



Stochastic model for spontaneous formation of molecular wires

J.A. Olmos Asar, M.M. Mariscal, E.P.M. Leiva^{*,1}

Unidad de Matemática y Física, Facultad de Ciencias Químicas, INFIQC, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

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ABSTRACT

A stochastic model which may be used to analyze the formation of bonds connecting the interface formed by a substrate surface and a scanning tunneling microscope (STM) tip is presented. The model is tested by means of kinetic Monte Carlo simulations, and analytical predictions are given for some limiting cases. In the case of long time observations, the model may be applied to obtain information on the rate constants associated with the process and on the number of molecules trapped at the gap. In the case of short time observations, the results of the model for the probability of observing a given number of molecules bridging the gap are compared with the experimental results from the literature, showing a good predicting power.

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1. Introduction

A major advance towards the development of the design of molecular nanoelectronic devices has been the synthesis of different types of nanowires consisting of a single-molecule attached to two macroscopic metallic contacts, forming a metal–molecule–metal junction. These molecules are able to transport charge over long distances and also to work as interconnects, switches, transistors, rectifiers, etc.

One of the most widely studied of these systems consists of α,ω -alkanedithiolates attached to two gold surfaces or monoatomic wires. Single-molecule experiments using a mechanically controllable break-junction [1] and an atomic force microscope (AFM) [2] provided the first insights into their response to an externally applied electric voltage [3], allowing the determination of their electrical conductivity and the measurement of the properties of molecular junctions under mechanical stress.

Several methods to measure the conductivity of single-molecules chemically attached to two metal electrodes have been developed by Cui et al. [4,5], Xu and co-workers [6,7], Reichert and co-workers [8,9], and Haiss et al. [10,11]. For instance, in the method devised by Cui et al. [4,5], 1,8-octanedithiol molecules were inserted into an octanethiol monolayer adsorbed previously on a Au(111) surface using a replacement reaction whereby one of the two thiol groups became chemically bound to the gold substrate. The thiol groups at the top of the film were brought into contact with a suspension of gold nanoparticles. A gold-coated conducting AFM probe

was used to locate and contact individual particles bonded to the monolayer. I/V measurements on different nanoparticles produced only five distinct families of curves, corresponding to multiples of a fundamental curve. These normalized curves were attributed to the polarization of a single metal–molecule–metal contact (see Ref. [12]).

Xu and co-workers [6,7] also developed a technique to obtain single-molecule contact conductance measurements. They were able to create single-molecular junctions by means of a scanning tunneling microscope (STM) tip. The method involves a mechanical contact between the tip with a Au(111) surface in a solution containing the sample molecules (i.e. alkanedithiols). After withdrawal of the Au tip, a molecule (or eventually more) is linked between the end-atoms (from tip and substrate surface) and the conductance is measured at the same time that the system is elongated.

A different approach to measuring conductance was developed by Haiss et al. [10,11] founded on trapping alkanedithiol molecules between a STM tip and a substrate without mechanical contact between them. These authors considered two types of experiments. We follow here their notation. In one of these types of experiments, denominated $I(t)$, the STM tip was approached to the surface of a substrate covered with a small surface concentration of α,ω -alkanedithiol molecules, and held at a constant distance from it. Then, the tunneling current at the tip–substrate junction was monitored as a function of time. Under these conditions, current jumps were observed, that were assigned to the formation of molecular wires between tip and substrate. In another type of experiments, denominated $I(s)$, the STM tip was brought close enough to the Au surface so as to allow for the spontaneous formation of stable molecular wires between the tip and the sample. The tip was then lifted while keeping a constant x – y position, and the current–distance relation was measured. A statistical analysis of

* Corresponding author. Tel.: +54 351 4344972; fax: +54 351 4344972.

E-mail address: eleiva@fcq.unc.edu.ar (E.P.M. Leiva).

¹ ISE member.

the current steps observed under these conditions showed that different numbers of molecules became trapped at the tip-substrate gap. Thus, these two types of experiments showed strong evidence for the formation of molecular entities bridging the gap between the metal substrate surface and the STM tip. In the present work we devise a stochastic model to describe the spontaneous formation of molecular wires via jump of molecules at the gap between a substrate and a tip that may be helpful for the understanding of this phenomenon and may provide information on some of the parameters associated with this phenomenon.

Although experiments have been carried out both in air and in an electrochemical environment, we think that the latter conditions should be the more suited to study the present problem. In fact, electrochemical experiments provide separate control of tip and substrate potentials with respect to a reference electrode. This would allow the precise separate control of some of the rate constants addressed below.

2. The model

The model does not consider the physical nature of the bonds, but proposes a statistical description of the processes taking place in the system. As depicted in Fig. 1, it assumes that N molecules are present at the gap between a substrate and the STM tip, and that the S-terminated end of the dithiols may jump between both contacts. It is assumed that each of the molecules may adopt mainly three states: one with both ends attached to the substrate, another with both ends attached to the tip, and a third one where it is bridging the gap. All other possible configurations (i.e. a molecule with an unbonded end) are neglected. Thus, all the events taking place at this interface may be interpreted as detachment–attachment steps, where a thiol group detaches from the substrate and attaches to the tip, or viceversa.

For a given dithiol molecule adsorbed on the substrate (or tip), there may be associated, in principle, two processes with different rates: the transfer of the first thiol group (for example α) and the transfer of the second thiol group (for instance ω). The difference in these two rates will be given by the interaction of the hydrophobic chain of the thiol with the substrate. For the present calculations, we will neglect the difference between the transfer rate of α and ω thiol groups; however, this feature could be easily incorporated into the model.

Since $I(s)$ and $I(t)$ experiments are usually performed at low coverage degrees of the adsorbed dithiols, it can be assumed that their interaction is negligible. Thus, two successive events taking place at this interface may be considered as independent. This should be a reasonable assumption given the low concentration of adsorbed species present on both surfaces. We will make two further assump-

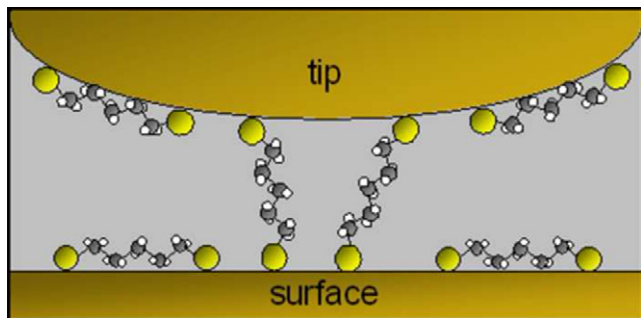


Fig. 1. Schematic representation of the model employed to describe spontaneous formation and rupture of molecular wires at a nanocontact between a substrate and an STM tip. A molecule may assume three states: one with both ends attached to the substrate, another with both ends attached to the tip and a third one where it is bridging the gap.

tions. The first is that any particular transition which becomes possible at time t can potentially occur at any later time $t + \Delta t$ with a probability $\nu \Delta t$, where ν represents its rate and is independent of the events before time t . The second assumption is that probability that more than one event occur in the interval Δt is of order higher than one in Δt . According to these assumptions, we can describe the present phenomena in terms of the framework of Poisson processes.

The more general framework to analyze this type of events, regardless of the complexity of the problem, is that provided by kinetic Monte Carlo (KMC) simulations. Within this approach, dynamic processes can be simulated following the following procedure [13]:

- The possible k events that may take place in the system must be first identified and their rates calculated. This set of rates will be here referred to as $\{v_1, v_2, \dots, v_k\}$.
- The probability of a process to occur can be thus represented on a straight line by a segment proportional to its rate.
- If the sum of all the segments is normalized to unit length, then the occurrence of a process can be selected by generating a random number between 0 and 1, and choosing the process corresponding to the segment on which the random number has been found to fall. Since the probability of changing the current state has a constant rate, the time elapsed Δt until the accepted change has an exponential distribution. Thus, a time increment Δt can be calculated from $\Delta t = -(\ln(\eta))/\sum_{i=1}^k v_i$ where η is a random number uniformly distributed on the (0,1) interval, and the sum index runs over all possible processes at a given time step.
- After letting the time advance in the amount Δt , the configuration of the system is updated, a new set of rates $\{v_i\}$ is calculated, and a new process is again selected randomly and so forth.

KMC methods have been used successfully in electrochemistry to address the simulation of different problems [14], like electrochemical nucleation and growth [15–17], trench filling [18], metal film formation [19] and anion electrosorption [20].

In the present work we perform KMC simulations to describe the spontaneous formation of molecular wires by the simple model described previously. In some cases the results of the simulation can be predicted by simple analytical procedures, but it should be noted that the simulations could be straightforwardly employed to predict the behavior of more complex models.

3. Results and discussions

Simulations were performed using different initial conditions and sets of parameters to describe processes in different time scales and different experimental conditions.

3.1. Long time simulations

They refer to simulations of processes occurring in a time interval that is large as compared with that of a single-molecular jump.

As described in Section 2, we assumed that the transfer rates of all the S-ended groups are the same. Thus, we denote the rate of transfer of S-groups from the substrate to the tip with $\nu_{s \rightarrow t}$ and the rate of transfer of S-groups from the tip to the substrate with $\nu_{t \rightarrow s}$. The parameter that we monitor is the number of substrate–tip bonds $n(t)$ at different stages of the simulation, since this quantity corresponds to an observable. This quantity should be linearly related to the tunneling current flowing at the substrate–tip gap, provided the interaction between the molecules appears as negligible, which is clearly the case for a hydrocarbon backbone.

Fig. 2 shows $n(t)$ vs. t for different time intervals at the steady state obtained with $N = 20$, assuming $\nu_{s \rightarrow t} = \nu_{t \rightarrow s} = 1$.

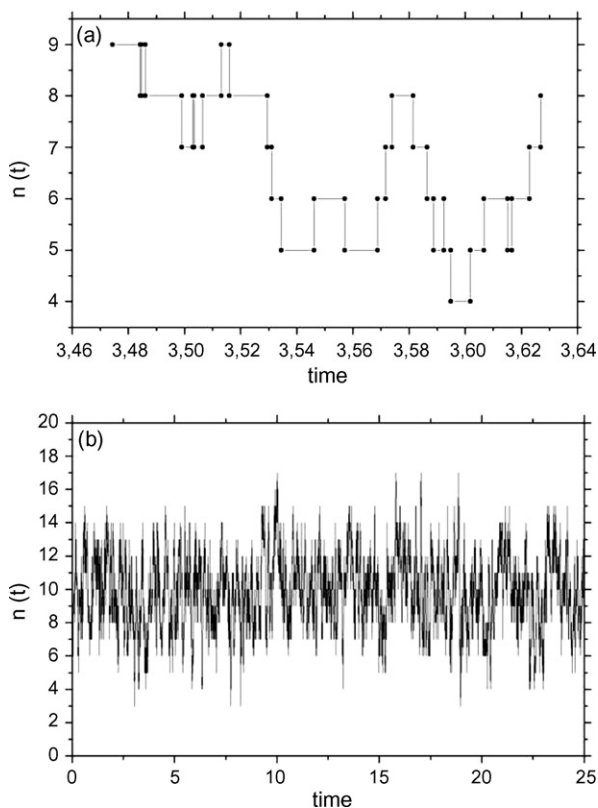


Fig. 2. Number of substrate-tip bonds as a function of time for 20 dithiol molecules at the tip-substrate gap. The transfer rates were $\nu_{s \rightarrow t} = \nu_{t \rightarrow s} = 1$. (a) Corresponds to the monitoring of a short while (b) to the observation of the system along a longer period of time.

Although not evident in Fig. 2a, since the system is monitored over a short period of time, the simulated average number of bonds (n) shown in Fig. 2b appears to be close to one-half the number of molecules.

This is more systematically found in Table 1, where we present results of simulations that were performed with different numbers of molecules N .

The reason why $\langle n \rangle \approx N/2$ can be understood from the geometrical argument shown in Fig. 3, where we indicate the possible configurations for a molecule. There, we have denoted the different ends with α and ω . The molecule may attach with both ends to the tip, both ends to the substrate or one end on each side of the junction. Thus, the relative weight for the configuration for one end attached to the tip and another one attached to the substrate is exactly 1/2. A little bit less straightforward to understand is the correlation between the standard deviation of $\langle n \rangle$, denoted with σ_n , and N . Fig. 4 shows that σ_n follows a linear relationship with \sqrt{N} . To examine this, we turn to consider the stochastic nature of the process under analysis. Let us define a random variable ξ_i , specify-

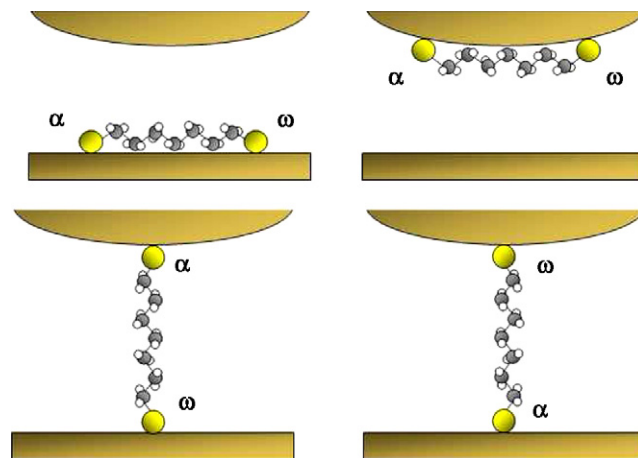


Fig. 3. Schematic representation of the ways in which a molecule may be bonded at the substrate-tip junction.

ing the status of molecule i . This variable will be assigned the value $\xi_i = 1$ (or $\xi_i = 0$) when it connects (does not connect) the substrate and the tip, respectively. Thus, the number of substrate-tip bonds will be given by

$$n = \sum_{i=1}^N \xi_i \tag{1}$$

Since $\{\xi_i\}$ is a set of independent random variables, the properties of n can be easily calculated from the properties of ξ_i . Thus, for the mean value $\langle \xi_i \rangle$ and the variance $\sigma_{\xi_i}^2$ of ξ_i we have:

$$\langle \xi_i \rangle = \frac{0 + 1}{2} = 0.5 \tag{2}$$

$$\sigma_{\xi_i}^2 = \langle \xi_i^2 \rangle - \langle \xi_i \rangle^2 = 0.25 \tag{3}$$

From these values we can obtain the corresponding ones for n :

$$\langle n \rangle = \langle \xi_i \rangle N = 0.5N \tag{4}$$

$$\sigma_n^2 = N \sigma_{\xi_i}^2 = 0.25N \tag{5}$$

From the latter equations we can now easily understand the results of Table 1 and the correlation observed in Fig. 4.

The present model may be used to consider not only steady states as those reported above, but also transient processes. For

Table 1

Average number of bonds (n) and its variance for σ_n for different number of molecules present at the substrate-tip gap. σ_n^p is the prediction according to the expectation assuming independent processes.

N	$\langle n \rangle$	$\sigma_n = \sqrt{\langle n^2 \rangle - \langle n \rangle^2}$	$\sigma_n^p = 0.5\sqrt{N}$
5	2.53	1.13	1.12
10	4.98	1.58	1.56
50	24.9	3.56	3.54
100	50.2	4.99	5
500	250	11.3	11.2
1000	501	15.7	15.8
5000	2501	35.3	35.4

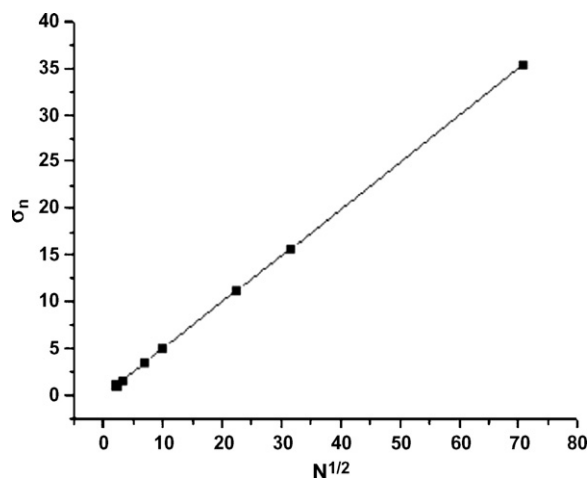


Fig. 4. Standard deviation of the number of substrate-tip bonds $\sigma_n = \sqrt{\langle n^2 \rangle - \langle n \rangle^2}$ as a function the square root of the number of molecules at the junction.

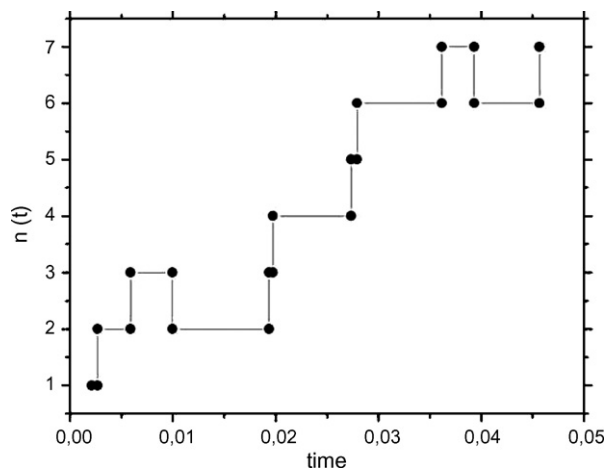


Fig. 5. Time evolution of the number of bonds at the nanojunction when 20 molecules of alkanedithiol are initially only attached to the surface of the substrate. System parameters as those of Fig. 2.

example, Fig. 5 shows the evolution of the number of bonds in a system where 20 alkanedithiol molecules are, in the initial state, completely attached to the substrate surface, and allowed to jump to the tip from $t=0$ on. The transient shows that, as time progresses, the number of bonds between the substrate and the tip increases. Depending of the parameters provided to the system, diverse behaviors can be found in these transient responses. We will analyze here a case that it is particularly simple and may be

useful to gather information on the system. We consider initial conditions such that a certain number N of molecules is adsorbed on the substrate, none are present at the tip, and the electrostatic potentials applied to the substrate and the tip are such that only the transfer of the molecules in one direction (from substrate to tip) is allowed. In terms of the notation defined above, we will analyze the case where $\nu_{s \rightarrow t} = 1$ and $\nu_{t \rightarrow s} = 0$. This condition may be difficult to achieve experimentally, but provides a simple limiting case where the results of the simulations may be compared with analytical results. These types of simulations are analyzed in Fig. 6 for different number of particles initially adsorbed on the tip. The occurrence of a maximum is a remarkable feature of these transients, which can be understood as follows. At short times $t \rightarrow 0$, all the molecules remain attached to the substrate surface, since no time has elapsed allowing for the Poisson events to proceed. Thus, in this limit the number of contacts is zero. As time passes, the probability of observing no events decreases exponentially, and connections start to form. At some later point, the number of contacts reaches a maximum and begins to decrease, since whole molecules start to be attached to the tip and no longer contribute to the formation of substrate-tip bonds. In order to provide an analytical description of this phenomenon, we will analyze the process in terms of differential equations. Let us consider a differential change dn in the number of molecules bridging the substrate-tip gap, under the present conditions, namely when the transfer of molecules occurs only from the substrate to the tip. The number of substrate-tip bonds n will decrease with a rate proportional to the number of molecules bridging the gap (which is also n) since these molecules may transfer their substrate-bonded end to the tip. On the other hand, n may increase due to the transfer

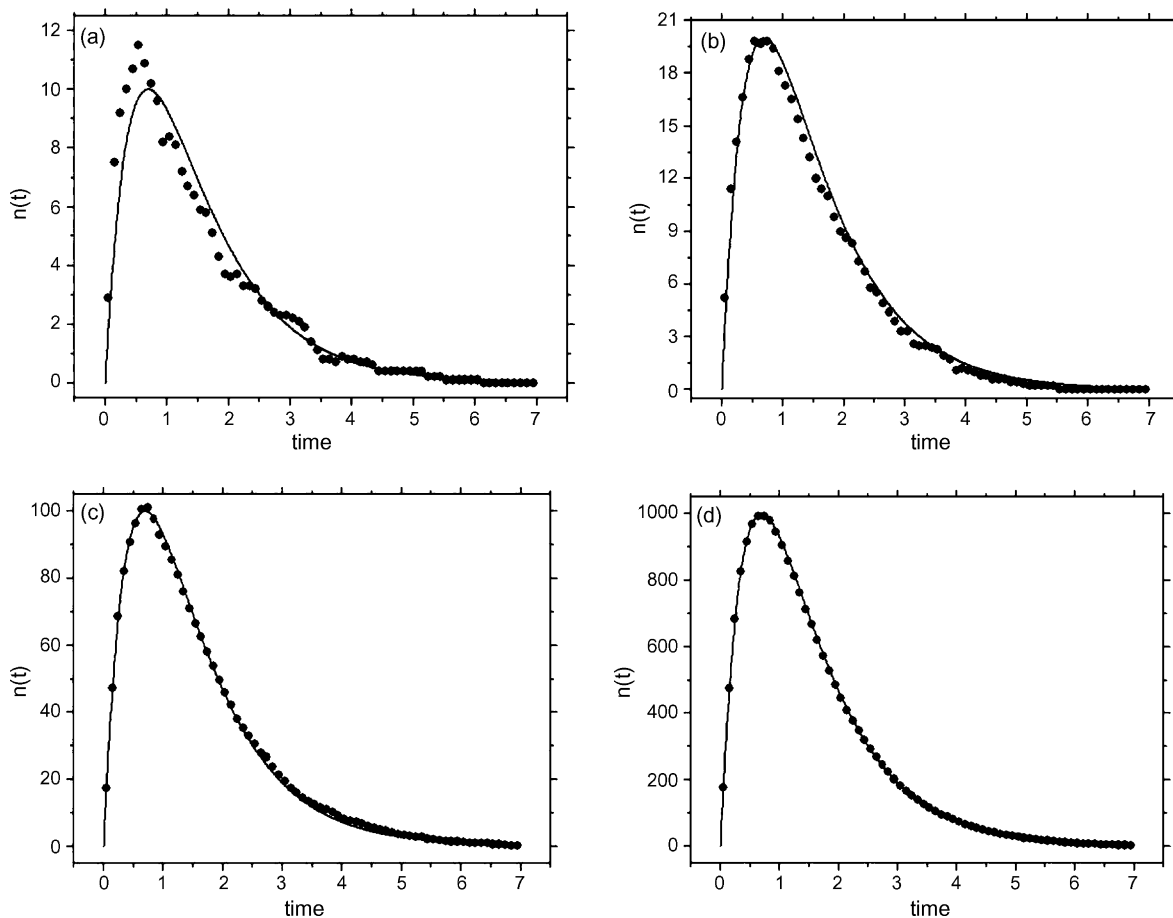


Fig. 6. Transient behavior of the number of bonds $n(t)$ as a function of time when different number of molecules N are initially adsorbed on the substrate and are allowed to make contact with the tip starting from $t=0$. The transfer rates were $\nu_{s \rightarrow t} = 1$ and $\nu_{t \rightarrow s} = 0$. (a) $N=20$; (b) $N=40$; (c) $N=200$; (d) $N=2000$. Filled circles correspond to kinetic Monte Carlo results averaged over 10 simulation runs. The continuous curve is the prediction given by Eq. (10).

of one of the thiol ends of the molecules completely attached to the substrate. In equations this reads:

$$dn(t) = v(N_r(t) - n(t))dt \tag{6}$$

where $N_r(t)$ is the number of molecules remaining with both ends attached to the substrate. Consistently with the assumption of our simulation, we have assumed a unique rate for the transfer of the molecule ends, independent of whether the molecule is bonded to the substrate with one or two ends.

In order to solve Eq. (6), we need a relationship between $N_r(t)$ and t . To get this, we define an intermediate variable $N_r^S(t)$, which denotes the number of thiol groups on the substrate that belong to molecules with both ends attached to the substrate. Clearly, $N_r(t) = N_r^S(t)/2$. When the time dt has elapsed, we get a decrease in $N_r^S(t)$ given by

$$dN_r^S(t) = -2vN_r^S(t)dt \tag{7}$$

where the factor 2 occurs because the desorption of one thiol group results in the decrease of a factor of 2 in $N_r^S(t)$. In fact, on one side we have the thiol group being detached, on the other side the other remaining attached to the substrate no longer counts for $N_r^S(t)$. Since $N_r(t) = N_r^S(t)/2$, Eq. (7) may also be written as

$$dN_r(t) = -2vN_r(t)dt \tag{8}$$

So that the time evolution of $N_r(t)$ will be given by

$$N_r = Ne^{-2vt} \tag{9}$$

Replacing (9) into (6) and solving for $n(t)$ leads to the relationship:

$$n(t) = 2N e^{-vt}(1 - e^{-vt}) \tag{10}$$

which exhibits the same qualitative behavior as that of the transients shown in Fig. 6. This function presents a maximum for $t = t_{max} = \ln(2)/v$ and $N = N_{max} = N/2$. Theoretical transients according to Eq. (10) are superimposed as dashed lines with the results of the simulations in Fig. 6, where a good agreement is found, especially at large number of molecules.

3.2. Short time simulations

They refer to those simulations in which the time interval considered is such that only few events occur.

To discuss this item in analytical grounds first, we will assume that the initial state of the system is one where a relatively large number of molecules is adsorbed in a flat orientation of the surface of the substrate.

According to the theory of Poisson events, we expect that the probability that m events take place in a certain time interval t_{obs} will be given by the following equation:

$$P_n = \frac{(\int_0^{t_{obs}} r(t)dt)^n e^{-\int_0^{t_{obs}} r(t)dt}}{n!} \tag{11}$$

where $r(t)$ is, in principle, a time-dependent rate. As stated above, if we restrict our observation to a relatively short times (few events) and a large number of molecules, we can assume that $r(t) \approx Nv$, so that Eq. (11) becomes:

$$P_n = \frac{(Nvt_{obs})^n e^{-Nvt_{obs}}}{n!} \tag{12}$$

Interestingly, Eq. (12) can be compared with available experimental results. To this end, we revisit the work of Haiss et al. in Fig. 4c, the authors show a number of histograms of conductance, where five maxima are found at multiples of a basic current unit. For the present purposes, we are not focused on the spread of the conductance values, but rather on the number of molecular wires

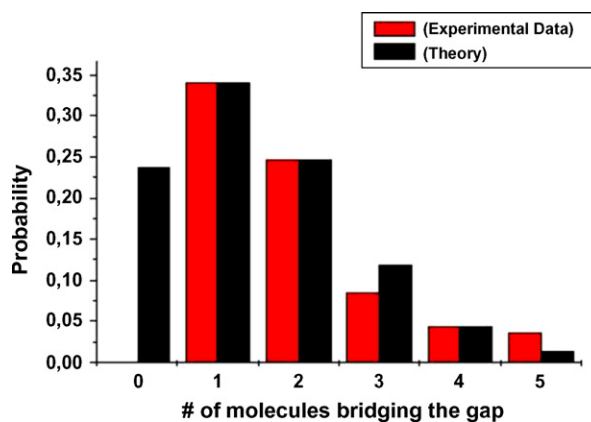


Fig. 7. Histograms showing the probability of finding a certain number of molecules trapped between a substrate and a tip. The light bars show the data of Fig. 4c of Ref. [11] re-plotted upon collecting together all the counts corresponding to the same number of molecules at the gap. The black bars are predictions according to Eq. (12). Note that the theoretical prediction also considers the observation of none molecule bridging the gap.

detected in the $I(s)$ experiments and that were formed while the tip was held close to the substrate. Thus, we have replotted these experimental data in a more compact form in Fig. 7. The height of each of the light bars represents the probability of observing a given number of molecules at the gap. In the same figure, black bars describe the prediction according to Eq. (12). The theoretical results involve only one fitting parameter, namely the product Nvt_{obs} , obtained from the experimental value of the ratio $(2P_2/P) = Nvt_{obs} = 1.443$. It can be noted that the theoretical prediction closely resembles the experiment. Furthermore, the results predicted also include P_0 , the probability that no molecule is adsorbed at the gap. This is a quantity that should also be measured and could provide relevant information on the present phenomenon.

As discussed above, Eq. (12) is an approximation assuming that the number of molecules adsorbed at the substrate remains unchanged. If the number of molecules is small, Eq. (12) could not be a good approximation, since the factor $r(t)$ in Eq. (11) will be a function of $n(t)$ and as a result, of time. In order to analyze this point, we have performed KMC to test the effect of a relative small number of molecules at the gap on the histograms. We have chosen to simulate a period of time t_{obs} that fulfills the condition $Nvt_{obs} = 1$.

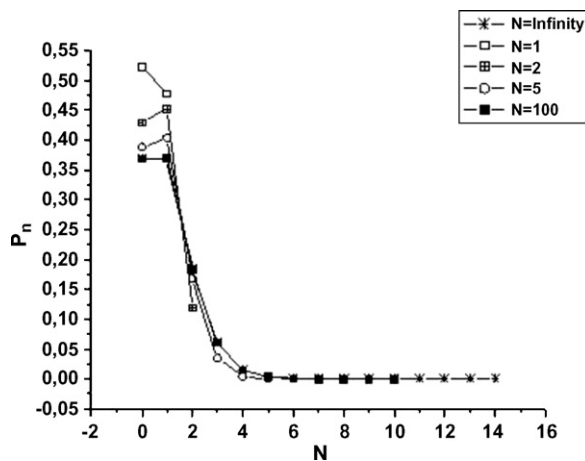


Fig. 8. Values of the probabilities of finding a certain number of molecules trapped between a substrate and a tip according to simulations with different number of molecules for the case where the simulation time is such that $Nvt_{obs} = 1$. The case labeled as "Infinity" corresponds to the application of Eq. (12).

Fig. 8 displays the results found for different numbers of molecules trapped at the gap. The case labeled as “Infinity” corresponds to the straightforward application of Eq. (12). It is interesting to note that the case of $N = 100$ yields results which are practically identical with the prediction of Eq. (12). Moreover, even a small number of molecules such as 5, exhibits a behavior that is qualitatively similar to the “Infinity” case. However, the distinct feature is that in the case of a finite number of molecules and for this observation time, P_1 is slightly larger than P_0 .

4. Conclusions

We have set up the basis of a stochastic model that can be used to analyze the development of bonds at the interface formed by a substrate surface and a STM tip. The model was analyzed by means of kinetic Monte Carlo simulations and, in some cases, analytic predictions were made. In the case of long time observations, the model may be applied to obtain information on the rate constants associated with the process and the number of molecules trapped at the gap. In the case of short time observations, the results of the model were compared with experimental results, which led to predictions in good agreement with experiment.

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