states of Au atoms studied by Repp et al [34] tend to remain stable at moderate voltages during the whole experiment, while charging of the InAs clusters studied in Stomp et al [31] is compared to the time resolution of AFM, so the reaction of their state to bias changes appears to be immediate. The most interesting case, in which the charging and discharging rates were comparable to the dAFM frequency, was encountered, e.g., in experiments with the Au QDs [30] and in fact also with the InAs cluster, as shown in Cockins et al [32]. In such a case, the frequency shift signal depends on the charging rate and a signal in the energy dissipation channel can also be detected [30, 32]. A more complex setup of this type was reported by Zhu et al [37] where a gold nanoparticle served as an electroscope attached to a carbon nanotube and the oscillating tip was able to periodically change the charge of this Au particle using its electric field.

The aim of this paper is to develop a numerical model that allows us to simulate the EFS response to the charge switching in QDs at various time scales. While the gating effect of the biased AFM tip was crucial for the explanation of charging in the above quoted experiments on Au atoms or InAs nanostructures [30, 31, 34, 35, 38], our focus in this paper will be on cases where an electron tunneling from the tip has the decisive effect. We should note that the model could also be easily adapted to charge gating processes, but this is beyond the scope of the paper. We implement and compare two complementary approaches, stochastic and deterministic, to simulate the charge dynamics. Such insight into the response of an oscillating probe driven by charging processes helps to better understand the complex behavior observed in EFS experiments. In addition, we will establish relatively simple analytic formulas providing, in the limit of small amplitudes, relations between frequency shift $\Delta f$, dissipated energy $E_{\text{diss}}$, and characteristic tunneling rates ($\nu_1, \nu_2$) driving the charging processes.

2. Model

The outline of the model we propose (sketched in figure 1(a)) is as follows. Consider a QD (be it an atom, molecule, or a nanostructure) on a surface. Assume the dot can accept or release an electron, thus switching between two possible charge states. The AFM probe is sensitive to the charge state of the QD due to the electrostatic component of force between the charged dot and the probe apex. Several parameters determine the characteristic time scales of the model:

- Tunneling rate between the AFM tip and the QD on the surface $\nu_1$.
- Discharging rate of the charged dot by tunneling to a conductive substrate $\nu_2$.
- Resonant tip oscillation frequency $f_0$.
- Sampling rate $\nu_S$, while $t_m = 1/\nu_S$ is the time spent measuring one particular point of the $\Delta f(V)$ spectrum.

Furthermore, the tunneling probability between the tip and the dot depends on tip position (z) and on applied voltage bias (V).

2.1. Forces

We aimed to create a model as simple as possible, but that still captured the essential features of charge dynamics coupled to tip oscillations. The force between the AFM tip and the surface consists in the following components:

- Non-electrostatic bias-independent force $F_{\text{Ham}}$, derived from the Hamaker model to describe the long-range part of the van der Waals (or, more precisely, London dispersion) interaction between a spherical tip of radius $R_{\text{tip}}$ and a planar surface. The Hamaker model approximates the tip with a homogeneous sphere and the substrate material with a homogeneous half-space delimited by the surface plane [39].

\[
F_{\text{Ham}}(z) = -\frac{A_H R_{\text{tip}}}{6(z - z_{\text{surf}})^{\frac{3}{2}}}.
\]  

- The electrostatic part $F_{\text{cap}} + F_Q$. We describe the long-range part of the electrostatic force $F_{\text{cap}}$ as the force between two electrodes of a capacitor, one of which is planar and represents the surface and other one is spherical and represents the tip [40]. The same geometry, that is the same tip radius and distance from the surface, is assumed as in the Hamaker model used above. To calculate the local part of the electrostatic force $F_Q$, we treat the charge of the QD as a point charge corresponding to one electron. The point charge $q$ may be present or absent, depending on the immediate ‘charge state’. If absent, the local electrostatic contribution is assumed to be zero. If present, we assume an interaction of the point charge with (i) an electric field from the tip, and (ii) another static point charge $Q_{\text{apex}}$ positioned on the very end of the AFM tip. The electric field is assumed to depend linearly on the voltage bias and be inversely proportional to the tip distance from the QD (as if the field were homogeneous) while the apex charge is assumed to be characteristic for the tip and independent.
from the bias.

\[ F_{\text{cap}}(z, V) = -\frac{\pi \varepsilon_0 R_{\text{tip}}^2 (V - V_{C\text{PD}})^2}{(z - z_{\text{surf}})(R_{\text{tip}} + z - z_{\text{surf}})} \approx -\frac{\pi \varepsilon_0 R_{\text{tip}}^2 (V - V_{C\text{PD}})^2}{z - z_{\text{surf}}} \]  

(2)

and

\[ F_{Q}(z, V) = \frac{\varepsilon_0}{4\pi \varepsilon_0 (z - z_{\text{dot}})^2} + \frac{\varepsilon_0}{2} \frac{q(V - V_{C\text{PD}})}{z - z_{\text{surf}}} \]  

(3)

where \( \varepsilon_0 \) is the vacuum permittivity and \( e_0 \) is the elementary charge. The charges \( q \) and \( Q_{\text{apex}} \) are expressed here in the unit of the electron charge (negative elementary charge), so they are themselves dimensionless quantities.

The total force by which the surface with the QD pushes the tip is then \( F(z, V) = F_{\text{Ham}}(z) + F_{\text{cap}}(z, V) + F_{Q}(z, V) \). The mechanical dynamics of the tip is characterized by its (undamped) resonant oscillation frequency \( f_0 \), cantilever stiffness \( k \), and quality factor \( Q \). For the instantaneous vertical position \( z(t) \) of the tip, the equation of motion

\[ \frac{d^2z}{dt^2} + \frac{2\pi f_0}{Q} \frac{dz}{dt} + (2\pi f_0)^2 (z - z_{\text{eq}}) = F(z) \]  

(4)

holds, where \( z_{\text{eq}} \) is the equilibrium position of the tip determined by the piezoelectric positioning system of the AFM cantilever and \( F \) is the total force applied on the oscillating tip by its interaction with the surface below it. The quality factor \( Q \) and resonance frequency (in the absence of damping) \( f_0 \) characterize the cantilever.

2.2. Model for the electronic states of the tip apex and on the surface

The electronic state at the QD to which the electrons are tunneling when the charge state changes, is characterized by its mean energy \( \varepsilon_{\text{dot}} \) and a broadening \( w_{\text{dot}} \) around this mean energy. The broadening \( w_{\text{dot}} \) of the final state for tunneling is a consequence of an interaction with the substrate and, in particular, of the mechanism that stabilizes the charge on the QD. We chose to represent the shape of this energy level broadening by a Gaussian distribution for simplicity. The density of states \( \rho_{\text{dot}} \) is then

\[ \rho_{\text{dot}} = \frac{1}{\sqrt{\pi} w_{\text{dot}}} \exp\left(\frac{\varepsilon - \varepsilon_{\text{dot}}}{w_{\text{dot}}}^2\right). \]  

(5)

Two models of the electronic structure of the tip were implemented: (i) either the tip carries a single electronic state capable of participation in the tunneling (this model may represent a tip with a localized state, like a dangling bond, on its terminal apex); or (ii) the tip hosts a continuum of electronic states with a constant density of states near the Fermi level (a metallic tip). In this paper, we discuss only the localized-state tip model as the continuum model gives very similar results (see discussion later). For the tip model with the localized apex state, we describe the corresponding density of states on the tip \( \rho_{\text{tip}} \) by a Gaussian distribution, similarly to the QD state:

\[ \rho_{\text{tip}} = \frac{1}{\sqrt{\pi} w_{\text{tip}}} \exp\left(\frac{\varepsilon - \varepsilon_{\text{tip}}}{w_{\text{tip}}}^2\right). \]  

(6)

The Fermi–Dirac distribution of occupancy probabilities is invoked to account for a finite temperature of the tip \( T \). Temperature effects on the substrate are disregarded.
tunneling probability per unit time from the tip to the QD ($\nu_1$) is assumed to exponentially decay with tip distance from the surface. Further, this tunneling probability $\nu_1$ resonantly depends on the voltage bias through the Gaussian densities of states on the dot and tip in a way that corresponds to the assumption of exclusively elastic tunneling. Taking all these conditions into account, the tunneling probability from the tip to QD is expressed as:

$$\nu_1(z, V) = \nu_0 \exp(-\beta z) N_{\text{norm}} \times \int_0^\infty \delta \rho_{\text{dot}}(\epsilon) \delta \rho_{\text{tip}}(\epsilon - e_0 V) f_{\text{FD}}(\epsilon - e_0 V, T).$$

(7)

Figure 1(b) displays a schematic diagram of the tunneling process. The normalization factor $N_{\text{norm}}$ in equation (7) will be chosen in such a way that the tunneling rate at $V = (e_{\text{tip}} - e_{\text{dot}})/e_0$ and $z = 0$ becomes $\nu_1 = \nu_0$. The prefactor $\nu_0$ is a $z$- and $V$-independent parameter, which characterizes the overall feasibility of tunneling from the tip to the dot. In the model presented here we do not consider the possibility of tunneling in the opposite direction, i.e. from the dot to the tip. While this may seem to be an unrealistic assumption, as the probability of elastic tunneling should be the same in both directions, it may in fact be a reasonable approximation for cases similar to Au on NaCl. The negative Au$^-$ ion, once created, becomes stabilized by interaction with the substrate and does not change back to its original neutral state at the same tip bias [34]. Such stabilization would be an inherently inelastic process. An electron tunneling from the QD in the stabilized charged state back to the tip would therefore carry less energy than it carried when it was tunneling in the direction towards the QD. If the applied voltage brings tunneling towards the QD on resonance, tunneling back to the tip becomes off resonance. Possible non-zero probability of such back tunneling then only occurs due to the tails of the energy distribution around the resonance. We consider such a probability to be negligible. However, our model allows the charged dot to resume its neutral state by giving up an electron to the substrate. The probability of this event in a unit of time is a constant parameter ($\nu_2$) of the model. Our model is thus different from (and in a sense complementary to) that of Roy-Gobel et al [30]. The system considered in their paper [30] had negligible probability of tunneling from the quantum dot to the substrate while the back tunneling to the AFM probe is a crucial component of it. Realistic systems may conceivably combine both features, but we nevertheless consider it useful to explore the other limiting case to see what the suppression of back tunneling does to the EFS measurement.

2.3. Stochastic versus deterministic model

We compare two approaches to simulating the charge dynamics, to which we will refer as the stochastic and the deterministic approach. In both cases the probabilities of electron tunneling from the tip to the dot ($\nu_1 dt$) and from the dot to the substrate ($\nu_2 dt$) are evaluated in each time step for the current position of the tip. In the deterministic approach, the charge $q$ of the QD is allowed to assume a fractional value between 0 and 1. The fractional charge should be interpreted as a mean value of the actual stochastic charge or, equivalently, as the probability that the extra electron is present in the QD. The rates $\nu_1$ and $\nu_2$ are then to be interpreted as charge flows. Time evolution of the charge is controlled by the first-order differential equation

$$\frac{dq}{dt} = \nu_1(1 - q) - \nu_2 q.$$  

(8)

In the stochastic case, the tunneling rates are treated as genuine probabilities and a pseudo-random number generator is used to decide whether the charge state of the QD should be changed or not based on these probabilities and the pseudo-random value. Only charges 0 or 1 (meaning no or one extra electron) were allowed in the stochastic approach. When $0$, it changes to 1 in the next step with probability $\nu_1 dt$; when 1, it changes to 0 with probability of $\nu_2 dt$.

2.4. Numerical parameters of the model

All simulations of the tip dynamics were carried out using the following parameters: $\zeta_0 = 4.0 \ \text{Å}$, $f_0 = 46.858 \ \text{kHz}$, $k = 3681 \ \text{N m}^{-1}$, $Q = 2438$ and a small amplitude of $A = 0.1 \ \text{Å}$. The curves were sampled with the step of $\Delta V = 0.02 \ \text{V}$. The bias voltage $V$ was kept constant for 1000 oscillation periods of the cantilever to measure one point on a $\Delta f(V)$ curve, unless stated otherwise ($\nu_2 \approx f_0/1000$). The following values were chosen for the parameters that determine individual force components in our model: $R_{\text{tip}} = 400 \ \text{nm}$, $A_H = 0.029 \ \text{eV}$, $\zeta_{\text{surf}} = -4.8 \ \text{Å}$, $\zeta_{\text{dot}} = -3.2 \ \text{Å}$, $V_{\text{CPD}} = 0$, $Q_{\text{apex}} = -0.5$. The decay constant for tunneling probability was $\beta = 2.3 \ \text{Å}^{-1}$. This choice of parameters is mostly arbitrary but should be quite realistic, as it was motivated by several (unpublished) STM/AFM measurements carried out in our department’s lab by our experimentalist colleagues.

3. Results

Figure 2 presents the results of the deterministic model for various charging and discharging rates determined by parameters $\nu_1$ and $\nu_2$. The values of $\nu_0$ are indicated indirectly, in terms of $\nu_0^2 = \nu_0 \exp(-\beta z_0) \approx 10^{-4} \nu_0$. Such rescaling by the exponential factor facilitates a direct comparison between the different time scales.

Figure 2 displays a set of curves that represent the simulated frequency shift $\Delta f$ and the dissipated energy $E_{\text{diss}}$ as a function of voltage bias $V$. The occurrence of resonant tunneling though a localized QD electronic state $\epsilon_{\text{dot}}$ introduces a variation in the frequency shift $\Delta f$ at the corresponding voltage, as seen in figure 2(a). This effect is accompanied by the appearance of a pronounced signal in the dissipated energy channel $E_{\text{diss}}$. Here we should note that similar phenomena at bias voltages near the threshold for tunneling are also observed with the metallic-tip model, which is not discussed here further. The only difference between results obtained with a localized-state and a metallic tip is that in the latter case the system stays in the charged
state for higher voltages as a consequence of the continuum density of tip states. Similarly, if we replaced the Gaussian distributions for the densities of states with slower-decaying Lorentzian functions, the behavior at the resonance and towards the low-bias side of the spectra would remain qualitatively similar to the Gaussian case, but the high-bias side of the spectra obtained with Cauchy–Lorentz distribution might be more similar to the metallic case, depending on the discharging rate.

Both the variation in the frequency shift $\Delta f$ and the dissipated energy $E_{\text{diss}}$ are directly related to the charging process occurring during the resonant tunneling. In our model, the local electronic states in the QD and on the tip apex are chosen so that a resonance for tunneling occurs around the bias of $0.5 \text{ V}$. The relevant parameters were: the dot state energy $E_{\text{dot}} = 0.5 \text{ V}$ with respect to the substrate Fermi level, the apex state energy $E_{\text{tip}} = 0$ (right at the Fermi level of the tip), and Gaussian smearing for both states was given by the full width at half maximum of $0.03 \text{ eV}$ (corresponding to $\sigma_{\text{dot}} = \sigma_{\text{tip}} \approx 0.05 \text{ eV}$). As expected, the QD stays discharged (neutral) most of the time for out-of-resonance values of voltage bias. In the neutral state, the $\Delta f(V)$ dependence follows a parabolic curve as known from traditional Kelvin probe measurements, see figure 2(a) dashed line. Note that the dissipation signal in figure 2(e) is negligible out of resonance.

The situation changes when the tunneling junction is brought to resonance ($V$ around $0.5 \text{ V}$) and the tip is sufficiently close. Provided the prefactor $\nu_0$ of equation (7) is also sufficiently large, the tunneling rate between the tip and the QD becomes much larger than the discharging rate, $\nu_1 \gg \nu_2$. Consequently, the QD will be found in the charged state most of the time. In such a case, the parabolic curve just shifts downwards (or upwards) by a constant amount of $\Delta f$ with respect to the neutral case, depending on the sign of an extra Coulomb force $F_Q$. Here we consider the attractive interaction $F_Q$ so the frequency shift $\Delta f$ is more negative.

One can expect that the system oscillates between two (neutral and charged) states represented by idealized Kelvin parabolas, one for the charged (dotted line) state and the other for the neutral state (dashed line). However, the simulations reveal that the frequency shift does not have to always lie between the two parabolas, see figures 2(b) and (d). In other words, the changes in the frequency shift with respect to the neutral state sometimes tend to ‘overshoot’ the curve that would correspond to the $\Delta f(V)$ of a fully charged state. We observe this effect, in particular, when the charging and discharging probabilities $\nu_1$, $\nu_2$ are of comparable magnitude and the QD therefore often changes its charge state. Such a situation occurs in two different regimes. First, for high resonant tunneling rates $\nu_0$, at the ‘edges’ of the resonance, where the high resonant tunneling rate $\nu_0$ becomes partially

![Figure 2](image-url)
compensated by being slightly off-resonance. Thus it makes the actual tunneling rate \( n_1 \) from the tip comparable to the discharging rate \( n_2 \). Second, it happens for moderate resonant tunneling rates \( n_0 \) just at the center of the resonance. The regions of the overshoot partially overlap with regions of large dissipation, cf figures 2(b) and (d), and figures 2(f) and (h). Nevertheless the dissipation tends to increase for slower charging and discharging rates (closer to the tip oscillation frequency \( f_0 \)) while for fast charging and discharging rates, the dissipation is small even at voltages corresponding to the overshoot.

One may wonder if the deterministic approach, which disregards the discrete nature of the charge state of the quantum dot, correctly captures all pertinent features of the EFS measurement. We therefore compare it to the stochastic approach. The outcome of the stochastic simulation naturally depends on the bandwidth determined by the sampling rate \( \nu_S \). Figure 3 demonstrates that the stochastic simulation agrees perfectly with the deterministic one if the bandwidth given by the sampling rate is narrow enough to sufficiently filter the fluctuation. Even for the fastest sampling rate (widest bandwidth) shown, \( \nu_S = f_0/10 \), the frequency shift and dissipation calculated in the stochastic way tend to fluctuate around the values given by the deterministic simulation. However, the fluctuations are large in that case, so they almost mask the functional dependence. The agreement between results of the two distinct approaches demonstrates that the replacement of discrete charge states by a continuous value of a mean charge does not compromise the predictive power of the deterministic approach.

Figure 4 demonstrates how the results change if we completely disregard the stabilization effect and allow tunneling from the QD to the tip with the same probability as in the opposite direction. The peaks in \( \Delta f(V) \), which signify the ‘overshoot’ effect, become largely suppressed in such a setup. The reason for such sensitivity of the frequency-shift peaks to the asymmetry of tunneling will be clear from the theoretical analysis in the next section.

4. Theoretical analysis

First, we will analyze the effect of the (dis)charging process of the QD under the tip on the measured frequency shift \( \Delta f \).
In this paragraph, we provide an intuitive qualitative explanation of the relation between frequency shift $\Delta f(V)$ and the charging rates $\nu_1, \nu_2$. A detailed derivation of quantitative formulas for the frequency shift in a small-amplitude limit can be found in appendix A. If the system stood in the neutral state indefinitely, the frequency shift $\Delta f(V)$ would follow one Kelvin parabola as sweeping the voltage bias through a finite range; see dashed lines in figures 2(b) and (e). Similarly, in the charged state, the system follows a different parabola, see dotted lines in figures 2(b) and (e), which is rigidly shifted with respect to the neutral case. Now, for a suitable voltage, a resonance between the electronic state on the tip apex and the electronic state of the QD is established. This initiates the electron transfer from the oscillating tip into the dot.

If the rate of QD charging $\nu_1$ is comparable to the rate of discharging $\nu_2$, the average charge on the QD will be something between 0 and 1 electron. This mean value of the charge corresponds accordingly to a frequency shift $\Delta f$ somewhere in between the two above mentioned parabolas. However, the mean charge does not yet explain why the frequency shift sometimes falls outside the area between the two parabolas. In particular, it goes below the lower parabola that corresponds to the fully charged state, as seen in figures 2(b) and (e).

To understand this extra frequency shift, correlation between the dynamics of the charge and tip oscillations has to be taken into account. As the tunneling is more probable when the tip comes closer to the QD during its oscillation, the charge of the QD will be on average closer to 1 when the tip goes through its lower positions. Conversely, the charge will on average be closer to 0 when the tip is in its upper positions. This variation of charge during the tip oscillation creates an extra effective gradient of the electrostatic force between the tip and the sample, on top of the usual distance dependence arising, e.g., from the $1/r^2$ factor in the Coulomb law.

The first term on the right-hand side of equation (9) is a contribution to the frequency shift, which includes all charge-independent forces as well as the charge-dependent force component evaluated for the time-averaged value of the charge $\bar{q}$. The second term corresponds to the modification of the frequency shift by the charge dynamics. We can see that the relative frequency shift $\Delta f/\nu_0$ corresponding to this second term tends to be maximal when $\nu_1(\bar{q}, V) \approx \nu_2 \gg \nu_0$. In such instances, peaks on the $\Delta f(V)$ curve can be expected to appear.

If it were not for the charge stabilization effect on the QD, which causes asymmetry in the tunneling between the tip and the QD by suppressing the possibility for an electron to...
tunnel from the charged QD back into the tip, the overshoot effect would be hardly visible, as demonstrated in figure 4. Once the tunneling is possible in both directions, the z-dependence of the mean charge on the QD becomes much weaker because any effect due to the increased probability of tunneling into the QD is compensated by the equally increased probability of tunneling from the QD.

Similarly, correlation between the temporal charging and probe dynamics is also manifested by the appearance of an enhanced signal in the energy dissipation channel [31, 32]. \( E_{\text{diss}} \). This means that energy has to be supplied to the cantilever (or sometimes retrieved from it, if the dissipation is negative) in order to maintain constant amplitude \( A \) of the oscillation. From the results shown in figure 3 we can see that the dissipation signal appears at the \('edges\) of the resonance.

To get more insight into the origin of the dissipation signal \( E_{\text{diss}} \) during the (de)charging process, let us analyze the dynamics of the probe driven by time-dependent Coulomb force \( F_Q \). Figure 5 illustrates correlation between the dissipation signal \( E_{\text{diss}} \) and time-dependent Coulomb force \( F_Q \) during two tip oscillation periods. The cosine function in the bottom panel represents the immediate position \( \Delta z(t) = z(t) - z_{\text{eq}} \) of the tip with respect to its equilibrium position \( z_{\text{eq}} \). The second panel from the bottom shows what the time development of the Coulomb force \( F_Q(t) \) may look like. The force \( F_Q(t) \) directly relates to the charge \( q(t) \) of the QD. By definition, the Coulomb force equals zero \( (F_Q = 0) \) for \( q = 0 \) and it jumps to a non-zero value when the state of the QD switches from the neutral to the charged one. The charge-dependent component \( F_Q \) is a sizable contribution to the total force \( F \), shown in the second panel of figure 5 from the top. All other components of \( F \) besides \( F_Q \) are assumed to be conservative forces. The dissipated energy \( E_{\text{diss}} \) is tied to the mechanical work consumed by the tip; it can be calculated by integrating the total force over the path given by \( \Delta z(t) \). Alternatively, because all forces except \( F_Q \) are conservative, \( E_{\text{diss}} \) can also be calculated by integrating \( F_Q \Delta z \) alone, as indicated in the top panel of figure 5.

The presence of a positive mean dissipation signal \( E_{\text{diss}} \) is related to a phase delay of the Coulomb force \( F_Q \) with respect to the tip oscillations. The rate \( \nu_1 \) of electron tunneling from the tip to the QD is given by equation (7), which depends exponentially on the z-distance. Therefore, the charging process occurs more frequently when the tip is closer to the QD. The actual charging tends to happen only some time after the tunneling conditions become favorable for it, resulting in a QD charge that on average oscillates with some lag behind the tip oscillations. This lag in turn gives rise to a non-conservative force component, hence non-zero mean dissipated energy \( E_{\text{diss}} \) during the oscillation cycle. In particular, if the Coulomb force is attractive, as we consider in our example, there is positive dissipation. Figure 5 illustrates a typical series of charge switching events, which result in a net energy loss (positive dissipation) over two oscillation cycles, although there is negative dissipation during the first cycle due to the random nature of the process. A similar mechanism creating a dissipation signal was also reported, e.g., in [30, 32, 37], although there the dependence of the charge state on tip distance arises in a somewhat different way: the tip acts as a gate electrode rather than a source of electrons.

The dissipation signal diminishes if the force \( F_Q \) acts during the whole oscillation period, as is the case when \( \nu_1 \gg \nu_2 \), or if it is zero almost all the time, as is the case when \( \nu_1 \ll \nu_2 \), or finally if the phase shift between \( F_Q \) and \( z \) is negligible because \( \nu_1 \gg \nu_0 \). On the other hand, the signal is maximal when both tunneling rates and the oscillation frequency are comparable, \( \nu_1 \approx \nu_2 \approx \nu_0 \). Then the force \( F_Q \) switches frequently during one oscillation cycle. To justify the condition \( \nu_1 \approx \nu_2 \approx \nu_0 \) for the maximum dissipation signal more rigorously, we derived an analytic expression for the dissipated energy \( E_{\text{diss}} \) (for details see appendix B):

\[
E_{\text{diss}} = -\frac{\partial F}{\partial q} \left( \frac{2\pi^2 A^2 \beta_{\text{q}} \nu_1\nu_2}{\sigma f_0^2} \right)
\]

From the expression above, we see that the dissipated energy is proportional to the force derivative with respect to the charge. From a detailed analysis we can also see that the dissipated energy tends to be large when \( \nu_1 \approx \nu_2 \approx \nu_0 \), where \( \nu_1 = \nu_2 (\text{eq}, V) \).

Because of the stochastic nature of the charge dynamics, random fluctuations in the measured values of both the frequency shift and energy dissipation have to be expected, as exemplified by the results of the stochastic simulations plotted in figure 5. Although such fluctuations are usually regarded as imperfections of the measurement, which should be avoided if possible, e.g. by reducing the sampling rate and thus narrowing the bandwidth, they may also carry a useful information about the properties of the measured system, as we show below. Fluctuations are suppressed when \( \nu_1, \nu_2 \ll \nu_0 \), because charge changes are rare then. Similarly, when
\(\nu_1 \ll \nu_2\) or \(\nu_2 \ll \nu_1\), the QD spends most of its time in only one of the possible charge states and the fluctuations are suppressed too. Finally when \(\nu_1, \nu_2 \gg f_0\), the fluctuations mostly form high-frequency noise, which becomes filtered out due to the limited bandwidth of the measurement. With a given bandwidth, the largest fluctuations should therefore be expected when \(\nu_1 \approx \nu_2 \approx f_0\). We indeed observe this in figure 3 in the frequency shift as well as in the dissipation channel. The region in the parameter space in which large fluctuations appear coincides with the region of large dissipation. More specifically, the root mean square deviations that characterize the fluctuations can be shown, under certain approximations, to be proportional to the square root of the dissipated energy per oscillation cycle. For the frequency-shift fluctuations, \(\delta \left( \frac{\Delta f}{f} \right) = \frac{1}{\pi K} \frac{\nu_2}{f_0^2} \frac{\partial f}{\partial q} \frac{|E_{\text{diss}}|}{2\beta} \). (11)

Refer to appendix C, where equation (11) is derived as equation (C21) for the notation and more details.

From the discussion above, we can deduce that the characteristic shape and observed instabilities in a Kelvin parabola encode temporal information about the charge states. Thus it can be seen as a complementary tool to pump-probe STM experiments [41], but providing only qualitative information about characteristic tunneling rates \(\nu_1, \nu_2\), i.e. about the lifetime of the generated charge state). In principle, we have established a set of three equations (9)–(11) that could be employed to determine, e.g., the characteristic rates \(\nu_1, \nu_2\). Nevertheless, this is not immediately possible, because the equations contain more unknown variables such as \(\beta\) or derivatives of force. Some of these parameters could be perhaps estimated from independent measurements on a given QD system (e.g. \(\beta\) from the current measurement). However, more elaboration on the strategy is beyond the scope of this paper.

5. Conclusions

In conclusion, we have discussed in detail the temporal response of a dynamic AFM probe to charge-state switching in QDs at different time scales. We presented numerical simulations that captured the coupled dynamics of both the switching charge states and the oscillating probe. We tested two complementary approaches to the simulation: a stochastic (based on pseudo-random decisions at each step) and a deterministic one (based on numerical solution of differential equations for mean values). The analysis shows that the joint effect of tunneling between the tip and QD (\(\nu_1\)) and between the QD and the substrate (\(\nu_2\)) gives rise to a peak structure in bias-dependent frequency shift \(\Delta f (V)\) and to enhanced dissipated energy \(E_{\text{diss}}\) under certain conditions.

In addition, we derived approximate analytic formulas for the frequency shift and the dissipated energy in the limit of small amplitudes. These formulas allow us to relate the frequency shift \(\Delta f\), its fluctuation \(\delta (\frac{\Delta f}{f})\) and dissipation \(E_{\text{diss}}\) to the characteristic rate parameters that control the charging and discharging process, i.e. to the electron tunneling rates \(\nu_1\) (tip–QD) and \(\nu_2\) (QD–substrate). Firstly, we found that the observed frequency shift \(\Delta f\) can be much larger than the frequency shift corresponding to the permanently charged QD. This effect is maximized when the tunneling rates \(\nu_1\) and \(\nu_2\) are of comparable magnitude. Secondly, the dissipated energy \(E_{\text{diss}}\) and the frequency-shift fluctuations \(\delta (\frac{\Delta f}{f})\) are enhanced under the condition \(\nu_1 \approx \nu_2 \approx f_0\). Thirdly, the frequency-shift fluctuation magnitude \(\delta (\frac{\Delta f}{f})\) is proportional to the square root of the expectation value of the energy dissipation \(E_{\text{diss}}\). Finally, we discussed how the characteristic shape and observed instabilities in Kelvin parabolas encode information about temporal variations of QD charge states. We believe that these features can be, in principle, exploited in future research to obtain more quantitative information concerning the dynamical properties of chargeable QDs from Kelvin probe measurements.

Acknowledgments

We thank M Švec, J Berger, and J Repp for valuable discussions. This work was financially supported by a Czech Science Foundation grant no. 14-02079S.

Appendix A. Frequency shift

We are now going to demonstrate the origin of the ‘frequency shift overshoot’ and of the dissipation signal by deriving analytic formulas for both the frequency shift and energy dissipation under certain approximations. Our goal is not to find completely general analytic formulas that would be able to replace the numerical simulation. Instead, we want to understand qualitatively the influence of the three time scales \(f_0\), \(\nu_1\) and \(\nu_2\) on the measurement. We will assume a case in which the deterministic model is a ‘good enough’ description. Therefore we disregard the stochastic nature of the charging process. We will consider only the small amplitude limit of the cantilever oscillations, so that we can restrict the changes of the short-range force and tunneling probabilities to the first order in Taylor expansion. This means that we only consider constant terms and terms linear in the position \(z\). With this approximation, the tip oscillation is well described by a sinusoidal function

\[\Delta z (t) \approx A \cos (2\pi ft) = A \Re \{ \exp (2\pi i ft) \} \] (A1)

as a function of time \(t\) (where \(\Delta z = z - z_{eq}\)). We have arbitrarily chosen \(t = 0\) in such a way that \(\Delta z (t)\) is the cosine function with a zero phase shift. In what follows, the phase of other periodically oscillating quantities will be given relatively with respect to the phase of \(\Delta z (t)\). We will look for a harmonic solution to also describe the temporary
changes of the charge \(q(t)\):
\[
q(t) = \dot{q} + A_q \cos(2\pi ft + \phi_q) = \ddot{q} + \Re[\dot{q} \exp(2\pi ift)].
\] (A2)

In the second form of the above expression, we have introduced the complex amplitude \(\hat{q} = A_q \exp(2\pi i\phi_q)\). The complex formalism will be more convenient for the next steps of the derivation than working with sine and cosine functions. The \(z\)-dependence of the tunneling rate, equation (7), can be rewritten as
\[
\nu_1(z) = \nu_1 \exp(-\beta \Delta z),
\] (A3)
where \(\nu_1 = \nu_1(z_{eq})\). In the small amplitude approximation, the \(z\)-dependence of \(\nu_1\) can be linearized as
\[
\nu_1 = \nu_1(1 - \beta \Delta z).
\] (A4)
With \(\Delta z\) given by equations (A1) and (A4) can be rewritten as
\[
\nu_1 = \nu_1(1 - \beta A \Re[\exp(2\pi ift)])
\] (A5)
and if we then substitute equations (A2) and (A5) into (8) while neglecting a term proportional to \(A \times A_q\) (justified in the small amplitude limit), we get
\[
\Re[2\pi if\hat{q} \exp(2\pi ift)] = \nu_1(1 - \beta A \Re[\exp(2\pi ift)])
\]
\[
\times \left( 1 - q \right) - \nu_1 \Re[\dot{q} \exp(2\pi ift)]
\]
\[
- \nu_2 (q + \Re[\dot{q} \exp(2\pi ift)]).
\] (A6)

After rearrangement, equation (A6) becomes
\[
\Re[(2\pi if + \nu_1 + \nu_2)\hat{q} \exp(2\pi ift)]
\]
\[
= -\beta A \nu_1 (1 - q) \Re[\exp(2\pi ift)] + \nu_1 - (\nu_1 + \nu_2)q
\] (A7)
The last equation will be satisfied for arbitrary \(t\) if
\[
\dot{q} = \frac{\nu_1}{\nu_1 + \nu_2}
\] (A8)
and
\[
\dot{\hat{q}} = -\beta A \frac{\nu_1 \nu_2}{(\nu_1 + \nu_2)(\nu_1 + \nu_2 + 2\pi if)}.
\] (A9)
The time dependence of the charge \(q(t)\) in the small amplitude approximation can be thus obtained by substituting the expressions (A8) and (A9) into equation (A2).

The frequency shift measured in AFM is given by [42]
\[
\Delta f = -\frac{f_0}{kA} \left( F \Delta z \right),
\] (A10)
assuming \(\Delta f \ll f_0\) and thus \(f \approx f_0\). The angled brackets denote simultaneous temporal and ensemble averaging. Showing only the time averaging explicitly, we can write
\[
\Delta f = -\frac{f_0^2}{kA^2} \int_0^{T_e} F(t) \cos(2\pi ft) dt,
\] (A11)
where \(T_e = 1/f_0\) is the period of the cantilever oscillation. The interaction force \(F(t)\) felt by the oscillating tip depends on the tip position \(z(t)\) and on the quantum-dot charge \(q(t)\). For small amplitudes, we can linearize \(F(z, q)\) and write (retaining the \(f \approx f_0\) approximation from now on)
\[
F(t) = \frac{\partial F(z = z_{eq}, q)}{\partial z} \Delta z(t)
\]
\[
+ \frac{\partial F(z_{eq}, q = \hat{q})}{\partial q} \Re[\dot{\hat{q}} \exp(2\pi if_0 t)].
\] (A12)
The partial derivatives should be derived from a particular model of the interaction force, for instance from equations (1)–(3) in our case. Let us rewrite the time dependence of \(F(t)\) in terms of trigonometric functions.
\[
F(t) = \frac{\partial F}{\partial z} A \cos(2\pi f_0 t) + \frac{\partial F}{\partial q} \Re(\dot{\hat{q}}) \cos(2\pi f_0 t)
\]
\[
- \Im(\dot{\hat{q}}) \sin(2\pi f_0 t).
\] (A13)
Here, we have abbreviated the notation for partial derivatives by omitting the arguments in parentheses. We can finally insert equation (A13) into (A11) to obtain
\[
\Delta f = -\frac{f_0}{2k} \left( \frac{\partial F}{\partial z} + \frac{\partial F}{\partial q} \Re(\dot{\hat{q}}) \right),
\] (A14)
Using equation (A9),
\[
\Delta f = \frac{f_0}{2k} \left( \frac{\partial F}{\partial z} + \frac{\partial F}{\partial q} \left( \frac{\beta \nu_1 \nu_2}{(\nu_1 + \nu_2)^2 + (2\pi f_0)^2} \right) \right)
\] (A15)
The first term in the round brackets on the right-hand side of the above equation corresponds to a frequency shift that would be observed for a stationary charge \(q = \hat{q}\). The second term is the part of the frequency shift contributed by the charge dynamics on the QD. This second term may lead to the frequency shift ‘overshoot’ observed in the results of our simulations when it becomes large at \(\nu_1 \approx \nu_2 \gg f_0\).

Appendix B. Dissipation

Energy dissipation per cycle can be expressed as
\[
E_{\text{diss}} = -W = -\int_0^{T_e} F(t) \frac{dz}{dt} dt = 2\pi A f_0 \int_0^{T_e} F(t) \sin(2\pi f_0 t) dt.
\] (B1)
The dissipation, apart from a constant contribution from the finite quality factor, originates only from the electrostatic force related to the switching charge, because all other forces are conservative. Consequently, in the small amplitude approximation
\[
E_{\text{diss}} = 2\pi A f_0 \frac{\partial F}{\partial q} \int_0^{T_e} \Re[\dot{\hat{q}} \exp(2\pi if_0 t)] \sin(2\pi f_0 t) dt
\]
\[
= -\pi A \frac{\partial F}{\partial q} \Im(\dot{\hat{q}}).
\] (B2)
So finally, the dissipation will be

\[ E_{\text{diss}} = -\frac{\partial F}{\partial q}(\bar{\nu}_1 + \nu_2)((\bar{\nu}_1 + \nu_2)^2 + (2\pi \nu_0^2)^2) \]  

(B3)

The above expression for dissipated energy assumes its maximal absolute value when

\[ \nu_1 = \nu_2 = \pi \nu_0. \]  

(B4)

To prove this statement, consider that according to equation (B3), the dissipated energy is proportional to

\[ E_{\text{diss}} \propto \frac{f_0 \nu_0 \nu_2}{(\bar{\nu}_1 + \nu_2)((\bar{\nu}_1 + \nu_2)^2 + (2\pi \nu_0^2)^2)} \]

= \frac{2f_0 \nu_0 \nu_1 \nu_2}{(\bar{\nu}_1 + \nu_2)((\bar{\nu}_1 + \nu_2)^2 + (2\pi \nu_0^2)^2)} = \frac{1}{4(\bar{\nu}_1 + \nu_2)((\bar{\nu}_1 + \nu_2)^2 + (2\pi \nu_0^2)^2)}. \]  

(B5)

The term \((\bar{\nu}_1 - \nu_2)^2\) in the numerator of the right-most side of equation (B5) always reduces the absolute value of the whole expression for \(E_{\text{diss}}\). This term can never be negative, it must be at least zero, in which case the whole expression will be maximized. To make it zero, one should require

\[ \bar{\nu}_1 = \nu_2 \equiv \nu. \]  

(B6)

Now, equation (B5) simplifies to

\[ E_{\text{diss}} \propto \frac{f_0 \nu_0^2}{8\nu(\nu^2 + (2\pi \nu_0^2)^2)} = \frac{1}{\nu - \nu_0^2 + 2\nu_0 \nu} \]

\[ = \frac{1}{8\nu - \nu_0^2 + 16\pi}. \]  

(B7)

The last expression is obviously a maximum if the first term in the denominator becomes zero, which happens when \(\nu = \nu_0\). This completes the proof of equation (B4).

**Appendix C. Fluctuations**

Let us now turn our attention to the random fluctuations seen in the measurable quantities \(\Delta f\) and \(E_{\text{diss}}\). These fluctuations become apparent in results obtained within the stochastic model, see figure 3. We will now try to estimate the dependence of these fluctuations on \(f_0 = 1/T_0, \nu_1, \) and \(\nu_2\) quantitatively. In addition to these parameters, the fluctuations obviously depend on the sampling rate \(\nu_S\) or, equivalently, on the number of periods \(N = f_0 / \nu_S\) completed by the oscillating tip while measuring a single point of the \(\Delta f(V)\) and \(E_{\text{diss}}(V)\) curves. We will characterize the fluctuations quantitatively by root mean square deviations:

\[ \delta(\Delta f) = \sqrt{\langle (\Delta f - \langle \Delta f \rangle)^2 \rangle}, \]

(C1)

\[ \delta E_{\text{diss}} = \sqrt{\langle (E_{\text{diss}} - \langle E_{\text{diss}} \rangle)^2 \rangle}, \]

(C2)

where

\[ \Delta f = \frac{f_0^2}{N A K} \int_0^{N_T} F(t) z(t) dt \]

= \frac{f_0^2}{N A K} \int_0^{N_T} F(t) \cos(2\pi f_0 t) dt, \]

(C3)

\[ E_{\text{diss}} = \frac{1}{N} \int_0^{N_T} F(t) \frac{dz}{dt} dt \]

= \frac{2\pi f_0 A \nu_0}{N} \int_0^{N_T} F(t) \sin(2\pi f_0 t) dt, \]

(C4)

cf equations (A11) and (B1). As before, the angled brackets denote ensemble averaging.

We will start with general considerations about \(\delta(\Delta f)\) and \(\delta E_{\text{diss}}\), valid for arbitrary amplitudes, and we will then switch to the small amplitude approximation to derive analytic formulas for \(\delta(\Delta f)\) and \(\delta E_{\text{diss}}\). The non-random conservative components of the total force \(F\) do not contribute to either \(\delta(\Delta f)\) or \(\delta E_{\text{diss}}\). Furthermore, we now work within the stochastic model. Thus we assume that the charge can only be either \(q = 0\) or \(q = 1\). Therefore the charge dependence of the force can be simplified as

\[ F_Q(z, q) = F_Q(z)q, \]

(C5)

where \(F_Q(z)\) is the charge-dependent component for \(q = 1\). As we will shortly see, the restriction of \(q\) to only two possible values will be a great help in the evaluation of the fluctuations. Furthermore, we neglect the \(z\)-dependence of \(F_Q(z)\) over the range of the oscillating tip\(^1\). This allows us to rewrite equations (C3) and (C4) in terms of \(q(t)\) as

\[ \Delta f = \frac{f_0^2}{N A K} \int_0^{N_T} q(t) \cos(2\pi f_0 t) dt, \]

(C6)

\[ E_{\text{diss}} = \frac{2\pi f_0 A \nu_0}{N} \int_0^{N_T} q(t) \sin(2\pi f_0 t) dt. \]

(C7)

We now substitute equation (C6) into (C1), and equation (C7) into (C2) to get

\[ \delta(\Delta f) = \frac{f_0^2}{N A K} \times \sqrt{\int_0^{N_T} dt \int_0^{N_T} dt' C_q(t, t') \cos(2\pi f_0 t) \cos(2\pi f_0 t')} \]

(C8)

and

\[ \delta E_{\text{diss}} = \frac{2\pi f_0 A \nu_0}{N} \times \sqrt{\int_0^{N_T} dt \int_0^{N_T} dt' C_q(t, t') \sin(2\pi f_0 t) \sin(2\pi f_0 t')}, \]

(C9)

where

\[ C_q(t, t') = \langle q(t) - \langle q(t) \rangle \rangle \langle q(t') - \langle q(t') \rangle \rangle \]

\[ = \langle q(t)q(t') \rangle - \langle q(t) \rangle \langle q(t') \rangle \]

(C10)

is the correlation function of the charge deviation from the mean charge value. Because the charge may only switch between 0 and 1, we can interpret \(\langle q(t) \rangle\) as the probability

\(^1\) This simplification need not be valid for large amplitudes. We could postpone introducing it until we fully embrace the small amplitude approximation. Working with \(z\)-dependent \(F_Q\) would prevent us from extracting \(F_Q\) in front of the integrals in the subsequent steps. Instead, we would have to keep \(F_Q(z) = F_Q(e_{\text{magn}} + A \cos(2\pi f_0 t))\) inside the integrals. Otherwise, the derivation would not change. At the point when we eventually start using the small-amplitude approximation in a consistent way, we would set \(F_Q(z) = F_Q\) anyway.
that \( q(t) = 1 \). Moreover, \( \langle q(t)q(t') \rangle \) equals the probability that \( q = 1 \) at both times \( t \) and \( t' \). For \( t' \geq t \), it can be expressed as

\[
\langle q(t)q(t') \rangle = \langle q(t) \rangle \langle q(t') \mid q(t) = 1 \rangle,
\]

where \( \langle q(t') \rangle \) is the conditional probability that \( q(t') = 1 \), assuming \( q(t) = 1 \). This conditional probability can be found by solving a differential equation of the type of equation (8) for \( q(t') \) in time \( t' \geq t \), with the initial condition at \( t \) defined as \( q(t) = 1 \). Let us denote such conditional probability or conditional mean charge value at \( t' \) by \( q(t') \). In order to distinguish it from both the unconditioned mean value \( \langle q(t') \rangle \) and from a particular (non-averaged) instance of the random variable \( q(t') \). Briefly, we denote \( q(t') \equiv \langle q(t') \mid q(t) = 1 \rangle \). With such a careful notation, equation (8) can be rewritten as

\[
\frac{dq(t')}{dt'} = \nu_1(t') - (\nu_1(t') + \nu_2(t'))q(t') \mid q(t) = 1; t' \geq t,
\]

stating now every possible time dependence explicitly. With the solution \( q(t') \) of the above equation available, we can easily evaluate the correlation function \( C_q \) by combining equations (C10) and (C11) if we also know \( \langle q(t) \rangle \):

\[
C_q(t, t') = \langle q(t) \rangle \langle q(t') - \langle q(t') \rangle \rangle \quad \text{for } t' \geq t.
\]

Actually, we can use the solution of the differential equation for \( q(t') \) to also find \( \langle q(t) \rangle \). The charge dynamics is driven by the periodic oscillations of the cantilever, so we can expect that after long enough time, the mean value of \( q(t') \) will converge to a stationary periodic solution:

\[
\lim_{N \to \infty} q(Nt_0 + t') = \langle q(t') \rangle.
\]

Considering the above explained prescription to derive the correlation function, it would be convenient if we needed to evaluate \( C_q(t, t') \) only for \( t' \geq t \). This can be indeed achieved thanks to the fact that the integrands in equations (C8) and (C9) are symmetric with respect to the exchange \( t \leftrightarrow t' \).

\[
\delta(\Delta f) = \frac{f_0^2 F_q}{N K} \int_0^{Nt_0} dt \int_t^{Nt_0} dt' C_q(t, t') \cos(2\pi f_0 t) \cos(2\pi f_0 t')
\]

and

\[
\delta E_{\text{diss}} = \frac{2\pi f_0 F_0 \Delta A}{N} \int_0^{Nt_0} dt \int_t^{Nt_0} dt' C_q(t, t') \sin(2\pi f_0 t) \sin(2\pi f_0 t').
\]

What remains to be done so as to find the fluctuations defined by equations (C1) and (C2) is to solve equation (C12) for \( q(t') \), thus finding the correlation function \( C_q(t, t') \), substituting \( C_q(t, t') \) into equations (C15) and (C16) and evaluate the integrals. In order to solve equation (C12), however, we have to specialize to a particular model for \( \nu_1(t) \) and \( \nu_2(t) \). At this point, the following observation may be worth emphasizing: although the existence of fluctuations in measurable quantities such as \( \Delta f \) or \( E_{\text{diss}} \) is a consequence of the stochastic nature of the charging and discharging process, a crucial step needed to quantify these fluctuations consists in solving the differential equation equation (C12), which can be done numerically within what we call the deterministic approach. But we would also like to find an analytical expression for the fluctuations, and in order to do so we will go back to the small amplitude approximation. We again assume a time-independent discharging rate \( \nu_2 \). Moreover, we are going to content ourselves with the lowest-order term from the expansion of \( \delta(\Delta f) \) and \( \delta E_{\text{diss}} \) in powers of the amplitude. For that, we will need only the amplitude-independent part of \( C_q(t, t') \), which can be obtained by assuming that the charging rate \( \nu_1 \), formerly given by equation (A5), also becomes time-independent, \( \nu_1 = \tilde{\nu}_1 \). We now have the solution of equation (C12) (with time-independent rate constants)

\[
q(t') = (1 - \tilde{q}) e^{-(\tilde{\nu}_1 + \nu_2)(t' - t)} + \tilde{q}.
\]

For \( C_q(t, t') \), it follows that

\[
C_q(t, t') = (1 - \tilde{q}) e^{-(\tilde{\nu}_1 + \nu_2)(t' - t)}
\]

\[
= \frac{\nu_1 \nu_2}{(\tilde{\nu}_1 + \nu_2)^2} \exp[-(\tilde{\nu}_1 + \nu_2)(t' - t)].
\]

When evaluating the double integrals in equations (C15) and (C16), we will consider only terms proportional to the measuring time \( Nt_0 = 1/\nu_2 \). Because the square root is taken of the double integrals and there is a prefactor that involves \( 1/N \) in front of the square root, such terms will eventually decrease as \( 1/\sqrt{N} \) with increasing \( N \). All other possible terms would decrease faster and they can be thus neglected unless \( N \) is too small. We should also note that the terms which decrease with \( N \) faster than \( 1/\sqrt{N} \) are sensitive to the exact initial and final conditions of the measurement, in particular on the phase of \( \Delta \zeta(t) \) at \( t = 0 \) (the beginning of the measurement) and at \( t = Nt_0 \) (the end of the measurement). While we have chosen \( \Delta \zeta(t) = A \cos(2\pi f_0 t) \), so \( \Delta \zeta(0) = +A \), and we have furthermore assumed \( N \) to be a natural number, so \( \Delta \zeta(Nt_0) = +A \) too, this particular choice is obviously arbitrary and it cannot be usually controlled in a realistic experimental setup anyway. Neglecting terms that are sensitive to this choice is therefore justified. With this last approximation, final expressions for the fluctuations can be given.

\[
\delta(\Delta f) \approx \frac{f_0^2 F_q}{N K} \frac{\nu_1 \nu_2 N t_0}{(\tilde{\nu}_1 + \nu_2)^2 + (2\pi f_0)^2}
\]

\[
= \frac{f_0^2 F_q}{K A} \left( \frac{\nu_1 \nu_2}{(\tilde{\nu}_1 + \nu_2)^2 + (2\pi f_0)^2} \right)
\]

and

\[
\delta E_{\text{diss}} \approx \frac{2\pi f_0 F_0 \Delta A}{N} \left( \frac{2\pi f_0 \tilde{\nu}_1 \nu_2 N t_0}{(\tilde{\nu}_1 + \nu_2)^2 + (2\pi f_0)^2} \right)
\]

\[
= \sqrt{2\pi} f_0 A \left( \frac{\nu_1 \nu_2}{(\tilde{\nu}_1 + \nu_2)^2 + (2\pi f_0)^2} \right).
\]
Note that the magnitude of relative fluctuations of the frequency shift scales with the rate and frequency constants $\nu_1$, $\nu_2$, and $f_0$ as the square root of the dissipation, as follows from the combination of equations (C19) and (B3) (noting that $\partial F / \partial q = F_0$):

$$\delta \left( \frac{\Delta f}{f} \right) = \frac{1}{\pi A^2} \sqrt{\frac{\partial F / \partial q}{f_0}} \left| E_{\text{diss}} \right|. \quad (C21)$$

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