

Electric force microscopy of samples having an appreciable impedance

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Scanned probe microscopy (SPM) techniques that measure electrostatic forces have revealed the fate of charges in a broad array of semiconductor electronic and photovoltaic devices. The equation commonly used to interpret frequency-modulated scanning Kelvin probe force microscopy (KPFM) measurements of electric forces is

$$\Delta f = -\frac{f_0}{4k_0} C'' (V_{ts} - \Phi)^2, \quad (1)$$

where Δf is the time-dependent cantilever frequency shift, f_0 is the cantilever resonance frequency, k_0 is the cantilever spring constant, C'' is the second derivative of the tip-sample capacitance with respect to the vertical direction, V_{ts} is the applied tip-sample voltage, and Φ is the sample surface potential. Recent experiments have called the validity of this equation into question.

Figure 1 shows one striking example [1]. The sample was a thin film of the perovskite semiconductor CsPbBr₃ prepared on a conductive indium tin oxide substrate, illuminated from above with visible light (Fig. 1(a)). The cantilever frequency shift and amplitude were measured at different applied tip-sample voltages to determine the curvature of the frequency- and dissipation-versus-voltage parabolas (Fig. 1(b)). Figure 1(c) and (d) show how these parabola curvatures depend on the light intensity.

According to Eq. 1, the curvature of the frequency-shift-versus-voltage parabola is proportional to the tip-sample capacitance derivative C'' . The capacitance and its derivatives should be proportional to the free carrier density. In a semiconductor, this free carrier density has a power-law-dependence on the light intensity. The capacitance data, in contrast, increases rapidly but then flattens out as the light intensity is increased. Likewise, the dissipation should increase linearly with the carrier density. The experimental data contradicts this prediction even more dramatically, showing a sharp peak in dissipation at moderate light intensity, and decreasing dissipation at high light intensities, even as the free carrier density surely continues to increase.

The source of these apparent contradictions is not the sample or the microscope, but Eq. 1. Why can't Eq. 1 be used to sensibly interpret the Fig. 1 data? The problem lies in two hidden, seldom-stated assumptions needed to derive Eq. 1. The two assumptions are

1. the tip charge oscillates exactly in phase with the cantilever motion to keep the tip voltage constant, and
2. any changes in the tip-sample interaction happen slowly.

In the Fig. 1 experiment, the problem is that the increased dissipation implies a tip charge oscillating out of phase with the cantilever motion — a clear violation of assumption 1.

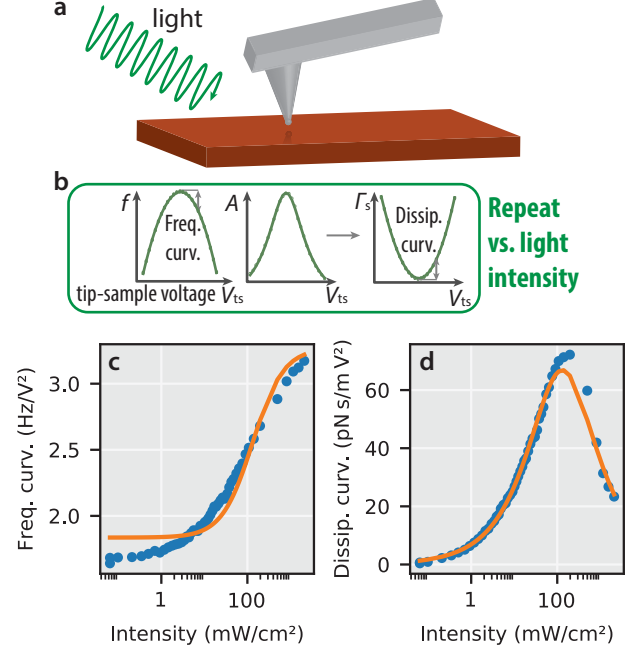


FIG. 1. Apparent violation of Eq. 1 in an illuminated thin-film semiconductor, CsPbBr₃. Modified from Tirmzi et al., 2017, *ACS Energy Lett.*; copyright American Chemical Society [1].

To move forward, we needed a model that describes the cantilever frequency shift and dissipation even when these assumptions are violated. We use Lagrangian mechanics to describe the coupled motion of cantilever tip displacement, tip charge, and sample charge. Based on its usefulness in electrochemical impedance spectroscopy, we describe the sample using a complex impedance. Using this new model, we derived two equations that *replace* Eq. 1. The frequency shift is

$$\Delta f = -\frac{f_0}{4k_0} \left(C_q'' + \Delta C'' \operatorname{Re}(\hat{H}(\omega_0)) \right) V^2 \quad (2)$$

and the sample-induced dissipation is

$$\Gamma_s = -\frac{1}{4\pi f_0} \Delta C'' \operatorname{Im}(\hat{H}(\omega_0)) V^2, \quad (3)$$

with $\Delta C'' = 2(C')^2/C$ and $C_q'' = C'' - \Delta C''$ two distinct capacitance derivatives, and

$$\hat{H}(\omega) = \frac{1}{1 + j\omega C Z(\omega)} \quad (4)$$

the transfer function between the applied tip-sample voltage and the tip voltage drop, which depends on the tip capacitance C and the complex sample impedance $Z(\omega)$. These two

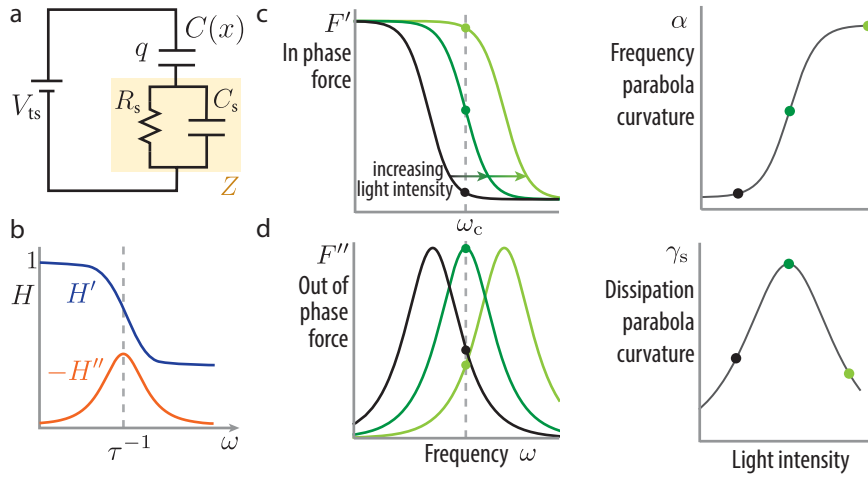


FIG. 2. A Lagrangian-impedance treatment of the tip-sample interaction and a parallel- RC model of the sample explains the seemingly anomalous results of Fig. 1. Modified from Tirmzi et al., 2017, *ACS Energy Lett.*; copyright American Chemical Society [1].

equations should replace Eq. 1 whenever the tip charge does not oscillate exactly in phase with the cantilever motion.

To explain the data of Fig. 1, we model the sample as a capacitor C_s and light-dependent resistor R_s operating in parallel (Fig. 2(a)). The central new quantity is $\hat{H}(\omega_c)$, the transfer function evaluated at the cantilever resonance frequency. Figure 2b shows that the transfer function has a roll-off frequency determined by the time constant $\tau = R_s(C + C_s) \approx R_s C_s$. The real part of the transfer function H' causes a force F' oscillating in phase with the cantilever motion which results in a cantilever frequency shift Δf . The imaginary part of the transfer function H'' causes a force F'' oscillating out of phase with the cantilever motion which results in sample-induced dissipation — this is the component of the tip-sample interaction completely neglected in Eq. 1. We can explain the dramatic peak in dissipation by assuming R_s is large in the dark and small under illumination. The peak in dissipation occurs at an illumination intensity where τ^{-1} equals the cantilever frequency ω_0 . The lines in Fig. 1(c,d) are a fit of the data to Eqs. 2 and 3. The joint fit nicely captures the nonlinear behavior of both the frequency and the dissipation versus illumination intensity.

Figure 3 shows the power of this new model of the tip-sample interaction to connect and integrate the results of a wide variety of scanned probe experiments. Figure 3(a–c) shows a broadband local dielectric spectroscopy measurement [2] carried out on the CsPbBr_3 film of Fig. 1. The measured quantity is the difference in cantilever frequency shift caused by modulating the tip-voltage at a frequency f_m . According to our Lagrangian-impedance model, this experiment mainly measures the real part of the transfer function at the modulation frequency $H'(f_m)$ at the modulation frequency f_m . The change in the spectrum's knee with increasing light intensity is in qualitative agreement with the light-dependent R_s used to explain the Fig. 1 data, validating the use of a relatively simple RC sample impedance model to explain a wide range of experiments carried out on the photovoltaic CsPbBr_3

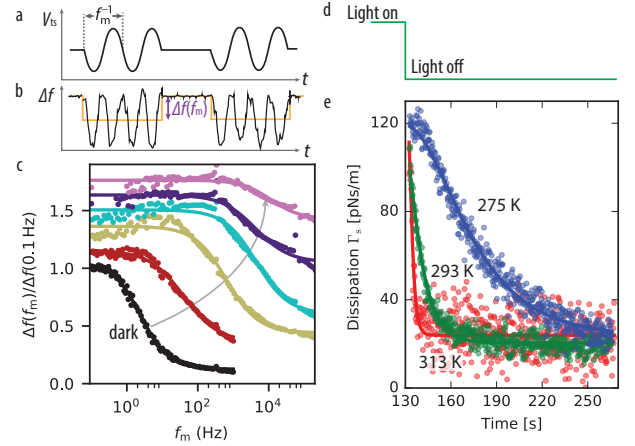


FIG. 3. The Lagrangian-impedance model provides a framework for interpreting (a–c) broadband local dielectric spectroscopy, and (d–e) cantilever ringdown dissipation measurements. Modified from Tirmzi et al., 2017, *ACS Energy Lett.*; copyright American Chemical Society [1].

sample.

To gain a better understanding of the microscopic origin of this light-dependent resistance R_s in CsPbBr_3 , we examined the kinetics of the resistance recovery in the dark at different temperatures. Figure 3(e) shows measurements of the sample-induced dissipation inferred from repeated cantilever ringdown measurements acquired just after turning off the light. The increased dissipation, caused by a reduction in the sample resistance R_s , decreases slowly with a time constant ranging from 2 seconds at 313 K to over 30 seconds at 275 K. An Arrhenius plot shows that the process by which the resistance goes back to its dark value is highly activated, with an activation energy $E_a = 0.52 \pm 0.03$ eV. This slow, highly activated process rules out many simple explanations of the sample-induced resistance [3, 4] and supports the suggestion

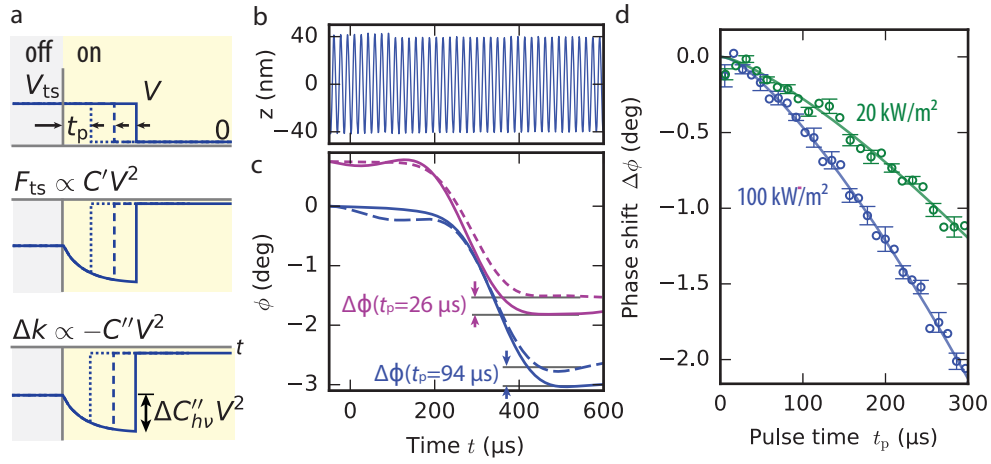


FIG. 4. Phasekick electric force microscopy accurately measures light-induced changes in the tip-sample interaction even when the light or voltage induces abrupt changes in the tip-sample interaction, in violation of assumption 2. Modified from Dwyer et al., 2017, *Sci. Adv.*; copyright CC-BY ND 4.0 [9].

that light *creates* mobile ionic vacancies in CsPbBr₃ [5]. The Lagrangian-impedance model links each experiment shown in Figs. 1 and 3 back to the sample impedance $Z(\omega)$, allowing the experiments to be interpreted in a common framework.

The data and models in Figs. 1–3 show how the Lagrangian-impedance model helps interpret results where the assumption that the tip charges oscillates exactly in phase with the cantilever is violated (assumption 1). What about the other assumption, that any changes in the tip-sample interaction occur slowly? This assumption can be violated in experiments that follow the time evolution of photocapacitance in response to illumination [6–8]. These experiments have pushed the limits of time resolution in electric force microscopy, with claimed time resolutions down to less than 1 percent of the cantilever period [8]. Our analysis shows that the standard equation for frequency shift in KPFM cannot be used to analyze these single-shot, transient EFM experiments because the abrupt changes in the tip-sample force shift the cantilever’s amplitude and phase. The Lagrangian formalism, however, can be used to interpret these results and design experiments that can accurately measure abrupt changes in the tip-sample interaction.

The phasekick electric force microscopy experiment sketched in Fig. 4 shows how. The light is turned on at time $t = 0$, inducing a possibly abrupt change in the capacitance. The voltage is turned to zero abruptly at a time t_p after the light is turned on (Fig. 4(a)). We infer the light-induced phase shift as a function of the stepped delay time t_p (Fig. 4(b)). Representative data at two pulse times is shown in Fig. 4(c). A photocapacitance-induced phase shift is computed by comparing relative phase-shift data in the dark (dashed line) and under illumination (solid line). Figure 4(d) shows representative phase-shift versus pulse-time data acquired for 768 pulse times at two different light intensities over a polymeric solar-cell film. In Ref. 9, the Fig. 4(d) data was analyzed to reveal that the photovoltaic sample’s photocapacitance had biexponential dynamics.

The Lagrangian-impedance approach to understanding electric force microscopy highlighted here has a number of advantages. It accounts for dissipation of energy in both the sample and the cantilever; treats both steady-state and transient phenomena in a unified way; and captures the effects of sub-cycle changes in sample capacitance, conductivity, and tip charge that are missing from previous treatments of the cantilever-sample interaction in EFM and KPFM. The Lagrangian-impedance point of view has inspired new measurements and has forced us to rethink established measurements. The phasekick EFM measurement of Fig. 4 enables the measurement of sample charge motion on a timescale much shorter than even a single cantilever period. The assumptions underlying Eq. 1 are questionable in many interesting samples. Equations 2 through 4 should be used in place of Eq. 1 in any frequency-modulated KPFM experiment carried out on a sample with appreciable impedance, including photovoltaic films, battery materials, and mixed electronic-ionic conductors.

Methods

The data in Figs. 1, 3, and 4 were acquired on a custom-built vacuum/variable-temperature scanned probe microscope in Marohn’s laboratory at Cornell.

Acknowledgements

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Biographical sketches



John Marohn earned a B.S. in Chemistry and a B.A. in Physics from the University of Rochester. His Chemistry Ph.D. research was carried out at the California Institute of Technology under the mentorship of Daniel Weitekamp. He did postdoctoral work at the U.S. Army Research Laboratory with Doran Smith as a U.S. National Research Council Postdoctoral Associate. In 1999 he joined the faculty at Cornell University, where he is presently a Professor of Chemistry and Chemical Biology, serves as his department's Director of Undergraduate Studies, is a member of the Cornell Center for Materials Research, and is a member of Cornell's graduate field of Materials Science and Engineering. In 2006, Professor Marohn created the 1st International Conference on nanometer-scale Magnetic Resonance Imaging; the 6th International nano-MRI conference will be held in February 2018. In 2012 he landed a Ruth L. Kirschstein National Research Service Award from the National Institutes of Health that allowed him to work for a year as a visiting scientist at The Scripps Research Institute in La Jolla, California. His research group has three themes: (1) developing a microscopic view of organic and hybrid electronic materials using high-sensitivity electric force microscopy, (2) performing nanoscale magnetic resonance imaging using mechanical detection, and (3) studying near-surface fluctuations using microcantilevers.



Ryan Dwyer earned a B.S. in Chemistry from the University of Notre Dame. His chemistry Ph.D. research was performed with John Marohn at Cornell University. He is presently an Assistant Professor of Chemistry and Biochemistry at University of Mount Union where he teaches general and physical chemistry.