

Effect of a STM tip on the surface-diffusion measurement: A Monte Carlo study

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Monte Carlo simulations are performed to study the effect of an electric field on the surface diffusion of adatoms in a method that measures scanning tunneling microscopy tunneling-current fluctuations. The correlation function of the tunneling-current fluctuations is proportional to the adatom density fluctuation. Diffusion coefficients are inversely proportional to the time constant of the correlation function. Both the shape of the correlation and the measured time constant are calculated as a function of the ratio of the temperature to the characteristic electrostatic energy (i.e., strength of the electric field) and as a function of the initiating time of the measurement. The effect of the field is more pronounced when the measurement is carried out in the early nonequilibrium time regime while the adatom density evolves towards its equilibrium distribution under the spatially dependent electrostatic potential due to the electric field. [S0163-1829(98)06912-4]

I. INTRODUCTION

The adatom arrangement within surface overlayers in atomic-scale growth processes is largely controlled by the adatom mobility. The mobility of the adatoms is the essential mechanism for transporting mass across the surface to achieve either a well-equilibrated configuration or technologically important metastable structures. The importance of the time-dependent tunneling current measurement has been described before.^{1,2} Recently, a real-time technique based on scanning tunneling microscopy (STM) has been developed to measure diffusion coefficient by monitoring the current fluctuations at the tip.³ The technique is based on the expectation that any changes in particle density under the tip should induce fluctuations in the measured tunneling current. Since density fluctuations are related to the particle mobility through a dissipation-fluctuation theorem, the measurement of current fluctuations provides a means for measuring the diffusion constant.¹ This technique has been applied experimentally to measure surface diffusion for O/Si(111) at low coverage.³ Recent Monte Carlo studies examined the effect of adsorbate-adsorbate interactions on the single site⁴ and patch^{5,6} density correlation functions measured in fluctuation experiments. Time dependent correlation functions in connection to field-emission experiments also have been studied theoretically with the real-space dynamic renormalization group methods.⁷

As with all STM methods, a major problem is to ascertain the role of the electric field in influencing adatom diffusion. It has been demonstrated that the electric field can be used to manipulate adsorbed atoms and molecules to form organized structures on surfaces.⁸ In STM fluctuation experiments,³ the correlation function of the tunneling current can be measured immediately after the STM bias is turned on or after a sufficient time to allow the overlayer to reach equilibrium. The presence of the tip potential will disturb the distribution of particles on the surface, particularly for highly polarizable adatoms. A qualitative discussion of the role of the field was given previously by Gomer.¹ The quantitative estimate of such effects on the diffusion constant has not been examined

previously. This Monte Carlo study aims to address this question.

II. METHOD

We perform Monte Carlo simulations on a two-dimensional square lattice ($l=60$) in the presence of a predefined tip potential $U(r) = -U_0/(r/a+1)^\alpha$, where r is the distance measured from the position directly under the dip and a is the distance of the tip above the surface. α measures the decay of the potential and is taken to be 3 in this study. A similar expression was derived in Ref. 3 as an approximate expression to describe the electrostatic interaction between the tip (treated as a point charge) and an infinite flat equipotential surface (typical of metallic substrates but also consistent with the highly doped semiconductor surfaces used for STM experiments). Such a picture has been invoked to explain how the electric field is used to manipulate growth and produce well-controlled nanostructures.⁸ It changes the potential well minimum, so the sites closer to the tip are deeper than the ones further away. The present problem of diffusion under an electric field can be thought as a two-dimensional (2D) biased random walk where a diffusive atom has a higher probability of moving towards the tip than away from the tip. A calculation is performed either when the system approaches equilibrium or after the equilibrium is established. The question we address is whether the density correlation function calculated under these conditions is different from the one expected on a flat potential surface. Biased-random-walk problems are found in textbooks⁹ on surface diffusion whenever a constant field is assumed. Our problem involves a biased walk in a field that depends on the distance from the tip, with the electric field practically zero after a cutoff distance determined by the distance of the tip from the surface (approximately 4 times the size of the tip-surface distance). Interparticle interactions are neglected for simplicity.

In the absence of a field, a particle hops with equal probability in the four possible directions, overcoming a constant diffusion barrier E_0 between the nearest-neighbor sites. In the presence of an interaction potential $U(r)$ with the electric

field on, the probability of moving to a neighbor site r' will necessarily depend on the potential energy $U(r')$. In this work, the diffusion of adatoms under the influence of the tip potential $U(r)$ is simulated with a Montropolis algorithm. In particular, the probability of an adatom at site i moving to an empty nearest-neighboring site j , P_{ij} , is given by

$$P_{i,j} = P_0 \exp\left(\frac{U(r_i) - U(r_j)}{kT}\right), \quad (1)$$

where $P_0 = p_0 e^{-E_0/kT}$ is the probability in the absence of the field, which itself is thermally activated, with E_0 the activation energy for zero field. In this work, we have taken P_0 as a constant for convenience, implying a time scale that is exponentially varying with temperature.

The simulation is performed as follows. The initial configuration is taken as a random distribution of particles with coverage θ , which corresponds to an equilibrium configuration in the absence of the field. At $t=0$ the electric field is turned on and particles begin to diffuse towards the tip. A randomly chosen particle is tested to move to one of the neighboring sites with probability P_{ij} given by Eq. (1). Periodic boundary conditions are applied. Following the convention, a Monte Carlo step (MCS) corresponds on the average to one attempt for each particle. For sufficiently long times, the system will acquire a new equilibrium configuration determined by $U(r)$, with a nonuniform distribution of particles. With an attractive potential, more particles will occupy sites under the tip since these sites have lower potential energy.

With the fluctuation STM method³ the time scale of fluctuations in the tunneling current corresponds to the time for an atom to either cross or revisit the probe area. A current pulse is expected (above the average value of the current) whenever an atom is in the tunneling region. The diffusion coefficient can be obtained² from the pulse width (which corresponds to the time for the atom to cross the area) or from the average time separating the pulses, which corresponds to the average time between visits. The time to cross the probe region is simply proportional to the decay constant of the correlation function while the time between the visits is determined by the time necessary to attain the $1/t$ tail for 2D diffusion.³ The tunneling current fluctuations are simply determined by the density fluctuation that was calculated in the simulations,

$$C(t, t_0) = \langle N_p(t) N_p(t_0) \rangle - \langle N_p \rangle^2, \quad (2)$$

where $N_p(t)$ is the total number of particles within the probe area at a given time t and $\langle N \rangle$ the average number of particles in the probe area. t_0 is the starting time of the correlation function calculation and the angular bracket represents an ensemble average over independently prepared initial equilibrium configurations.

In the absence of $U(r)$, $C(t, t_0)$ is independent of the starting time t_0 and obeys a well-known form in the hydrodynamic limit,^{10,11}

$$C(t) \sim \int_A \frac{1}{4\pi D_c t} \exp\left(-\frac{(\vec{r} - \vec{r}')^2}{4D_c t}\right) d\vec{r} d\vec{r}', \quad (3)$$

where the integration is over the probe area A . The chemical diffusion constant D_c can be extracted by comparing the experimentally measured form with expression (3). In the long time limit, a simplified form of $C(t)$ can be used to extract the diffusion constant, $C(t) \approx A/4\pi D_c t$. In practice, the Fourier transform is compared instead. The $1/t$ asymptotic limit at longer time leads to a $\ln(f)$ dependence at low frequency, the coefficient of which is inversely proportional to the diffusion constant D_c .^{3,11} The effect of probe area and interactions has been investigated previously.⁴⁻⁷ In the absence of adatom-adatom interactions, D_c is a constant independent of the coverage.¹² Thus we expect that the normalized correlation function has the same form [Eq. (3)] independently of the average density.

As discussed before with the electric field on, the potential surface is modified by $U(r)$. This implies that the uniform density system is no longer in an equilibrium state and will evolve in time to attain a new equilibrium state that is described by position-dependent density. Thus $C(t, t_0)$ will depend on the starting time of the measurement t_0 . In determining the correlation function according to Eq. (2) we have used the long-time saturation value $N_{sat} = N_p(\infty)$ in the probe to be subtracted as the average particle number, instead of the average particle number for uniform distribution $N_p = A\theta$, where θ is the coverage. One expects the measured correlation function to deviate from the form (3) if the starting time t_0 is well before the equilibrium time. The readjustment in the particle positions to their new equilibrium introduces additional “nonequilibrium” fluctuations since fluctuations are measured from the final saturated density in the probe area. This should affect the shape of the correlation functions. It is not clear whether for long enough time such an equilibrium is attained that the shape of the correlation function and the extracted diffusion constant from them are the expected ones based on Eq. (3). Deviations still might be possible since the system even at equilibrium is undergoing a biased random walk with the probability of moving towards the tip higher than the probability of moving away.

Experimentally, it is easy to perform measurements for different t_0 : The tunneling voltage is applied either at the time (to measure how the system evolves in time to readjust particle density to the equilibrium configuration) or after the field has been on for a sufficiently long time such that the equilibrium configuration is attained. In practice, the configuration average can be carried out exclusively only in terms of independent configurations (as in the simulations) by turning the field off between acquisitions or by choosing a mixture of configurations and time average if the field is on continuously. The choice of the saturation value as the average density to subtract in Eq. (2) without any time average is better suited for studying the difference between equilibrium and nonequilibrium experiments.

Simulations have been performed on a 60×60 lattice size with a coverage $\theta = 0.2$ and an ensemble of at least 1000 configurations, under periodic boundary conditions. The tip is positioned at the center of the lattice at a distance of eight lattice spacings above the surface. An area of 8×8 directly under the tip is taken as the probe area. Simulations are performed at several temperatures or potential U_0 . Obviously, only their ratio is important, as is evident from Eq. (1). The particle density within the probe area is recorded for

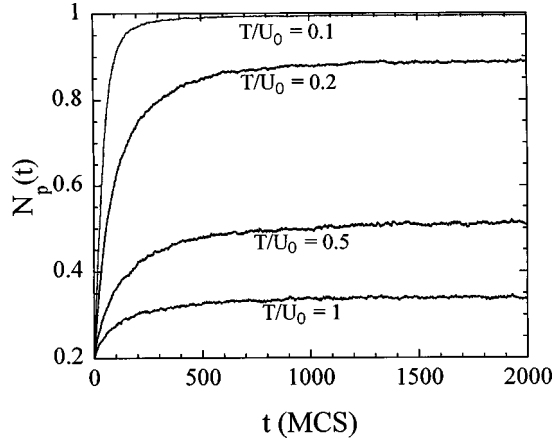


FIG. 1. Average density in the probe area as a function of the Monte Carlo simulation time. The electric field is turned on at $t = 0$.

each Monte Carlo step and the correlation function is then calculated starting from time t_0 .

Several related questions are investigated. First we determine the time scale for the system to reach the new equilibrium state at a different ratio of the temperature to the potential, T/U_0 . To characterize this time scale, we investigate the time dependence of the density within the probe area. The average density starts at the initial coverage θ and saturates to a constant value N_{sat} at a long enough time. This saturation time of the density should be taken as a lower bound of the equilibration time. One can look at the correlation function measured both before and after the equilibration time to see how they differ. from Eq. (3).

The second question addresses our primary interest: To what extent does the electric field affect the diffusion constant at different temperatures measured by both the shape and the decay constant of the correlation function? There are primarily two factors contributing to this effect: the time dependence of the density and the biased random walk towards the tip. These two work together and are difficult to separate. However, correlating this with the time to attain equilibrium will enable us to reach partial conclusions regarding the relative importance of the two.

III. RESULTS

Figure 1 shows the evolution of the average particle density in the probe area with time for different ratios of the temperature to the potential, $T/U_0 = 0.1, 0.2, 0.5, \text{ and } 1$. These curves show a fast increase in the density at the beginning and a much slower increase at the saturation stage. The initial fast increase occurs when particles from the surrounding area move into the probe area under the influence of the electric field. This initial stage is fast since the initial drive for the particle redistribution is large and the movement involved is short ranged. However, achieving the state of equilibrium requires a mass movement over the whole lattice. Thus the final stage of equilibration happens on a much slower time scale than the time scale of the fluctuations out of the probe area. Note that the particle density in the probe area increases at the end by as much as 70% even when the potential is comparable to the temperature

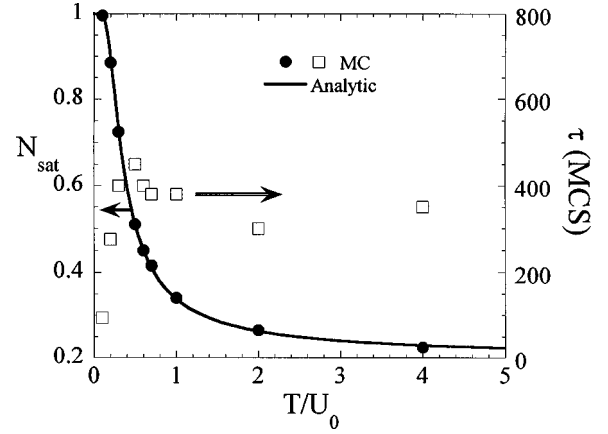


FIG. 2. Saturated density in the probe area N_{sat} and the density saturation time, τ_{sat} for different temperature to electrostatic potential ratios T/U_0 . The analytical result is from Eq. (4).

($T/U_0 = 1$). Much larger increases are found at lower temperatures (or larger fields). In Fig. 2 we have plotted the saturation density as a function of the ratio T/U_0 . If we approximate the probe area as a trap of one site with an effective trap potential $\langle U \rangle$, one expects the average density in the trap site to follow a simple form

$$N_{sat} = \frac{\theta}{\theta + (1 - \theta)e^{-\langle U \rangle/k_B T}}. \quad (4)$$

Indeed, this simple analytical relation describes the saturated density well (Fig. 2) with an effective average potential $\langle U \rangle = 0.713U_0$. At high temperatures the excess density in the probe area over the coverage θ varies as $\langle U \rangle/T$. Shown also in Fig. 2 is the density saturation time T_s , defined as the time when the density reaches 85% of the saturated value. The saturation time decreases rapidly with decreasing temperature for $T/U_0 < 0.5$. For $T/U_0 > 0.5$, the density saturation time does not vary significantly. It should be noted that our unit of time is temperature dependent. In an actual experiment, the saturation time will be much longer at lower temperatures due to the rescaling of the time by the thermally activated factor $e^{-E_0/k_B T}$.

Figure 3 shows the particle distribution in the lattice at $t = 2000$ MCS for different $T/U_0 = 0.5, 1, 2, \text{ and } 4$ averaged over a large number of samples. The saturation of density is already achieved at this time. Clearly, one sees an increased density at the center directly under the tip [Figs. 3(a) and 3(b)] gradually flatten out away from the tip. However, the increase is much smaller at higher temperatures and is hardly visible at $T/U_0 > 2$ [Figs. 3(c) and 3(d)].

Figure 4 shows the correlation function, measured immediately after the electric field is turned on and with the saturation density at the given temperature subtracted out as the average in Eq. (2). At low temperatures the correlation function (2) deviates strongly from the correlation function at high temperatures which is closer to the expected form (3). This suggests a direct way to measure the degree of influence of the electric field on the diffusion coefficient, i.e., to measure the correlation function immediately after the voltage is applied and search for a difference from the theoretical form. It is interesting to notice that the deviation is first towards a

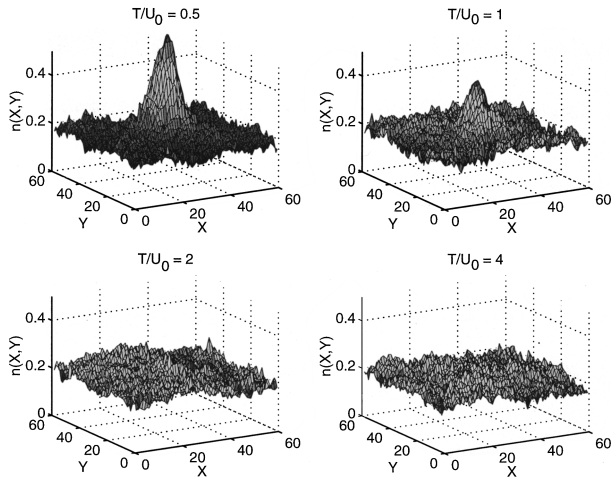


FIG. 3. Equilibrium particle distribution under the electrostatic potential $U(r)$ at different temperatures. The STM tip is positioned at the center of the lattice.

slower decay (which results from the smaller probability of an atom to revisit the tunneling region since the probe area acts as a trap); as the temperature is lowered the decay is faster than for zero field as a result of the rapid reequilibration to a new saturation density level seen in Fig. 1. It follows that there are two contributions to the change in the shape of the correlation function from the theoretical form: the readjustment of the density to a new value and the biased walk towards the potential-energy minimum underneath the tip. Since the correlation function is plotted in a scaled form (where the time is divided by the time it takes for the correlation function to drop to half its initial value), it does not show the expected increase of the absolute time constant at lower temperatures. Such comparisons of the shape can be easily done experimentally.

It is a standard question to identify the importance of the field in STM diffusion experiments. Other methods that measure the tracer diffusion with the STM that rely on scanning full images detect the role of the electric field for times longer than the image acquisition times but, since the experi-

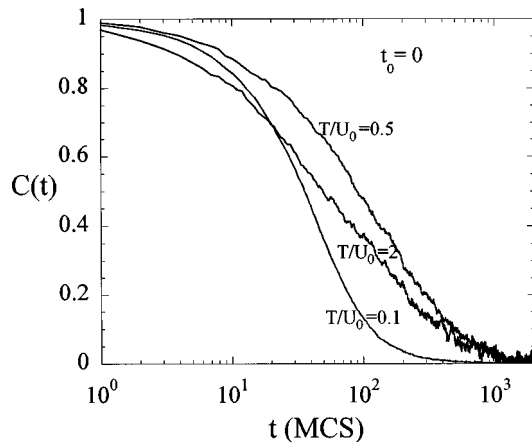


FIG. 4. Normalized correlation function calculated immediately after the electric field is turned on for temperature $T/U_0 = 0.1, 0.5,$ and 2 . Deviations from the zero-field (or high-temperature) shape are expected for a strong field.

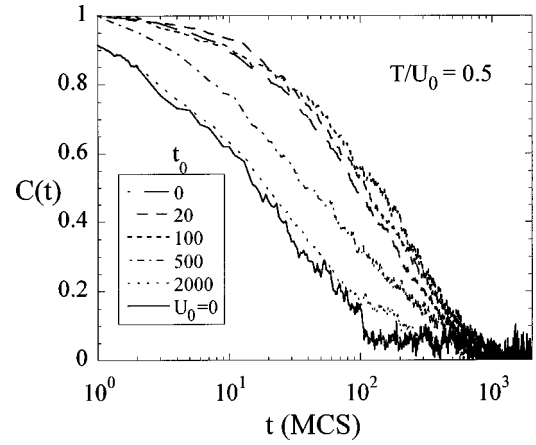


FIG. 5. Normalized correlation function calculated with different starting times t_0 for $T/U_0 = 0.5$. For long enough time $t_0 = 2000$ MCS the correlation function is the expected shape (3) obtained through Monte Carlo simulation at zero electric field, independent of the coverage.

ment is done by following the movement of a single atom, cannot exploit the response of the system to the chemical potential (and therefore concentration) gradient that is established by the electrostatic interaction of the tip surface. The decay of the density fluctuations as measured in our experiment³ is sensitive to this gradient both because of the equilibration necessary and because of the additional trapping effects.

Experiments on O/Si(111) were carried out as a function of the applied voltage (i.e., increasing the value of the electrostatics energy U_0) and at $t_0 = 0$ to search for possible field effects. Experimentally, power spectra were measured that contain the same information as the correlation function since the two quantities are simply related by a Fourier transform. The expected theoretical form (3) can be easily worked out for the power spectrum. The rescaled spectra obtained from three values of the tunneling current $V = 1, 2, 3$ V follow exactly the expected theoretical expression, which verifies that no field effects should be expected on such a covalently bonded substrate and oxygen, a low polarizability atom.

Figure 5 shows the normalized correlation function, at $T/U_0 = 0.5$, a sufficiently low temperature, at different starting times t_0 . Also shown in the same plot is the correlation function for a system under zero electric field obtained from Monte Carlo simulations as the standard form to be compared with. We have explicitly verified that this standard correlation function is independent of the coverage. Again, a deviation of these curves from the standard form given by Eq. (3) is clearly seen for small t_0 . The effective diffusion constant, defined by the time at which the value of the correlation drops to half its initial value $\tau_{0.5}$, depends strongly on the starting time t_0 (Fig. 5). At $t_0 = 2000$ MCS, the system has already achieved equilibrium and the curve follows the standard expression. It is surprising that the correlation function after equilibrium is attained follows the same shape as the case of diffusion on a flat surface with zero field. One might expect that although the final distribution of particles is attained and the nonequilibrium driving force does not operate, there is still a higher probability to diffuse towards the tip than away from the tip. In problems where a constant

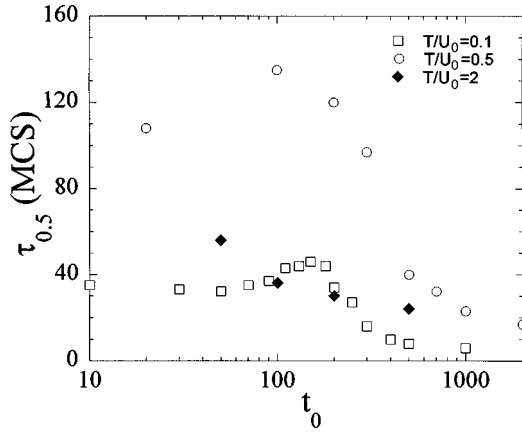


FIG. 6. Decay time constant $\tau_{0.5}$, defined as the time it takes for the correlation function to drop to half its initial value, for different ratios $T/U_0=0.1, 0.5, 2$ and different starting times t_0 . For low ratios ($T/U_0=0.1$) the time constant deviates from the expected one ($\tau=A/4D$) at long times t_0 , although the shape of the correlation function agrees with Eq. (3).

field extending over the whole system is present (i.e., diffusion in the presence of gravity), it has been shown⁹ that the final density distribution depends on position (with higher density towards the regions of lower energy, i.e., sedimentation), but it is not clear what the form of the correlation function for spontaneously generated density fluctuations should be, as in our problem.

We have plotted $\tau_{0.5}$ as a function of t_0 , the starting time of the current fluctuation and correlation measurement, for different T/U_0 ratios (Fig. 6). The measured τ are higher for small t_0 as a result of the contribution of the nonequilibrium driving force to a new saturation value of density. For sufficiently long t_0 (when equilibrium is attained) the $\tau_{0.5}$ value becomes constant to the value expected for the case of zero field, $\tau_{0.5}=A/4D=16$ MCS. We observe that the time for $\tau_{0.5}$ to reach the expected value of the diffusion constant seems to be longer than the density saturation time, which is 94, 450, and 380 MCS for $T/U_0=0.1, 0.5,$ and 1, respectively (see Fig. 2). This is clearly an indication that even though the density in the probe area is already very close to its equilibrium value, the system still has not reached complete equilibrium as reflected in the deviation of the time constant $\tau_{0.5}$ from the value expected for the case of zero field. It is also interesting that there is a deviation of $\tau_{0.5}=8$ for very long starting times from the expected one 16 MCS at strong field $T/U_0=0.1$. This is interesting in that although the shape of the correlation function is similar to the one observed for the case of no field, the measured $\tau_{0.5}$ is smaller, which amounts to a faster diffusion coefficient. Experimentally, this implies that although the shape is not a sufficient criterion to identify the role of the field, measuring the correlation function even in this regime when equilibrium is attained as a function of the applied voltage will lead to progressively smaller half times $\tau_{0.5}$ (and effectively larger diffusion constants at higher voltage). This is physically expected since the minimum of the potential energy

surface underneath the tip acts like a trap to speed up the diffusion of the atoms from the outside towards the tip.

In the past, the role of diffusion in STM measurements^{14,15} was identified either by varying the scanning rate (no field effect was indicated by diffusion-independent rate) or, by comparing experiments at temperatures (with the field on) with quench-and-look experiments (when the field is off during heating at the diffusion temperature) and the deviation of the diffusion coefficient from an Arrhenius dependence. As we have shown in the current study, using the shape and the decay constant of the correlation function as a function of the measurement time t_0 or as a function of tunneling voltage for long t_0 is a good method to identify the role of the field over a much wider range of time, from microseconds to seconds (since tunneling current can be measured at much higher acquisition speeds). In O/Si(111) it is no surprise that no field effect was observed³ because of the small polarizability of oxygen. Based on the free-atom value of the polarizability (and not accounting for the permanent dipole moment), the magnitude of U_0 is estimated to be $\frac{1}{2}\alpha_0 F^2$, where α_0 is the free atom polarizability and F the electric field strength. For oxygen,¹³ $\alpha_0=0.8\times 10^{-24}$ cm³. With a typical field strength $F=3\times 10^7$ V/cm and $T=400-500$ K in the experiment, we obtain $T/U_0=10$. On the other hand, field effects such as these discussed here can be more pronounced for Sb/Si(100) (Ref. 14) and Pb/Ge(111).¹⁵ For these systems, the free-atom values of the polarizability,¹³ $\alpha_0=6.6\times 10^{-24}$ for Sb and 6.8×10^{-24} for Pb, respectively, are larger by almost one order of magnitude. Using $T=300$ K for Pb, we have the ratio $T/U_0\approx 1$, so the correlation function could be a sensitive way to show field effects, especially for short measurement times t_0 .

IV. CONCLUSIONS

Monte Carlo simulations show how field effects can influence the measured diffusion constant in the STM fluctuation method. Such an influence increases with decreasing temperature or with the strength of the applied voltage. It can be identified either from a change of the shape of the correlation functions at early measurement times t_0 or from the dependence of the decay constant $\tau_{0.5}$ on applied voltage. The shape of the correlation function after equilibrium of a new value of the density underneath the tip is attained obeys the one expected theoretically for the case of zero field (in spite of the high probability to diffuse towards than away from the tip), but the time constant is lower. Experimentally, such results indicate how field effects can be determined by a measurement at a much faster time scale than typical STM image acquisition speeds.

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