A study of surface diffusion with the scanning tunneling microscope from fluctuations of the tunneling current

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A study of surface diffusion with the scanning tunneling microscope from fluctuations of the tunneling current

by

Manuel Leonardo Pasetes Lozano

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

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There are a couple of things that academic education can never accomplish: inculcate wisdom and build character.

The fear of the Lord is the instruction for wisdom, and before honor comes humility.
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ACKNOWLEDGEMENTS

It is almost impossible to find a work which was done, from start to finish, solely by one person. Usually it is the cooperative effort of a number of people who add bits and pieces, with one person who takes the time to organize and synthesize these numerous contributions into a whole. This work is not an exception.

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1. INTRODUCTION

1.1 General

The transport of atoms or molecules over surfaces has been an important area of study for several decades now, with its progress generally limited by the available experimental techniques to characterize the phenomena. A number of methods have been developed over the years to measure surface diffusion yet only very few systems have been characterized to this day mainly due to the physical limitations inherent in these available methods. Even the STM with its astonishing atomically-resolved images of the surface has been limited in terms of its capability to determine mass transport properties. This is because the STM is inherently a "slow" instrument, i.e., a finite time is needed for signal averaging in order to produce the image. A need exists for additional surface diffusion measurement techniques, ideally ones which are able to study varied systems and measure a wide range of diffusion rates. The STM (especially because of its highly local nature) presents itself as a promising tool to conduct dynamical studies if its poor time resolution during "normal operation" can somehow be overcome.

The purpose of this dissertation is to introduce a new technique of using the STM to measure adatom mobility on surfaces—one with a capacity to achieve excellent time resolution. We do this by monitoring the time dependence of the tunneling
current fluctuations, specifically from its power spectrum or autocorrelation function. We shall show later that diffusion parameters can be simply extracted from the decay of either of these two functions. We have tested this technique on oxygen adsorbed on stepped Si(111) and present the results here. Aside from possessing a high time resolution the technique is highly local and can measure a wide range of diffusion rates. To the author's knowledge there has been only one other attempt to use the STM for time-resolved studies [1] but because it attempted to attain both time and spatial resolution simultaneously, questionable assumptions were made in order to extract diffusion parameters. The technique we introduce here allows the STM to be both spatially and time resolved but not at the same time. When diffusion measurements are conducted and time resolution is necessary, spatial resolution is sacrificed but only during the measurement. It thus serves as an appropriate complement to the spatially resolved studies which the STM has exclusively been used for.

In addition, we have also conducted Monte Carlo simulations, in conjunction with the experiments, to understand possible limitations of the technique. These are discussed here as well.

This dissertation is organized as follows. In the next section we give a brief description of surface diffusion and introduce the surface diffusion coefficient. The first part of Chapter 2 explores how the STM is currently utilized for surface diffusion studies, from which a different method of using the STM so that high time resolution may be achieved is proposed. Our experimental set up is described in Chapter 3, followed by a presentation and discussion of the results for O/Si(111). Chapter 4 discusses possible limitations of the method that may have to be considered: these are factors that could result in a measured value different from the true value; or
those that cause the act of measurement to interfere with the physical quantity being measured, possibly leading to spurious results. Finally a summary and a general assessment of the technique is given in Chapter 5.

1.2 A Brief Surface Diffusion Primer

When we think of surface diffusion the picture that usually comes to mind is that of a single atom diffusing on a crystal plane. In reality, however, the measured values of the diffusion coefficient require a more complex interpretation than just that of a single particle hopping. In fact, as we shall describe shortly, there are two "kinds" of surface diffusion coefficients and the current experimental methods have mostly been sensitive to only one kind.

When an atom or molecule adsorbs on a surface, the specific site at which it adsorbs—whether this be directly on top of a surface atom (an on-top site) or bridging nearest neighbors (a hollow site)—will just be a position of lowest potential energy, i.e., it is in an equilibrium position (see Figure 1.1). The difference in energy between the potential minima (or the trough) and that of the saddle point is customarily called the diffusion activation energy, $E_d$, while the energy required for an atom to desorb from the surface back into the gas phase is the binding energy, $E_b$. $E_d$ is usually a few percent of $E_b$ (in metals, it is found to be around 20% [2]). Due to the finite temperature of the substrate an adsorbate vibrates about its equilibrium position with a frequency comparable to the Debye frequency of the substrate. When it acquires enough energy from the phonon bath to overcome the barrier, $E_d$, the adatom "jumps" or "hops" to an equivalent site: another potential minima. So long as $E_d \gg k_B T$ (this is usually satisfied except at very high temperatures), the time an
Figure 1.1: A representation of adsorption sites and potential surface. (a) An atom may adsorb on a hollow site or an on-top site. (b) Where an atom adsorbs corresponds to an equilibrium position (1). The difference in energy between the potential minimum (1) and the saddle point (2) is called the diffusion barrier, $E_d$. Overcoming the diffusion barrier allows an adsorbate to move laterally on the surface while it takes a larger amount of energy, $E_b$, for an adsorbate to desorb back to the gas phase.

An adatom spends in an adsorption site is much greater than the time it takes to hop, making the jumping process Markovian and ensuring the unlikelihood of simultaneous events or hops occurring. Hence this thermally activated hopping process (or diffusion) would just be a random walk in two dimensions (assuming isotropic diffusion).

The mean square displaceament of the atom will then be proportional to the time:

$$\langle |r(t) - r(0)|^2 \rangle = 4D_z t. \quad (1.1)$$

$D_z$ is known as the self-diffusion coefficient or the tracer diffusion coefficient because it “traces” the path of the diffusing particle. For a system of $N$ particles, (1.1) can
be written as

\[ D_s = \frac{1}{4Nt} \sum_{i=1}^{N} (|\vec{r}_i(t) - \vec{r}_i(0)|^2). \]  

(1.2)

The "other kind" of diffusion coefficient, \( D \), is most familiar to us as the proportionality constant in Fick’s law,

\[ \vec{J}(\vec{r}, t) = -D \nabla n(\vec{r}, t) \]  

(1.3)

where \( \vec{J} \) is the particle flux and \( n \) the adsorbate number density. This is the chemical (or collective) diffusion coefficient, referring to mass transport in response to differences in chemical potential.

If we combine equation (1.3) with the continuity equation

\[ \nabla \cdot \vec{J} = -\frac{\partial n}{\partial t}, \]

we get

\[ \nabla \cdot \vec{J} = D \nabla^2 n \]  

(1.4)

if \( D \) is not a function of \( \vec{r} \) and is independent of the concentration.

The diffusion coefficient is also commonly expressed as the product of the mean-square jump distance, \( l^2 \), and the effective jump frequency, \( \nu \),

\[ D = l^2 \nu, \]  

(1.5)

the effective jump frequency being

\[ \nu = \nu_0 \exp(\Delta S/k_B) e^{-E_d/k_B T} \]  

(1.6)

where \( \nu_0 \) is the vibrational frequency of the adatom, \( \Delta S \) the difference in entropy between the potential minima and the saddle point in Figure 1.1, and \( E_d \) the diffusion
barrier. The diffusion coefficient can thus be written—and is customarily done—as

\[ D = D_0 e^{-\frac{E_d}{k_B T}} \]  

(1.7)

with the prefactor, \( D_0 = \frac{\hbar^2}{2m} \exp(\Delta S/k_B) \).

In most real systems it is almost impossible to measure the self-diffusion coefficient because of the requirement of observing a single atom hopping on a crystal plane [3, 4, 5, 6, 7, 8, 9]. Excluding field ion microscopy, surface diffusion measurements usually measure the chemical diffusion coefficient. For example, we can create a profile of atoms of known concentration in a region on the surface, allow it to evolve diffusively, and measure the profile as a function of time [10]. Even in field ion microscopy, observation of single atom diffusion is extremely limited to very small distances because of the size of crystal planes achievable with a sharp emitter, as is used in FIM. But while both the self (or tracer) and chemical diffusion coefficients arise from the random motion of atoms on the surface, in general, the tracer diffusion coefficient is easily interpretable in terms of single atom hops but the chemical diffusion coefficient is not.

To relate \( D \) and \( D_s \) we express the two diffusion coefficients in terms of velocity-velocity correlation functions [11]. Without loss of generality, we let \( \vec{r}(0) = 0 \) in equation(1.1) and write for the tracer diffusion coefficient,

\[
\langle |\vec{r}|^2 \rangle = \left\langle \left| \int_0^t v(t)dt \right|^2 \right\rangle
\]

\[
= \left\langle \int_0^t \vec{v}(t')dt' \int_0^t \vec{v}(t'')dt'' \right\rangle
\]

\[
= \int_0^t dt' \int_{-t'}^{t-t'} ds \left( \vec{v}(t') \cdot \vec{v}(t' + s) \right)
\]
\[
\langle \vec{r}^2 \rangle = 2t \int_0^t ds \langle \vec{v}(s) \cdot \vec{v}(0) \rangle = 2t \int_0^\infty ds \langle \vec{v}(s) \cdot \vec{v}(0) \rangle.
\]

Equation (1.1) can then be written as

\[
D_s = \frac{1}{2} \int_0^\infty dt \langle \vec{v}(t) \cdot \vec{v}(0) \rangle \tag{1.8}
\]

or for \(N\) particles,

\[
D_s = \frac{1}{2N} \sum_{i=1}^N \int_0^\infty dt \langle \vec{v}(t) \cdot \vec{v}(0) \rangle. \tag{1.9}
\]

We can use the Green-Kubo formula for the chemical diffusion coefficient (for brevity, we omit the lengthy derivation which can be found in reference [12]),

\[
DK \bar{n}^2 = 2k_B T A \int_0^\infty dt \langle \vec{J}(t) \cdot \vec{J}(0) \rangle, \tag{1.10}
\]

where \(\vec{J}(t) = \sum_{i=1}^N \vec{v}_i(t)\) is the total particle flux and \(K\) is the adlayer compressibility with

\[
K = \frac{\langle (\delta N)^2 \rangle}{k_B T \bar{n}^2 A} \tag{1.11}
\]

giving

\[
DK \bar{n}^2 = \frac{1}{2k_B T A} \int_0^\infty dt \langle \sum_{i=1}^N \vec{v}_i(t) \cdot \sum_{j=1}^N \vec{v}_j(0) \rangle. \tag{1.12}
\]
We can simplify equation (1.12) by separating the double summation into a summation over the same particle plus that involving different particles to get

\[
DK\bar{n}^2 = \frac{\bar{n}}{k_B T} \cdot \frac{1}{2N} \sum_{i=1}^{N} \int_0^\infty dt (\vec{v}(t) \cdot \vec{v}(0))
\]

\[
+ \frac{1}{2k_B T A} \int_0^\infty dt (\sum_{i \neq j} \vec{v}_i(t) \cdot \vec{v}_j(0))
\]

(1.13)

\[
= \frac{\bar{n}}{k_B T} D_s + \frac{1}{2k_B T A} \int_0^\infty dt (\sum_{i \neq j} \vec{v}_i(t) \cdot \vec{v}_j(0)).
\]

(1.14)

Clearly, if there are no correlations between the velocities of different particles, i.e.,

\[
\langle \sum_{i \neq j} \vec{v}_i(t) \cdot \vec{v}_j(0) \rangle = 0
\]

we have a simple relationship between the two diffusion coefficients:

\[
D = \frac{D_s}{k_B T \bar{n} K} = \frac{\langle N \rangle}{\langle (\delta N)^2 \rangle}.
\]

(1.15)

This result can also be derived from the so-called Darken equation [3, 11, 13, 14],

\[
D = \frac{\partial (\mu/k_B T)}{\partial (ln(\bar{n}))} D_s,
\]

(1.16)

where the chemical potential, \(\mu\), takes the form

\[
\mu = \mu_0 + k_B T \ln \frac{\bar{n}}{1 - \bar{n}}
\]

(1.17)

when there are no adsorbate-adsorbate interactions (\(\mu_0\) is the standard chemical potential).

As mentioned earlier, most measurements could only access the chemical diffusion coefficient and are macroscopic, i.e., diffusion lengths on the order of \(10^{-2}\) cm or greater are necessary in the measurement. Easily, diffusion at these length scales will
be subject to effects of discontinuities on the surface like steps and domain boundaries. There is no question that surface morphology affects adatom mobility and most current measurement techniques lack the capability of separating their effects mainly because of these techniques' macroscopic nature. Methods employing field ion microscopy and field emission [3], on the other hand, are microscopic by virtue of the small plane area at the tip of a sharp field emitter: typically 50Å–100Å. This limits the range of diffusion that may be investigated. Moreover, the high field employed in the measurement (~ $10^7 - 10^8$ V/cm) could modify the surface thus limiting the investigation to specific materials. Microscopic surface diffusion measurement on semiconductor surfaces have been virtually non-existent.
2. A PROPOSED MEASUREMENT SCHEME

2.1 Current STM Surface Diffusion Techniques and Their Limitation

With the discovery of the STM came the promise of more robust methods of studying adatom motion on the surface, free (or almost free) from the effects which may be induced by steps or other surface inhomogeneities. Now with the STM, these effects may be delineated: not incorporated to produce an average measured value, as is done with the macroscopic techniques, nor eliminated, as in field ion microscopy where the choice of substrates is limited and finite size effects need to be accounted for. The extent of the diffusion plane is now limited by the area of the surface that may be prepared perfectly\(^1\) and diffusion on semiconductor surfaces may now also be investigated. Likewise, experiments may now be conducted at much lower voltages (\(~a~few~volts\) as opposed to \(~10^3\) volts) although with still considerable fields: the voltages used are a few orders of magnitude lower than that for field emission or field ion microscopy, but the separation between electrodes is also reduced (a few angstroms as opposed to several centimeters).

Diffusion measurements with the STM could either have high spatial but low time resolution (like field ion microscopy) or have poor spatial but high time resolution (like the field emission methods). The astonishing spatial resolution achieved with the

\(^1\)Terraces as wide as 1 \(\mu m\) are not uncommon.
STM has driven the proliferation of spatially-resolved (but with poor time resolution) STM diffusion methods[15, 16, 18, 19]. To the author’s knowledge, no “real-time” diffusion measurements have yet been performed. Although it seems that atomic and time resolutions need not be mutually exclusive, the limited electronic response time of the STM may make this so, as we shall see later.

The usual method employed in taking advantage of the atomic resolution of the STM is the “freeze-and-look” method [15]. Here we take scans to record the surface morphology after certain events have been allowed to occur, i.e, look at the “freeze frame.” Detective work is then done to reconstruct the events (e.g., individual atomic hops and nucleation into islands) that must have led to the observed morphology to deduce surface diffusion parameters. Two general types of measurements using this method have been done to this day.

When adatoms are deposited onto a surface, they perform random walk and eventually agglomerate into 2D islands. An adatom on a terrace can have one of two fates. As it is performing random hops among lattice sites, it can join other adatoms and form islands, promoting nucleation, or it may find an edge (of an existing island, for example), thus promoting island growth. We can see that the morphology achieved will be very strongly influenced by the competing mechanisms of nucleation and growth. By varying the flux or the temperature we can change the number density and the size of islands. Assuming isotropic diffusion and a critical size cluster of one, for a given deposition rate, \( R \), the density of islands, \( N \), is related to the diffusion coefficient, \( D \), by

\[
N^3 = \frac{3R\theta}{D}
\]  

where \( \theta = Rt \) is the total dose after a time \( t \). Increasing the deposition rate, \( R \), gives
an adsorbate less time to find an existing island before the next atom is deposited and an increase in island density is observed, while increasing the temperature gives the adatoms greater mobility so that bigger islands (but fewer of them) are formed. Thus by varying the deposition rate and the substrate temperature, the diffusion coefficient is calculated by simply counting the number of islands in an STM image. This has been demonstrated with Si/Si(001) [15].

The second type of measurement using the "freeze-and-look" method operates on the same methodology but measures a different quantity. This time we monitor the random walk performed by adatoms on a surface. Atoms are deposited on the surface and an image is taken at a temperature \( T_0 \) while the adsorbed species are immobile. This records the initial position of the adsorbates. From immobility, adatoms are induced to execute random hops, usually by annealing the sample to a temperature \( T > T_0 \) for a duration \( \Delta t \), and then quickly quenching the sample back down to \( T_0 \). A scan done after quenching would then record the new position of the adsorbates. The motion from the "old" to the "new" position would then be solely due to the thermal bath at \( T \) for the duration \( \Delta t \). Several successive image–anneal–image sequences at different temperatures could then allow a statistically meaningful measurement of the mean square displacement of the adatoms, leading to the extraction of the self diffusion coefficient. This has been done with Sb/Si(001) [17] with Sb known to be immobile at room temperature.

It has been shown, however, that the scanning procedure may influence the motion of adatoms on the surface. For example, for the study of Sb/Si(001) previously mentioned, images taken when Sb was known to be mobile enhanced the measured diffusion rate by nearly an order of magnitude at 479K. Clearly, field-assisted diffu-
sion is heightened by the scanning process here. A similar study on Pb/Ge(111) [16] has been done where images were taken when the species were mobile. By prolonging the scanning time and observing no difference between the jump rates of the slow and fast scan rates, and because Pb is observed to be more mobile as the temperature is increased, it was concluded that the effect of the scanning process on the measured diffusion coefficient is negligible. This brings up two things. First, it is reasonable to assume that the effect of the scanning process, mainly due to the high, inhomogeneous (concentrated underneath the tip) electric field, on the diffusion of adsorbates is strongly system-dependent and thus it is necessary to understand the extent of these effects based on the physical properties of the adsorbates. Secondly, if atomic jumps are affected by the field over the temperature range of the experiment, it may not be possible to decouple the effect of the field except by comparison with the unaffected measurement. We will show from simulation results to be discussed in a later section that it is during the “early times” that the field has its maximum effect on the mobility of adatoms therefore prolonging the scan will not necessarily reveal any field effects. Likewise, whether the field affects adatom mobility or not, an increase in jump rate occurs with increasing temperature so that it is not reasonable to conclude that the mobility is not affected by the field because movement rate increases with temperature. Ultimately, much more reliable measurements using this methodology are made when images are taken when the adsorbates are immobile. This limits the technique to systems which are immobile at room temperature. In addition, the adsorbate species should also be distinct from the substrate under the STM. Alternatively, the sample can be cooled to low temperatures. Although this is already done, it still poses engineering challenges to avoid additional vibrational
and/or electrical noise coupling to the signal via whatever extra design specifications that have to be considered to achieve effective cooling of the sample.

We now pose the question, "Is it possible to do real-time diffusion measurements with the STM?" Using the current or more popular paradigm in devising STM-based surface diffusion measurement techniques basically requires the ability to take images (i.e., the frequency of taking images) at least as frequent as twice the fastest jump rate of adatoms. This, of course, also implies that the scanning process itself should be ultrafast! Considering the typical scanning rates which are limited by the electronics that drive the system (∼512x512 pixel points at a few μsecs per point), it would be necessary to cool the sample. In addition, the scan rates should be flexible enough to accommodate both fast and slow adatom motion. Moreover, if the diffusion barriers are not uniform throughout the whole temperature range (i.e, if the derived Arrhenius plot is not applicable to all temperatures of significance) and if the measurements are taken at low temperature, the measured values may only be applicable to the low temperature regime and possibly different at room and higher temperatures. Thus it seems that dynamical measurements requiring atomic resolution limits the time resolution achievable with the STM by several orders of magnitude. This cannot be avoided in the scanning process because a finite amount of time spent at each pixel-point buys enhancement of the signal-to-noise ratio, thereby producing the excellent spatial resolution. The tunneling time or typical time for an electron to traverse the barrier (tip-to-substrate separations are in the order of several angstroms) is $10^{-15}$–$10^{-14}$ seconds [20] which should afford, in principle, an excellent time resolution. The scanning process, therefore, limits the flexibility of the STM as a tool for dynamical studies. If a better time resolution is desired the scanning process may have to be
abandoned, even only for the duration of the measurement.

2.2 Adopting a New Paradigm in Using the STM

We therefore go back to the the basic physical process in the STM. The essence of the STM is the "controllable" quantum mechanical tunneling of electrons from one electrode to another. Hence, ideally, the physical limitation to the resolution of any time-resolved study conducted with the STM is only or should only be the tunneling time for the electron. Any surface process which we desire to measure has to, ultimately, affect the tunneling current or else remain undetectable. Given an ideal barrier, for example, the tunneling current would be constant for a set tip-to-substrate voltage. For a clean surface in a real system, the tunneling current will be broadened by random electrical and possibly vibrational noise inherent in the experimental set-up. In properly functioning microscopes, this noise is only a few percent of the tunneling current and is thus negligible and changes in the tunneling current would be about this mean current value. Adsorbates on a surface alter the local work function of the surface, therefore adsorbates on the surface in the vicinity of and including the area directly underneath the tip have a direct, static influence on the tunneling current. Now if these adsorbates were mobile, the tunneling current will be changing in response to the random motion of the adsorbates. Hence we expect the mobility of adatoms on the surface to cause tunneling current fluctuations because of the current's dependence on the local work function of the surface. We take advantage of this cause-and-effect relationship between adatom mobility and tunneling current fluctuations to devise a method of sensing and characterizing surface diffusion [21].

If a sharp tip is positioned few angstroms from a surface, an area on the surface
defined by the solid angle subtended by the apex of the atomically sharp tip can be labelled as the probe region, as in Figure 2.1 (a), from which most of the tunneling electrons go to or come from. If now the surface is covered with adsorbates, these adatoms will randomly hop from one lattice site to another in response to adsorbate concentration gradients locally, when the energy derived by the adatoms from the phonon bath is sufficient to overcome the diffusion barrier. Counting the number of particles in the probe region as a function of time would then give us Figure 2.1 (b), where the dotted line corresponds to the mean number of particles in the probe region, proportional to the surface coverage.

Two characteristic time scales can be defined: the time it takes for an adsorbate to cross the tunneling region, \( t' \); and the average time between visits of an adatom to the probe region, \( \tau \). In general, \( \tau \) is the more accessible quantity due to less stringent

![Figure 2.1: A proposed measurement scheme. (a) Atoms diffusing into or out of the probe region (shaded area) directly underneath the tip cause fluctuations in the number of atoms in the probe region. (b) In a graph of particle number versus time, two characteristic times can be defined: the mean time an atom stays in the probe region, \( t' \); and the mean time between visits of an atom to the probe region, \( \tau \). Both characterize adatom diffusion.](image)
demands on the electronic response of the instrument.

We now construct the number autocorrelation function\(^2\) of the number of particles wandering into or out of the probe region of area \(A\):

\[
\tilde{c}(t) = \langle \delta N(0) \delta N(t) \rangle \tag{2.2}
\]

where \(\delta N(t) = N(t) - \langle N \rangle\), and \(\langle N \rangle\) = mean particle number in \(A\). If we define the number density

\[
n(t) = \frac{N(t)}{A}
\]

then

\[
\tilde{c}(t) = \langle \int_A d^2 \vec{r} \delta n(\vec{r},0) \int_A d^2 \vec{r}' \delta n(\vec{r}',t) \rangle
\]

\[
= \int_A d^2 \vec{r} \int_A d^2 \vec{r}' \langle \delta n(\vec{r},0) \delta n(\vec{r}',t) \rangle. \tag{2.3}
\]

Assuming that these microscopic fluctuations decay according to macroscopic laws (Onsager's hypothesis) \([24]\) and thus follow the continuity equation:

\[
\frac{\partial}{\partial t} \delta n(\vec{r},t) = \nabla \cdot (D \nabla \delta n(\vec{r},t)) \tag{2.4}
\]

\[
= D \nabla^2 \delta n(\vec{r},t). \tag{2.5}
\]

This will be the form of Fick's second law applied to number density fluctuations.

If we multiply both sides of equation (2.5) by the density fluctuation at \(\vec{r} = 0, t = 0\) and take the ensemble average we can write equation(2.5) as

\[
\frac{\partial}{\partial t} \langle \delta n(\vec{r},t) \delta n(0,0) \rangle = D \nabla^2 \langle \delta n(\vec{r},t) \delta n(0,0) \rangle \tag{2.6}
\]

\(^2\) An excellent treatment of fluctuations and correlation functions in relation to measuring physical quantities is given in reference \([23]\).
where $\langle \rangle$ denotes averaging over the ensemble, or

$$\frac{\partial}{\partial t} S(\vec{r}, t) = D \nabla^2 S(\vec{r}, t) \tag{2.7}$$

where we define

$$S(\vec{r}, t) = \langle \delta n(\vec{r}, t) \delta n(0, 0) \rangle. \tag{2.8}$$

We can, in general, define[3]

$$S(\vec{r}, t) \rightarrow S(\vec{r} - \vec{r}', t) = \langle \delta n(\vec{r}, t) \delta n(\vec{r}', 0) \rangle \tag{2.9}$$

which, in the hydrodynamic limit becomes independent of time and can be approximated by a series of delta functions as in a perfect lattice. Then

$$S(\vec{r} - \vec{r}', t) = \sum_j e^{ik|\vec{r} - \vec{r}'|} = S(\vec{r}, t). \tag{2.10}$$

If we define the fourier transform

$$S(\vec{k}, t) = \int_{-\infty}^{\infty} d^2 \vec{r} e^{-i\vec{k} \cdot \vec{r}} S(\vec{r}, t) \tag{2.11}$$

Then

$$S(\vec{r}, t) = \frac{1}{2\pi^2} \int_{-\infty}^{\infty} d^2 \vec{k} e^{i\vec{k} \cdot \vec{r}} S(\vec{k}, t). \tag{2.12}$$

Upon substitution of equation (2.12) into equation (2.7),

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} d^2 \vec{k} e^{i\vec{k} \cdot \vec{r}} S(\vec{k}, t) = D \nabla^2 \int_{-\infty}^{\infty} d^2 \vec{k} e^{i\vec{k} \cdot \vec{r}} S(\vec{k}, t) \tag{2.13}$$

$$\int_{-\infty}^{\infty} d^2 \vec{k} e^{i\vec{k} \cdot \vec{r}} \left[ \frac{\partial}{\partial t} S(\vec{k}, t) - D \nabla^2 S(\vec{k}, t) \right] = 0 \tag{2.14}$$

or

$$\frac{\partial}{\partial t} S(\vec{k}, t) = D k^2 S(\vec{k}, t) \tag{2.15}$$
with solution

\[ S(\vec{k}, t) = e^{-k^2 D t} S(\vec{k}, 0) = S_0 e^{-k^2 D t}. \]  

Equation (2.12) then becomes

\[ S(\vec{r}, t) = \frac{S_0}{(2\pi)^2} \int_{-\infty}^{\infty} d^2 \vec{k} e^{i\vec{k} \cdot \vec{r}} e^{-k^2 D t} \]  

Going back to (2.3) and using (2.17),

\[
\bar{c}(t) = \int_A d^2 r \int_A d^2 \overline{r} \left[ \frac{S_0}{(2\pi)^2} \int_{-\infty}^{\infty} d^2 \vec{k} e^{i|\vec{k} \cdot \overline{r}|} e^{-k^2 D t} \right]
\]

\[ = \frac{S_0}{(2\pi)^2} \int_{-\infty}^{\infty} d^2 \vec{k} \int_A d^2 r \int_A d^2 \overline{r} e^{i|\vec{k} \cdot \overline{r}| - \vec{k} \cdot \vec{r}} e^{-k^2 D t} \]

which upon integration over \( d^2 \overline{r} \) gives

\[ \bar{c}(t) = S_0 \int_A d^2 r \int_A d^2 \overline{r} \frac{e^{-|\vec{r} - \overline{r}|^2 / 4Dt}}{4\pi Dt} \]  

where the appearance of the diffusion coefficient becomes apparent. The constant

\[ S_0 = \langle \delta N^2 \rangle / A \]  

whence

\[ \bar{c}(t) = \frac{\langle \delta N \rangle^2}{A} \int_A d^2 r \int_A d^2 \overline{r} \frac{e^{-|\vec{r} - \overline{r}|^2 / 4Dt}}{4\pi Dt}. \]

This correlation function has a very simple physical interpretation if we recognize that

\[ \lim_{t \to 0} \frac{e^{-|\vec{r} - \overline{r}|^2 / 4Dt}}{4\pi Dt} = \delta(\vec{r} - \overline{r}, t = 0), \]

a delta function. A delta function fluctuation of uniform strength \( \langle \delta N \rangle \) is placed at \( \vec{r} \) in \( A \) at \( t = 0 \) and allowed to evolve diffusively (i.e., obeying Fick's second law) with time. What remains in \( A \) (integration over \( \vec{r} \) in \( A \)) is multiplied by the initial strength to get the correlation function. In other words, it is equivalent to solving for the concentration profile.
In summary, constructing the number correlation function easily affords the diffusion coefficient, $D$. The decay time $\tau$ in Figure 2.1 (b) is related to the correlation function by

$$\tau = \frac{r_0^2}{4D}$$

(2.23)

where $r_0$ is the radius of the probe area.

Alternatively, the spectral density of the fluctuations can be constructed instead of, or in addition to the correlation function since

$$\tilde{W}(f) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{c}(t)e^{i2\pi ft}dt$$

(2.24)

by the Wiener-Khinchin formula.

Going back to the STM geometry, we realize that since fluctuations in the number density of particles in the tunneling region result in changes in the local work function, thereby causing fluctuations in the tunneling current, the tip could act as a “counter” of the particles in the probe region. In other words, the same diffusion-related quantities may be extracted by constructing the time autocorrelation function of the tunneling current fluctuations,

$$c(t) = \langle \delta i(t + s) \delta i(s) \rangle$$

(2.25)

with $\delta i(t) = i(t) - \langle i \rangle$ (and $\langle i \rangle$ is the average tunneling current) or taking its power spectrum,

$$W(f) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \delta i(t + s) \delta i(s) \rangle e^{-i2\pi ft} dt.$$  

(2.26)

We point out that this is basically an extension of the field emission fluctuation method in the limit that the probe area shrinks to a “single site.” There are

---

3 This will be interchangeably called “power spectrum.”

4 $\delta i = k\delta n$, with $k$ constant for a given system.
immediately some advantages to this new technique compared to the field emission technique: a smaller probe area will contain less adsorbates so that fluctuations are dramatically a larger percentage of the mean number in the probe region than those observed in field emission current fluctuations; and signal discreteness, especially when measuring very fast processes, ceases to be a problem because of the enhanced fluctuation signals.
3. THE EXPERIMENT

3.1 The Experimental Set Up

To test the viability of this technique, we performed experiments with oxygen adsorbed on a stepped Si(111) substrate. Prior to data collection the STM is operated in the constant tunneling current mode with the tunneling current typically set to 700 pA. A tungsten tip is positioned on a spot in the middle of a wide terrace and the feedback loop suspended (while the data are taken) in order to maintain a non-varying tip-to-sample separation for the duration of the sampling. The power spectra of the tunneling current fluctuations at different substrate temperatures for both clean and oxygen-covered surface are measured. Several sets of these measurements were taken to get a statistically meaningful measurement.

Experiments were conducted in an ion-pumped vacuum chamber maintaining a base pressure of \(~5 \times 10^{-11}\) Torr. The STM itself is mounted on an 8-inch stainless steel flange and consists of two major solid blocks (also made of stainless steel): an outer movable block housing the sample; and an inner, stationary block containing the tip assembly. A more rigid design using a combination of mechanical (1/4-80 screws, and gear and lever reduction are used for coarse tip-to-sample approach) and piezoelectric (using a tube scanner, as soon as the feedback loop is established) methods are used to control the tip-to-substrate separation. PZT5A is used for the
tube scanner of length 0.50", outer diameter 0.250", thickness 0.02", and is coated with four 90°-sectioned nickel electrodes on the outside to control the position of the tip.

Tip-to-sample approach is achieved in three stages: the coarse, semi-fine, and fine motions. The sample block is held from the block housing the tip using springs and three 1/4-80 screws mounted on gears, which are also used to control the tip-to-sample separation. To approach with the coarse motion the three screws are retracted simultaneously so that the entire block where the sample is mounted moves toward the tip; resolution using coarse motion is limited to ~1μm. Approaching with the coarse motion is usually done outside vacuum where the tip and sample assembly may be observed by eye or with an optical microscope. It is not advisable, although sometimes it is unavoidable, to achieve tunneling while using coarse motion, i.e., while all three gears are engaged because minute turns of the linear-rotary feedthrough may cause the tip to crash into the sample. Two of the three gears are disengaged when shifting to semi-fine motion and the resolution is increased by a factor of twenty because of gear and lever reduction. Semi-fine motion is used to establish the closed current loop (i.e., to tunnel). Instead of retracting the lone engaged screw it is pushed away, resulting in the tilting of the sample toward the tip but at increments of <200Å that the feedback mechanism can avert the tip crashing into the sample. The feedback automatically kicks in when the tunneling current nulls out the preset current level. At this point, voltages are applied to the outer portion of the tube scanner to control the tip-to-substrate separation, i.e., the z-motion with a response of ~80Å/V. Motion using the piezoelectric tube scanner comprise the fine motion. Applying the same voltage to all four electrodes cause the tube scanner
to either contract or expand (i.e., motion is perpendicular to the applied field and along the axis of the tube), depending on the polarity of the applied voltage and the polarization of the piezoelectric tube. If the voltage is applied to only one of the electrodes, only that quadrant of the tube will contract or expand. This produces a "bending motion," this time perpendicular to the tube axis, which is equivalent to lateral or x-y motion. Larger displacements are achieved when voltages of opposite polarity are applied to diametrically opposed electrodes. Line scans are performed by ramping the voltage on two diametrically opposite electrodes while keeping the other two electrodes at constant voltage. Successive line scans produce a two-dimensional image. It should be noted that because only a single tube scanner is used, the x, y, and z directions are coupled. This is called the "cross-talk" and has to be corrected for in the images by an appropriate subtraction from the final voltage levels which are interpreted into the image.

The tip is made by a two-phase electrochemical etching procedure of 20-mil W wires. First, the W wire is AC-etched in a 1M NaOH solution at 8 V rms with respect to the counterelectrode for a total of 7 minutes, broken up in six stages, with the tip slowly immersed into the solution in some stages to achieve the desired shape. This gives the tip its conical shape without the tapered sides usually preferred for field emission tips. This is followed by a DC etch at +1.5 V for 15 seconds to avoid possible electroplating from the previous step. The tip is then rinsed in deionized water and inspected under an optical microscope.

The sample used was P-doped Si(111), \( \rho = 0.035 - 0.065 \ \Omega \cdot \text{cm} \), misoriented 1.2° toward the high symmetry (\( \text{\overline{1}12 \)) direction, and mounted on tantalum clips. The substrate is prepared [25] by first outgassing the sample at \( \sim 700^\circ \text{C} \) by in-situ resistive
heating for a few hours, followed by flashing several times to \( \sim 1250^\circ \text{C} \), maintaining the background pressure at \( \leq 5 \times 10^{-9} \) Torr. Steps and terraces are clearly seen in the miscut direction and bunching of steps to produce wider terraces are observed, consistent with other studies performed on vicinal Si\(111\) [26, 27, 28, 29, 30, 31]. To monitor the temperature, a W-5%-Re/W-26%-Re thermocouple was spotwelded to the underside of the tantalum clips in good contact with the sample.

Oxygen was administered by backfilling the vacuum chamber with research grade (99.99\% pure) \( \text{O}_2 \) at a pressure of \( 5 \times 10^{-9} \) Torr for 100 seconds with the sample at room temperature. Although previous studies have speculated on the production of "activated oxygen" or excited oxygen species due to hot filaments in the vacuum system, more recent studies have indicated that such effects on the oxidation rate of Si\(111\) are negligible [32]. The sample was grounded and the tip retracted during the dosing. Based on sticking coefficient measurements [32], we estimate the coverage to be \( \theta \leq 0.1 \) ML. Low coverage was intentionally used in order to preclude complications which may arise from interactions between adsorbates at higher coverage. After cleaning and dosing the sample with oxygen, the sample was allowed to equilibrate at a particular temperature (usually 2–6 hours) to make sure that thermal drift has been minimized. The first set of data is taken at the higher temperature (550K) and the temperature lowered subsequently.

A miscut of 1.2° produces vicinal silicon with mean terrace widths of 150–200 Å. Successive heat treatments at \( T > 800^\circ \text{C} \) cause step bunching thereby producing terraces as wide as 300–1000 Å. In the experiments, the tip is positioned in the middle of the terrace to minimize effects which may be induced by the presence of steps which are known to act as nucleation and pinning sites. Figure 3.1 is a typical
Figure 3.1: The tip is customarily positioned above the middle of the terrace, as indicated by the arrow, usually $\geq 150\text{Å}$ from a step edge.

terrace chosen for the measurements with the arrow indicating a site where the tip is usually positioned. Just before the actual measurement, the feedback loop is suspended. This is necessary for the following reason. In the constant current mode of operation (the "default") the tunneling current is kept equal to the pre-determined current by means of a negative feedback mechanism. In this experiment, an adatom wandering into the probe region will affect the tunneling current by effecting a change in the local work function while the response of the negative feedback circuit is to null this out by causing a retraction of the tip from the surface to restore the pre-set level of the tunneling current. However, this compensation may render the STM not fully sensitive (or maybe even insensitive) to fluctuations in the tunneling current brought about by adatom mobility. This necessitates suspension of the feedback circuit when taking the spectral density. This is achieved by simply utilizing the "Sample–and–Hold Circuit", as shown in Figure 3.2.

This is the same circuitry used when doing spectroscopy, i.e., when taking I-V
Figure 3.2: Schematic diagram of the feedback circuit used to control the STM. The sample-and-hold circuitry is an integral part of the feedback network.
measurements. Once the tip is positioned at the desired spot the feedback loop is suspended and the voltage ramped. Typical I-V measurements take anywhere from μsec–msec because a sample-and-hold circuit with a fast response time is necessary to avoid unnecessary damage to the tip and/or the substrate. The sample-and-hold circuit acts in two modes: the “sample” mode in which it acts as a unity gain follower with dc gain accuracy typically 0.002%; and the “hold” mode wherein the hold capacitor maintains the voltage output at the same voltage level just before the feedback was suspended. The absolute value of the voltage is immaterial; the voltage applied to the electrodes may be different from one case to another but the tip-to-substrate separation is the same. The sample mode is the normal mode at which the STM operates where the output voltage serves to maintain the tip-to-substrate distance. This voltage is fed into high voltage amplifiers connected to the four electrodes on the tube scanner. Any change in this voltage causes a change in the tip-to-sample separation. Normally, this “hold time” (time during which the output voltage at time of suspension remains fairly constant up to a certain tolerance\(^1\)) is made as short as possible. In the envisioned spectral measurements, it is required that a longer “hold time” than just a few milliseconds be available for the spectrum analyser to gather enough data in order to get a substantial enhancement of the signal-to-noise ratio in measuring the spectra. In practice, this is accomplished by attaching an external hold capacitor in parallel to the existing one for the duration of the measurement, lengthening the hold time from a fraction of a second to ~8

\(^1\)Strictly speaking, this output voltage does not remain constant but changes with a characteristic droop rate which is controlled by the external circuitry. This can be made very slow, however, so that the output is essentially constant for a certain duration.
minutes, sufficient for taking measurements.

The tunneling current is amplified outside vacuum by a Keithley 428 current amplifier set at a gain of $10^8$ V/A. At such gain inherent amplifier noise is a few femtoamps. This allows us to be sensitive to spectrum levels greater than $10^{-30}$ A² · sec.

Also, the response of the amplifier is linear within the measurement range used in the experiments. The output of the current amplifier is fed into a HP3582A Spectrum Analyser which can cover a frequency range of 0.02 Hz to 25.6 kHz.

After each complete run the sample is recleaned, desorbing the oxygen, before a new run is initiated.

3.2 Results and Discussion

Figure 3.3 shows, as discrete symbols, the spectral densities for clean Si(111) and for oxygen-covered Si(111) taken at $T=400$–550K. A few observations are immediately obvious. While the spectral densities for the clean surface, shown as solid symbols, are indistinguishable from background noise and show no temperature dependence, those for the oxygen-covered surface, shown in open symbols, are larger by more than two orders of magnitude and exhibit a strong temperature dependence. Moreover it is clear that as temperature is increased $W(f)$ broadens and the absolute level of the signal decreases. This suggests that the tunneling current is sensitive to a dynamic process exclusively related to the presence of oxygen atoms on the surface. This dependence of $W(f)$ on $T$ is intuitively expected for a diffusive process: an increase in temperature increases adatom mobility producing a relative increase in the high frequency components of the power spectrum, thus the observed broadening of $W(f)$ with increased $T$. To be able to extract diffusion parameters, however, a more
Figure 3.3: Power spectra for both clean (closed symbols) and oxygen-covered (open symbols) stepped Si(111). The spectra for the clean surface exhibit no temperature dependence and their levels are comparable to the background. Spectra for the oxygen-covered surface, on the other hand, show signals a hundred times larger and exhibit a broadening with increasing temperature. The continuous lines are fits to the expected theoretical expression, eq. (3.9), characteristic of diffusive motion.

careful look at the expression for the power spectrum of tunneling current fluctuations in the STM is in order. Theoretical expressions for the form of the correlation function of the STM tunneling current fluctuations for diffusive motion has been worked out before for a system in the field emission mode[21]. This procedure is done for the case of tunneling and is presented below.

In this derivation, a classical approach is used in arriving at the relevant expressions\(^2\).

\(^2\)A semi-classical approximation is also shown in the next section.
We should point out at this point that the form of the field used here is the same regardless of whether the substrate is conducting or non-conducting. For a dielectric substrate, a surface charge density, $\sigma_b$, is induced on the surface and the total field becomes the superposition of the field due to the tip and $\sigma_b$. However, the field due to $\sigma_b$, $E_{\sigma_b}$, is proportional to the field (component normal to the surface) due to the tip because $\sigma_b = P_n$, the normal component of the polarization vector. Hence the field on a dielectric surface is just equal to the field on a conducting surface multiplied by a factor involving the dielectric constant. By normalising the expression in terms of $F(0)$, we obviate the necessity of differentiating between conducting and non-conducting substrates\(^3\). We approximate the tip by a conducting sphere a distance $z_0$ from the surface. Using elementary electrostatics, the field on the surface can be worked out giving

$$ F(r) = \frac{F(0)}{(1 + r^2/z_0^2)^{3/2}} \quad (3.1) $$

where $F(0)$ is the field intensity at $r = 0$, i.e., directly below the tip. Using the equation for the tunneling current density we can get the relation

$$ \frac{\delta j}{j} = B \delta n \quad (3.2) $$

where $n$ is the adsorbate density in atoms/cm\(^2\), and $B$ a constant, by assuming that an adatom wandering into the probe region of area $A$ alters the work function by an amount

$$ \delta \phi = \left( \frac{2\pi P}{A} \right) \delta n. \quad (3.3) $$

Here $\phi$ is the local work function, $P$ is the permanent dipole moment of the adsorbate

\(^3\)See, for example, reference [22].
and $\delta n = n - \bar{n}$ is the fluctuation in adsorbate particle density in $A$. We can construct the time autocorrelation function

$$c(t) \equiv \langle \delta i(0) \delta i(t) \rangle$$

(3.4)

but relegate the derivation to the appendix for brevity and to preserve continuity of thought.

The resulting expression for the time autocorrelation function takes the form

$$c(t) = \frac{M}{D(t + t_0)}$$

(3.5)

where all the extraneous constants have been lumped to $M$. It is clear that equation (3.5) reduces to the hydrodynamic limit $1/t$ as $t \to \infty$. Here $t_0$ is proportional to the time it takes for an adatom to cross the probe region of area $A$. The Fourier transform of such a correlation function produces the theoretically expected power spectral density

$$W(f) \sim \frac{M}{D} E_1(ft_0)$$

(3.6)

where $E_1(x)$ is the exponential integral function defined as

$$E_1(x) = \int_x^\infty \frac{e^{-u}}{u} du.$$  

(3.7)

The theoretical expressions for the spectral density, equation (3.6), supports the experimental results: the inverse relationship of $W(f)$ with $D$ makes $W(f) \propto exp(1/T)$ which causes the absolute level of the spectrum to decrease with temperature. And because $t_0$ (which is proportional to the traverse time of an atom across the probe region) decreases with temperature, we expect the broadening of the spectra

---

4Averaging of particle number, $N$, or particle number density, $n$, will be interchangeably denoted by a bar (as in $\bar{N}$), or by brackets (as in $\langle n \rangle$).
because of the $E_1(ft_0)$ dependence of $W(f)$. The experimental data were fitted with the theoretical expression (3.6), using different diffusion parameters, $D$, and is shown as continuous lines in Figure 3.3. The extraction of diffusion parameters is achieved if we consider the low frequency end of the spectrum because for small $x$,

$$E_1(x) = -\gamma - \ln(x) - \sum_{n=1}^{\infty} \frac{(-1)^n x^n}{n \cdot n!}$$

where $\gamma = 0.58$ is the Euler--Mascheroni constant.

We now try to determine what diffusing species we have on the surface. The adsorption of oxygen on the silicon surface is probably one of the most studied systems because of the need to microscopically understand and control the Si/SiO$_2$ interface, important in semiconductor technology. Most studies have revolved around the sticking coefficient, bonding geometries, changes in surface morphology during adsorption, and the identification and characterization of the different oxygen states. Even with the heightened interest and effort in trying to answer these questions, results or their interpretation have been varied and sometimes contradictory. With improved experimental capabilities more reliable information has become available but still, a majority of the questions remain unanswered or only partially solved. Surprisingly enough, no studies on oxygen mobility on Si have been conducted save for a couple, one of which has set an upper bound on the diffusion coefficient [33] by conducting Laser Induced Desorption experiments: $D < 10^{-9}$cm$^2$/sec at 600°K. In LID experiments, the entire substrate is covered with adsorbates and a region of size $\sim 10^{-2}$cm is emptied of adsorbates through desorption. The difference in concentration (and hence in chemical potential) inside and outside the probe region causes adsorbates outside to diffuse into the probe area which are, in turn, desorbed and "counted." The evolution of the concentration then gives the diffusion coefficient. Only an up-
per bound has been set using this method simply because not enough refilling signal back to the probe area was measured. Such measurements are normally carried out at higher coverage.

It is agreed that oxygen adsorption on Si(111) is complex. It was found that depending on the O\textsubscript{2} partial pressure and the substrate temperature, oxygen adsorption may follow two different paths: production of volatile SiO which leads to etching of the surface; or formation of an oxide layer [34, 35]. The boundary between these two phases is distinct. It is believed that oxidation at certain O\textsubscript{2} partial pressures and substrate temperatures lead to the formation of activated or volatile SiO which thermally desorbs causing etching of the surface [36, 37, 38, 39, 40, 41] as seen from the retraction of step edges for both Si(100) and Si(111) and creation of pits which are one layer deep especially in regions where mean terrace lengths are larger. These “pits” or “holes” are believed to be vacancies as reconstruction of the second layer to the stable 7x7 and metastable 5x5 and 9x9 configurations are clearly seen. It is speculated that the observed aggregation of these holes into vacancy islands is caused by the mobility of these vacancies (even at 400° C) and maybe also oxygen.

On the other hand, oxidation at lower temperatures (as was done in our experiments) promote the formation and growth of SiO\textsubscript{2}, as well as other SiO\textsubscript{x}. Through a combination of electron diffraction, various high resolution electron spectroscopies, Optical Secondary Harmonic Generation (OSHG) experiments, Laser Induced Thermal Desorption (LITD), synchrotron radiation studies, and STM investigations, the kinetics of the initial stages in the oxidation of Si(111) is proposed to be as follows [42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54]. O\textsubscript{2} adsorption on Si(111) at all temperatures is characterized by an initial fast uptake in the submonolayer regime,
with the initial sticking coefficient found to be 0.13 at 300K. The initial sticking coefficient is temperature-dependent, ranging from 0.2 at 200K to 0.06 at 600K. It is believed that this decrease in oxygen uptake is due to energetic and/or steric hindrances caused by earlier adsorbed oxygen. Molecular oxygen adsorbs dissociatively on the Si(111) surface and except at high temperatures (T>1000K), molecular oxygen exists as a metastable precursor (to atomic oxygen) with a lifetime strongly dependent on coverage, temperature, impurities, and surface structure [49]. These molecular species are observed to dissociate into atomic oxygen, revealing at least two reaction sites on the Si surface. In one configuration an oxygen atom attaches to an adatom which is, in turn, bridged by another oxygen atom to a restatom; in the other configuration the oxygen atom is attached to a restatom adjacent to an oxygen-bridged adatom-restatom pair.

In relation to our experiments, we determine that the surface is mostly covered by atomic oxygen because of the extended annealing at T>450K which is believed to facilitate the dissociation of molecular oxygen. We rule out the possibility of Si vacancies because backfilling was done at low enough temperature for the oxygen partial pressure used that clearly puts us within the oxide formation regime rather than in the etching regime. Although oxidation is inhomogeneous in the 7x7 unit cell, step bunching (as we deliberately induced here in order to achieve wider terraces) are known not to interfere with the adsorption. We thus have to attribute the observed spectra to the diffusive motion of mostly atomic oxygen on the Si(111) surface.

Figure 3.4 shows a plot of $W(f)$ vs. $ln(f)$ for different temperatures. Breaks in the ordinate axes were necessary in Figure 3.4 since $W(f)$ varies over four decades at the temperatures spanned by the experiment. The inverse of the slopes of the
Figure 3.4: The power spectra graphed versus $\ln(f)$ show good linear fits at different temperatures indicating consistency with the expected $\ln(f)$ behaviour for $f \to 0$. The inverse of the slope values are used to make the fits in Figure 3.3.
straight lines in Figure 3.4 are used back into equation (3.6) to generate the theoretical curves in Figure 3.3. They are clearly excellent fits to the data. This enables us to extract a reliable value for the activation energy. However, due to the constant $M'$ in equation (3.6) which depends on specific information about the system (like absolute coverage and adlayer compressibility), a value for the prefactor may not be deduced only from the $f \to 0$ limit of power spectrum measurements taken at different temperatures. The inverse of the slopes in Figure 3.4 which are proportional to $D$ are used in an Arrhenius plot in Figure 3.5 from which we can extract the surface diffusion activation energy, $E_d = 0.92 \pm 0.15$ eV.

Since no other direct studies have been done on the diffusion of oxygen on Si(111),

![Graph](image)

**Figure 3.5:** Plot of the inverse of the slopes in Figure 3.4 versus $1/T$ to extract an activation energy of $E_d = 0.92 \pm 0.15$ eV.
no comparison of the extracted value for the activation energy can be done. The limit to the value of $D$ imposed by another investigation mentioned earlier[33] is not inconsistent with the value of $E_d = 0.92 \text{ eV}$ deduced from our experiments which would imply $D = 10^{-13} \text{ cm}^2/\text{sec}$ at $T=600^\circ K$ (using normal values of the prefactor, $\sim 10^{-4} \text{ cm}^2/\text{sec}$). This value is also consistent with recent STM studies on nucleation during oxidation [41] where if the diffusion barrier we have extracted for oxygen is used in a simple nucleation model, whereby it is assumed that two diffusing oxygen species consist a stable cluster, the predicted rates become consistent with the experimental findings. It is noteworthy that these measurements have been done spanning a rather wide range of temperatures ($\Delta T = 250K$), wider than what is normally used in other surface diffusion measurements.

3.3 A "Quantum Mechanical" Approach

For completeness, we briefly mention an alternative derivation of the expressions for the correlation function and the spectral density, specifically using a semi-classical approach. Expressions for the tunneling current have been derived by solving for appropriate electron wave functions using the WKB approximation. A similar approach was done recently including the effects of diffusing adsorbates in the formalism [55]. With no particles in the region between the tip and the substrate, the electron potential is assumed to be a constant, $V_0(r) = V_0$. The presence of mobile particles in the region complicates the problem not only through the interaction between the tunneling electrons and the particles but also because the motion of the atoms would cause a time-varying potential. The second predicament is easily circumvented by the following argument. An electron tunneling from one electrode to another typi-
cally takes $10^{-15} - 10^{-14}$ seconds while the time for an atom in the gas phase to cross the tunneling space between the sample and the tip and the time for an adatom to traverse a tunneling region several angstroms wide is $10^{-12} - 10^{-11}$ seconds. Hence an electron essentially "sees a static potential," at least momentarily. The relevant problem can then be solved statically (i.e., solve it for a moment in time, $t$) and then averaged in time. For an atom at $\vec{r}_i$, a spherically symmetric electron–atom interaction potential of the form

$$U(\vec{r} - \vec{r}_i) = \frac{-U_0 b^4}{(|\vec{r} - \vec{r}_i|^2 + b^2)^2}$$

may be assumed, where $b$ is a length scale on the order of the range of interaction. For $N$ particles the new potential then becomes

$$V(\vec{r}) = V_0 + \sum_{i=1}^{N} U(\vec{r} - \vec{r}_i).$$

We can then solve Schrödinger’s equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V(\vec{r})\psi = E\psi$$

for the electron wave function and calculate the current density, $j(t)$, for the configuration frozen at time $t$. By averaging over time (and hence over arbitrary locations of the particles, $\vec{r}_i(t)$), expressions for the correlation function and power spectrum may be derived. To no surprise, the form for the correlation function and the spectral density are identical and we leave out the mathematical derivation of these expressions. However, we point out two things derived from these semi-classical calculations which support the experimental results. The first is that adatom motion on the surface will produce signal levels much greater than that of thermal and shot noise. Secondly, gas atoms in the tunneling space do not affect the average current and their motion
is expected to be characterized by signals of the same strength as shot and thermal noise and therefore undetectable from the background. As seen from Figure 3.3, there is a clear indication of the signature of the oxygen diffusing on the surface: the signals are over and above that for clean Si(111) and contributions from O₂ or other species in the gas phase moving in the tunneling gap is small.
4. FACTORS THAT MAY COMPLICATE THE MEASUREMENT

In any measurement process it is imperative not only to ascertain how to conduct the measurement and how to extract the relevant parameters but also to ask the question, "how does the measurement procedure affect the measured quantity?" In an ideal situation, the measurement does not alter the state of the measurable quantity but this may be untenable in real measurements—if not due to inaccessibility set by the physical system measured, then to instrumentation capabilities or lack therof. We would want complicating factors to have negligible effect, but this becomes more challenging in measurements involving small signals. At the very least, the extent of the effect should be known so that any corrections to the measured value may be applied and the "true value" of the measurable quantity deduced. Thus in proposing this technique to measure surface diffusion by monitoring fluctuations in the STM tunneling current, it is but natural that a discussion of factors that may complicate the interpretation of the measured quantities be made—and is done here. We will consider three factors that may possibly cause measurement inaccuracy:

1. the consequences of a non-zero low frequency cutoff;

2. the effect of measuring simultaneous diffusion on the tip and on the substrate;
3. the role of the high, non-uniform electric field on the substrate in the vicinity of the tip.

These are considered separately in the following sections.

4.1 The Effect of a Low Frequency Cutoff

Recent studies [56] have indicated that the unavoidable use of a low-frequency cutoff, $f_i$, actually changes the shape of the correlation function. The low frequency cutoff naturally comes about because of the finite sampling time of the analyser or the correlator (there is also a prevailing inverse relationship between $f_i$ and the cost of analysers). Measurements have shown that the normalized decay constants, $\tau$, can differ by as much as a factor of 2 for $\tau f_i = 0.045$ [56]. This means that a substantial deviation should be observed with $f_i = 0.01$ Hz and $\tau = 4.5$ seconds. (Note that $f_i$ pertains to low frequency whereas $\tau$ generally refers to the high frequency end. $\tau$ is determined by the physical process while $f_i$ by the electronics. For a given value of $\tau f_i$, an approximate match between a process with $\tau$ and an instrument with $f_i$ may be made.) It is clear that if $f_i$ is high enough a deviation from the expected shape of $W(f)$ or $c(t)$ is observed. Now we want to determine how this affects our extracted value of the diffusion barrier.

We have conducted tests by taking spectra at $f_i = 0.02$Hz and $f_i = 2$Hz. Clearly measuring enough of the $\ln(f)$ regime, the spectrum taken with $f_i = 0.02$Hz resulted in the same slope (hence the same $D$) while the spectrum taken with $f_i = 2$Hz, as shown in Figure 4.1, outside the $\ln(f)$ regime, could not even be approximated properly by $\ln(f)$ at the low end of the spectrum taken. (It is conceivable, however, that the correct diffusion barrier may still be extracted once the other constants are
Figure 4.1: The spectrum graphed versus $\ln(f)$ does not show a good linear fit when $f_i = 2\text{Hz}$ was used, indicating that the graph is outside the $\ln(f)$ portion of $W(f)$ hence making the extraction of the diffusion barrier difficult.

determined.)

This should not be surprising because in extracting $E_d$ we basically utilized only that portion of the spectrum where $W(f) \sim E_1(f) \propto -\ln(f)/D$, i.e., the linear portion of the $W(f)$ vs. $\ln(f)$ graph. Therefore, since the low frequency cutoff effectively removes only that part of the spectrum $f < f_i$, if enough of the $\ln(f)$ regime is still measured, then no appreciable error is introduced to the extracted diffusion barrier. In fact, in these experiments, the data had to be fit to slightly different portions of $E_1(x)$ in Figure 3.2 (albeit the difference is minimal). Nevertheless enough of the $\ln(f)$ portion of $W(f)$ should be measured otherwise no diffusion barrier could
be simply extracted from the $f \rightarrow 0$ limit of $W(f)$.

Looking back at the data presented in Figure 3.2 and the temperatures at which the spectra were taken, it is not surprising that no deviation from the theoretical form was observed and hence no correction to the extracted diffusion barrier is necessary. At 400K, for example, for $E_d = 0.92\text{eV}$, using normal values of the prefactor, $\sim 10^{-5}\text{cm}^2/\text{sec}$, and assuming a probe area of $\sim 6\text{ Å}$ radius, $\tau f_1 = 10^{-3}$ with our analyser which has $f_1 = 0.02\text{Hz}$. At these values of $\tau f_1$, no substantial change in shape of the correlation function or the spectral density were reported [56].

4.2 Detecting Simultaneous Diffusion

Unlike other STM techniques which rely on topographic images of the surface to deduce diffusion parameters, the essence of this measurement is the fluctuation of the tunneling current attributed to the diffusion of adsorbates within the vicinity of the tip—either on the substrate, on the tip, or on both. Since it is not possible to rule out, a priori, the diffusion of adsorbates on the tip which may contribute to the fluctuations, it is important to determine whether or not this technique would be able to discriminate a single diffusion process from simultaneous diffusion on the substrate and on the tip which, in general, can have different diffusion coefficients.

We have attempted to induce simultaneous diffusion by increasing the substrate temperature to as high as 750-800K. Because increasing the temperature is accompanied by a decrease in the absolute current level of the spectrum, no meaningful conclusion can be drawn as noise levels become almost comparable. Up to 600-650K, however, no deviation from a single diffusion process was evident as shown in Figure 4.2.
Figure 4.2: Assuming that the tip was not at a high enough temperature for the adsorbates to be mobile, spectra were taken at higher temperatures but up to 650K, no deviation from the expected form is seen. Spectra taken at 700–800K had absolute levels comparable to background noise. This indicates that there is no simultaneous diffusion on the substrate and on the tip, at least up to 650K.

Our data, apparently indicating no simultaneous diffusion, lead us to ask: “If, in fact, simultaneous diffusion were present, how would it be manifested?” We addressed this issue in two different ways: by deriving an analytic expression for the form of the correlation function or the power spectrum when simultaneous diffusion is present and by conducting Monte Carlo simulations using the two-dimensional lattice gas model to mimic the experiments. We discuss the latter first.

Here and in the next section, simulation results will be presented in terms of both the correlation function and the power spectrum. However, a majority of the analysis
is done in terms of $c(t)$ just because provides a simpler and more intuitive physical picture than $W(f)$. In addition, $c(0)$ is finite at $t = 0$ whereas $W(f) \to \infty$, $f \to 0$. In comparing the experimental data with the simulation results, we use power spectra for both since we measure the spectra in our experiments. Where possible new experiments or extensions of the technique are proposed, either or both $c(t)$ and $W(f)$ are utilized.

Because a relatively low coverage was used in the experiments, the same was done for the simulations and no adsorbate–adsorbate interactions were assumed. A square lattice containing 31x31 sites with periodic boundary conditions was used and the circular probe region contained five sites. A fixed number, $N$, of particles corresponding to the desired mean coverage was thrown onto the surface at random. (Normally, if a higher coverage was used and adsorbate–adsorbate interactions were incorporated, the system would be allowed to attain its equilibrium configuration first before recording any diffusion runs.) A particle is chosen randomly and the jump direction is decided. Particles may only hop to nearest neighbour sites; no long jumps were allowed. If the neighbouring site is empty, a jump occurs with probability $D$. Otherwise, another particle is chosen. Each Monte Carlo Step (MCS) would then consist of $N$ such interrogations. At the end of each MCS, the number of particles in the designated probe region was counted. After completion of all MCS, the number fluctuation autocorrelation function was constructed,

$$
c(t) = \frac{1}{K} \sum_{i=1}^{K} \frac{1}{L} \sum_{j=1}^{L} \left[ n(t_j + t) - \bar{n} \right] \left[ n(t_j') - \bar{n} \right],
$$

where the $i$ summation is over different runs while the summation over $j$ is the time averaging. Except for very slow diffusion rates, $K = 3$ and $L = 10^5$ were typically used; these yielded reasonable statistics.
The foregoing describes the routine used when simulating single diffusion on the surface. To simulate simultaneous diffusion, two overlapping lattices were constructed, corresponding to the surface and the tip, with constant (but possibly different) coverage on each (see Figure 4.3). Atoms were confined to diffuse on their respective lattices with different probabilities, \( D_1 \) and \( D_2 \). Unlike the “co-adsorption model” where two or more species with different diffusion rates are allowed to diffuse on one surface, here we have a single species diffusing independently on two surfaces. Situations in which particles on both planes are “on top of each other” are not excluded. The same standard algorithm was used as described above, but the number of particles used in constructing the correlation function in equation (4.1) is the sum of the particles in both probe regions. Simulations were conducted for probability ratios \( D_1/D_2 = 0 - 5000 \).

The results are summarized in Figure 4.4 with a graph of \( c(t)/c(0) \) versus “normalized time,” \( t/t_{0.4} \), where \( t_{0.4} \) is the time it takes for the function to drop to 40% its value at \( t = 0 \). For a single diffusion process we have used rates of \( D = 0.0002 - 1.0 \) and it is observed that if graphed as in Figure 4.4, they all collapse into the same curve.

Figure 4.3: Simultaneous diffusion is represented by two overlapping lattices with adsorbates diffusing independently on each surface and having different diffusion probabilities, in general. No particles are allowed to hop from one lattice to the other.
Figure 4.4: Correlation functions scaled both horizontally and vertically graphed for different probability ratios, $D_1/D_2$. The correlation function for the single diffusion process is shown by the continuous line. $c(t)$ for simultaneous diffusion clearly deviates from the expected curve with the deviation increasing for larger values of $D_1/D_2$. $c(t)$ for $D_1/D_2 = 0, 1, \infty$ are indistinguishable from the single diffusion case, as expected. (solid line), irrespective of the diffusion rate, as expected. Different probabilities only correspond to different time scales. On the other hand, simultaneous diffusion on two lattices, which is a physically different process, produces a correlation function which distinctly deviates from that of a single diffusion process. In essence, they cannot be described by a single functional form and do not scale, as evident in Figure 4.4. The case where $D_1/D_2 = 0$ or $\infty$ is trivial because we really have only one process going on. It is also found that if $D_1/D_2 = 1$, i.e., for simultaneous diffusion on the surface and on the tip but with identical diffusion rates, we get the same curve as that for a
single diffusion process: we basically measure only one kind of process. In this case we will be measuring the correct $D$. 

In contrast, for rates with ratios greater than 5 a noticeable departure from the single diffusion process curve is seen. This corresponds to a difference in activation energies only greater than 0.08 eV, assuming the same temperature (600K) for the substrate and the tip. Increasing the ratio $D_1/D_2$ leads to a more pronounced difference in the correlation functions. Since there are two diffusion rates, one on the tip and one on the substrate, the decay of the correlations due to the faster process does not follow through to zero but is survived at long times by correlations due to the slower process. This is why the effect is more evident for larger ratios of diffusion rates. Naturally, in the limit where the atoms on one surface move much, much faster than on the other surface, i.e., $D_1/D_2 \to 0$ or $\infty$, the slower process is practically non-existent with respect to the faster one and we recover a single diffusion process. These results are not surprising. From the construction of the correlation function, equation (4.1), expressions for single and simultaneous diffusion can be written, respectively, as

$$c(t) = \langle (n(t) - \bar{n}) (n(0) - \bar{n}) \rangle$$
$$= \langle n(t)n(0) \rangle - \bar{n}^2$$
$$c'(t) = \langle \left( N(t) - \bar{N} \right) \left( N(0) - \bar{N} \right) \rangle$$
$$= \langle N(t)N(0) \rangle - \bar{N}^2$$

where $N(t) = n_1(t) + n_2(t)$. The correlation function for the simultaneous diffusion process, (4.3), may be expressed in terms of $c(t)$ as follows:

$$c'(t) = \langle (n_1(t) + n_2(t)) (n_1(0) + n_2(0)) \rangle - (\bar{n}_1 + \bar{n}_2)^2$$
A two-segment correlation function is thus expected, and is observed in Figure 4.4. Using (4.4), for $D_1/D_2 = 1$, $c'(t) = 2c(t)$: the single diffusion correlation function. For $D_1/D_2 = 0$, adsorbates on one of the surfaces are immobile so that $c(t) = 1$. Then $c'(t) = c(t)$ again, upon appropriate normalization. Equation (4.4) can also be generalized for surfaces having different coverages, using equations (1.15), (1.16), and (2.21).

Because of the relationship between the correlation function and the power spectrum, a clear departure from the expected theoretical curve should be evident for a simultaneous diffusion process. Figure 3.2 shows the experimental data fitting the exponential integral function, indicating that for the temperatures at which the spectra were taken, it represents a single diffusion regime—that of O/Si(111). A correlation function or power spectrum indicative of a single diffusion process cannot, in principle, distinguish between diffusion on the tip from diffusion on the substrate. That 0.92 eV is the diffusion activation energy for O/W is immediately ruled out because of previous studies of O/W indicating that for O/W, $E_d \sim 0.6$ eV [6, 9] at low coverage.

We have transformed the simulation data to yield the spectral densities and Figure 4.5 shows representative normalized curves for both single and simultaneous
Figure 4.5: The spectra for simultaneous diffusion (discrete symbols), better represented by a power law, $f^{-\gamma}$, $\gamma > 0$, rather than the $E_1(f)$ characteristic of a single diffusion process (solid line).

While that for a single diffusion process fits the expected theoretical form, that for simultaneous diffusion diverges faster than $\ln(f)$, fitting a power law, $f^{-\gamma}$, $\gamma > 0$ better. This is indicative of a correlation function tail going as $t^{-\beta}$ with $\beta = 1 - \gamma > 0$, as can be deduced from the Fourier transform, instead of the diffusive $1/t$ tail. As previously mentioned, no such departure is observed of the experimental data, leading us to believe that no simultaneous diffusion process occurred at these temperatures, at least for the O/Si(111) system.

From the results of the simulations, we can infer that for simultaneous diffusion on the substrate and on the tip to be detectable, the ratio of diffusion rates must
fall within a certain “window.” This, however, is not a difficult criterion to fulfill. For example, for O/Si(111) at 600K, assuming that the tip stays at 300K because of conduction through the rest of the tip assembly, the ratio of diffusion coefficients if oxygen were diffusing on both the Si and W surfaces would be \( \frac{D_g}{D_t} \sim 200 \), which should produce a visible deviation from the expected form. For most systems, the difference in \( \frac{E_d}{kT} \) would be sufficient such that enough deviation from the theoretical form should be observable if simultaneous diffusion on the tip and the substrate occurred.

Finally we ask whether it would be necessary to have a “reference curve” for comparison to decide whether simultaneous diffusion is present or not. Measuring the power spectrum necessitates comparison with a reference curve but if we measure the correlation function, we can devise a method to obviate the necessity for a reference curve, as follows. The collected correlation function can be regraphed into a “normalized” correlation function as shown in Figure 4.6, with characteristic times, \( t_1 \) and \( t_0 \), corresponding to the times the correlation function drops to 50% and 40% its initial value, respectively. Since we know that for the STM the correlation

\[ \frac{c(t)}{c(0)} \]

Figure 4.6: For a single diffusion process, the shaded area below the normalized curve, \( \frac{c(t)}{c(0)} \), should be equal to \( t_1 \ln(2.5) \).
function takes the form

\[ c(t) = \frac{m}{t + t_1}, \]  

where \( m \) is an arbitrary constant, by graphing \( c(t) \) as \( c(t)/c(0) \) we determine that \( m = t_1 \). If we now calculate the area underneath the curve from \( t = 0 \) to \( t = t_0 \) we get

\[ A = \int_0^{t_0} \frac{d}{dt} c(t) c(0) = \int_0^{t_1} \frac{dt}{t + t_1} = t_1 \ln(2.5), \]  

represented by the shaded area in Figure 4.6. This is easily done by numerical integration with \( t_1 \) readily apparent from the normalized curve. Within experimental error, the area should be equal to \( t_1 \ln(2.5) \). Areas less than this may hence be indicative of simultaneous diffusion occurring. In fact, we can construct a difference parameter, \( \Delta \), defined as

\[ \Delta = t_1 \ln(2.5) - \text{calculated area.} \]  

Equal to 0 for \( D_1/D_2 = 0, 1, \) and \( \infty \), \( \Delta \) increases monotonically for \( D_1/D_2 > 1 \) until it reaches a maximum and subsequently drops back to zero for \( D_1/D_2 \to \infty \). We have done this with the curves in Figure 4.4 to yield Figure 4.7 for \( D_1/D_2 = 1 - 5000 \). This could prove to be a convenient construct: if the occurrence of simultaneous diffusion is suspected, by calculating \( \Delta \) we can get a rough estimate of the difference in \( E_d/T \).

### 4.3 The Effect of Inhomogeneities in the Surface Potential

Perhaps the biggest question in surface diffusion measurements with the STM is the role of the field in influencing adatom diffusion [21, 57, 58, 59]. A high, non-uniform electric field on the surface directly underneath the tip is produced even at
normal operating conditions. For example, for a tunneling gap of 5Å and typical tunneling voltages of 1-10 V, fields of $10^7 - 10^8$ V/cm are produced, enough to cause field ionization or field desorption for some species. This field, however, is concentrated to a small region underneath the tip, as shown in Figure 4.8, calculated for a tip with apex radius 100Å, a 10Å separation and 3V tunneling voltage. When interactions between the field and the induced dipole moment of the adsorbate is substantial, a potential gradient is created. This is believed to deform the surface potential energy, possibly resulting in biased or directional random walk of the adatoms because of the now asymmetric potential. This, in fact, has been shown to be the case for Cs on p-GaAs(110) [60]: by producing positive pulses from the initially negatively-biased tip, Cs atoms were observed to preferentially diffuse toward the location of the tip.
Any surface diffusion measurement with the STM has to eventually be also evaluated in terms of its sensitivity to the effects of the electric field on adatom mobility.

To respond to this concern, we have conducted experiments at different bias voltages to detect whether any changes in \( W(f) \) are evident. In addition, we have also addressed the more general question theoretically: is the shape of \( c(t) \) or \( W(f) \) different from the expected curves (3.5) and (3.6), respectively, if inhomogeneity in the surface potential, regardless of its specific nature, is present?

When field effects are present, it is reasonable to expect that the spectrum would "change" corresponding to changes in the field. (In what manner the spectrum changes will be discussed later.) Therefore by varying the bias voltage while keeping the tip-to-substrate separation the same, we should observe this change to be more prominent with increasing voltage. We therefore conducted tests by measuring...
the power spectra at room temperature utilizing different tunneling voltages, 1–3 V. (In the regular experiments, the bias voltage used was 2–2.5 V.) Care was exercised to prevent any differences in the tip-to-substrate separation among the different measurements. By using voltages of the same polarity, both below and above the typical voltages used in the experiments, we rule out the possible complications caused by a threshold field strength, if it exists. The raw data are shown in Figure 4.9 (a) and scaled for comparison in Figure 4.9 (b). The current levels increase with voltage, as seen in Figure 4.9 (a), consistent with the I-V characteristics of the tunneling junction but it is also clear from Figure 4.9 (b) that no deviation from the expected form is present, indicating that any effect the field is causing—aside from the effect due to the IV characteristics of the tunneling junction—is minimal. Alternatively, we have also divided $W(f)$ by $V^2$ to normalize the junction effects. The same diffusion barrier was extracted. This behaviour is not surprising for systems with very small polarizabilities. Investigations previously conducted on adsorbates with low polarizabilities (e.g., H, O on W) have indicated that no substantial effect on diffusion is observed. This is in sharp contrast to experiments with alkali and alkaline earth metals which show strong field effects [21]. In any case, whether the strong, non-uniform electric field affects adatom mobility, enough to be detectable, should be ascertained for each particular system. Adsorbates with high polarizabilities and dipole moments, in general, have a greater tendency to be affected by the field and the resulting measured diffusion values may be spurious. On the other hand, adsorbates with smaller dipole moments and polarizabilities may not be tangibly affected by the electric field.

Now to address this question theoretically, Monte Carlo simulations were carried out with the surface potential deformed so as to represent the effect of a non-uniform
Figure 4.9: Spectra of oxygen-covered stepped Si(111) taken at different tunneling voltages. While current levels increase with voltage (a), consistent with the I-V characteristic of the tunneling junction, no deviation from the expected form is seen in (b), as the normalized spectra clearly scale with each other. No field effects are thus evident.
field. An adatom in an electric field, $F(r)$, is known to become polarized with a dipole moment given by
\[ \vec{p} = \vec{\mu} + \alpha \vec{F} + \ldots \] (4.9)
to first order in $F$, where $\vec{\mu}$ is the static dipole moment and $\alpha$ the polarizability tensor.\(^1\) This results in a spatially-varying addition to the potential:
\[ \Delta U(r) = -\vec{p} \cdot \vec{F} - \frac{1}{2} \alpha F^2(r). \] (4.10)

In what specific manner (4.10) “adds on” to the constant surface potential is, however, not clear. It would be easy to understand why this seemingly simple configuration is actually complicated if we recall that an adatom may generally adsorb onto either a hollow site or an on-top site. Since local curvature differences between these two sites play a role in amplifying or attenuating the field, the fields may not be the same in these two sites. In addition, the static dipole moment and the polarizability may also be position–dependent.

In order to carry on with the simulation, we have simplified the situation by assuming uniform static dipole moment and polarizability. By further assuming the hollow sites as corresponding to the equilibrium positions on the surface (i.e., the troughs), and the on–top ones corresponding to the saddle points, the field at the saddle points will be much more enhanced relative to the field at the troughs and thus constitute the major contribution to the deformation, i.e., we have simply added (4.10) to the constant activation energy, $E_d$, so that the new diffusion barrier is now $E_d + \Delta U(r)$. Since oxygen has a static dipole moment equal to zero, we effectively\(^1\)

\(^1\)In general, this polarizability may be different from the free atom polarizability [61].
only have

\[ E_d \rightarrow E_d + \Delta U. \]  

(4.11)

This approximation is actually a “gentler” deformation because if, in addition, the equilibrium positions on the potential surface were also changed, a steeper gradient would result. However, the majority of the effect is produced by the approximation made here. Figure 4.10 illustrates how the potential surface is deformed by the non-uniform field where Figure 4.10 (a) is the potential at zero field. We have conducted simulations where adatoms tend to diffuse toward the tip, as in Figure 4.10 (b). The field, \( F(r) \), is given by equation (3.1):

\[ F(r) = \frac{F(0)}{(1 + r^2/z_0^2)^{3/2}} \]

where \( F(0) \) is the field at \( r = 0 \). For simplicity, we have also estimated the tip-to-substrate distance to be roughly three times the lattice spacing. The same procedure described in the previous section was followed in doing the diffusion runs: the lattice is randomly filled up to \( \theta = 0.1 \) and particles allowed to diffuse, but this time on an

![Diagram](image)

Figure 4.10: The surface potential not affected by the electric field is shown in (a). When coupling of sufficient strength between the adsorbate induced dipole moment and the field exists, the barrier heights in the vicinity of the tip may be changed which leads to preferred diffusion directions, as indicated by the arrow in (b).
inhomogeneous potential. The correlation function, \( c(t) \), is evaluated starting from \( t = 1 \) which corresponds to experimentally taking the data immediately after the field is turned on. The jumping probabilities are given by

\[
P = \exp \left[ -\frac{E_d + \Delta U}{kT} \right], \quad 0 < P \leq 1
\]

(4.12)

and values of \( \frac{1}{2} \alpha F^2/kT \) from 0 (corresponding to no field) to 6 were used. We show the results in Figure 4.11, scaled for easy comparison. The spectral densities are shown in Figure 4.12. It is clear that if the field affects the diffusion process a deviation of \( c(t) \) or \( W(f) \) from the no-field case will also be observed, with the effect increasing for larger values of the perturbation, \( \frac{1}{2} \alpha F^2/kT \). This is reasonable because the extent to which the field deforms the potential surface should be reflected in the deviation of the correlation function or the power spectrum from the expected form.

Figure 4.11: For \( \frac{1}{2} \alpha F^2/kT > 2 \), enough deviation from the expected (theoretical) form (solid line) shows, with the deviation increasing with the perturbation.
We also tried to answer the question: "is the effect of the field greater for weakly bound adsorbates?" To do this, we compared $c(t)$ for different values of $E_d/kT$, keeping $\frac{1}{2} \alpha F^2/kT$ constant. We found that the correlation functions for different values of $E_d/kT$ all scaled with each other, implying that the net effect does not depend on how strongly or weakly bound an adsorbate is to the surface but only on the perturbation, i.e., the strength of the coupling. In fact this result should not be surprising because by varying $E_d/kT$ we effectively vary only the time scale of the phenomena but not the net result. However, as we shall mention later, it makes it experimentally easier to detect field effects for strongly bound systems.

A better understanding of the nature of the effect can be gleaned if we compare the unnormalized correlation functions. In Figure 4.11, we calculated the correlation
function (and subsequently the spectral density) as in (4.1), subtracting the mean square number in the probe region. We can, instead, construct an unnormalized correlation function,

$$K(t) = \langle n(t)n(0) \rangle$$  \hspace{1cm} (4.13)

which is related to (4.1) by \(c(t) = K(t) - \bar{n}^2\). Results are shown in Figure 4.13. We observe that the mean coverage in the probe region changes as a result of the asymmetric potential. From an initial, uniform coverage, \(\theta_i = 0.1\), by the time the runs are concluded, the local coverage were as low as high as 83%. This immediately raises the following question: is the observed deviation from the expected theoretical form when there are no field effects mainly due to the directional walk an adatom undergoes or

![Figure 4.13: Unnormalized correlation functions for different values of \(\frac{1}{2} \alpha F^2/kT\) indicated on the right-hand side of the graph. Sufficient deformation of the surface potential causes a change of the local coverage in the probe region. This is seen as the differing plateau levels for different values of the perturbation, with final coverage, \(\theta_f\), farther from the initial \(\theta_i\) for greater values of \(\frac{1}{2} \alpha F^2/kT\).]
is it predominantly caused by the changing local coverage? We considered one of the runs which exhibited a substantial deviation in the correlation function and determined that it took roughly 10,000 MCS for the local density in the probe region to equilibrate to its final mean coverage of 83%. For times $t \leq 10,000$ MCS, the system is basically not in equilibrium. $c(t)$ was then constructed starting at different times to yield Figure 4.14. Correlating the number fluctuations from $t = 1$ MCS, as was done in Figure 4.11 yields the maximum effect. (This is experimentally equivalent to

![Figure 4.14: Correlation function calculated starting at different times, as indicated in the legend. The system achieves equilibrium in roughly 10,000 MCS. Including less and less of the non-equilibrium phase in constructing the correlation function results in the deviation of the shape of the correlation function from the theoretical curve to disappear. This indicates that the observed difference in shape in Figures 4.11 and 4.12 are primarily due to the changing adsorbate density in the probe region.](image)
measuring $c(t)$ or $W(f)$ immediately after the field is turned on.) Excluding more and more of the non-equilibrium time in the correlation function, however, reduces the deviation from the no-field case, as seen in Figure 4.14, until no field effects are detected at all when the correlation function is evaluated long after equilibrium has been established. We therefore conclude that the observed effect is brought about primarily by the relaxation of the system back to equilibrium after being quenched to a non-equilibrium state by turning on the field at $t = 0$. As mentioned earlier, varying $E_d/kT$ effectively changes the time scale of the phenomena. Because it is the non-equilibrium phase that causes the deviation, it is necessary that enough of the equilibration period is included in constructing $c(t)$. A larger diffusion barrier leads to a prolonging of the non-equilibrium phase and hence a better chance of capturing these processes. It should therefore be easier to detect field effects on a strongly bound system because it will take longer for the system to equilibrate.

Regarding the results in testing for field effects, we would have observed deviations from the theoretical form as the bias voltage was changed if, indeed, the field affected adatom mobility. This, of course was not observed. Using results from the simulations, these findings are substantiated because for O/Si(111) at room temperature, $\frac{1}{2} \alpha F^2/kT < 0.1$—no effect is detected from the simulations: there is no deviation from the theoretical form and there is no change in the local coverage.

At this point we might wonder how we would be able to differentiate between the effect caused by the electric field from that caused by simultaneous diffusion if both result in the correlation function decaying slower than the theoretical curve, as in Figures 4.4 and 4.11. This dilemma is easily resolved by using a different bias voltage to test for field effects because increasing (decreasing) the field should be
accompanied by a corresponding increase (decrease) in the deviation of \( W(f) \) or \( c(t) \) from the theoretical curve if field effects are present. Or another measurement, i.e., taking the spectrum or the correlation function, but using a bigger probe area can be done. Experimentally this corresponds to increasing the tip-to-substrate distance so that the solid angle subtended by the tip in Figure 2.1 covers a larger surface area. This could be easily achieved by decreasing the tunneling current at which the feedback loop is activated. Figure 4.15 shows that nothing happens to \( c(t) \) when the probe area is increased from 5 to 13 sites. Increasing the probe area, or equivalently the tip-to-substrate distance, does not cause any further change in the correlation function when there is only simultaneous diffusion.

On the other hand, changing the size of the probe region when field effects are

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**Figure 4.15:** Correlation functions of simultaneous diffusion evaluated for differently-sized probe regions (discrete symbols) scale with each other, and deviate from that of the single diffusion (solid line) in the same way.
present causes the already deviant \( c(t) \) to decay slower, as shown in Figure 4.16 where we have also increased the probe area from 5 to 13 sites. We have not yet ascertained why changing the size of the probe region causes this effect but it cannot be simply attributed only to the difference in final adsorbate densities. Although not yet completely understood, this nevertheless affords us another way of delineating field-induced effects from simultaneous diffusion: measuring \( c(t) \) or \( W(f) \) at a larger tip-to-substrate separation (corresponding to a larger probe area) should cause \( c(t) \)

![Graph showing correlation functions for field-affected diffusion deviating from the expected form as the size of the probe region changes.](image)

**Figure 4.16:** The correlation functions for field-affected diffusion deviate differently from the theoretical curve (continuous line) as the size of the probe region is changed. \( c(t) \) using 5 sites are represented by open symbols and those using 13 sites by shaded symbols. Increasing the probe area causes \( c(t) \) to decay slower if the deviation from the expected form is caused by the electric field.
to decay even slower for field-affected diffusion but not where simultaneous diffusion is concerned.

In the course of determining a satisfactory representation of the surface potential deformation caused by the field, we stumbled onto the potentials shown in Figure 4.17 which we briefly mention here. Unlike Figure 4.10 (b), representing the field-induced deformation where adatoms have a preferred jumping direction, a particle in a potential such as in Figure 4.17 is equally likely to jump to any of its available next-neighbour sites. What is happening, however, is the creation of a region wherein particles tend to be “trapped.” These may represent pinning sites (e.g., caused by impurities), which tend to agglomerate particles and form islands. Diffusion runs were likewise conducted with the probe region centered on these pinning or repulsion sites, with the results shown in Figure 4.18 and Figure 4.19.

Two things are worth mentioning at this point: (1) using the same perturbation strength a smaller effect is observed compared to Figure 4.11; and (2) equilibrium is reached faster by roughly a factor of ten with this new potential. We have previously said that it is the changing local adsorbate density that predominantly causes the correlation function to change. As we see, however, the type of asymmetry produced
that causes the change in $\bar{n}$ may also determine how $c(t)$ or $W(f)$ changes.

We have measured the power spectrum with the tip positioned over a region on the surface which acted as a pinning site. Figure 4.20 shows this location on the surface. Comparison of this spectrum with that taken over a region where no such agglomeration was observed is shown in Figure 4.21. The expected deviation, as predicted from the simulations and shown (scaled) in Figure 4.19, do appear but the effect is quite small. It should be noted, however, that scaling the frequency axis minimizes this effect because slightly differing points on the $f \to 0$ portion of $W(f)$ graph may have been used. But because of the divergent nature of $W(f)$ as $f \to 0$, tiny differences in the reference zero could lead to drastic minimization of the effect. The difference is quite evident when not scaled along the frequency axis but was graphed scaled in Figure 4.21 to show the difference in functional forms. Nevertheless, further confirmation needs to be done in this area.
Figure 4.19: Spectral density, centered on the pinning sites in Figure 4.17.

We have also calculated \( c(t) \) with the probe region distant from the asymmetry. This is similar to positioning the STM tip away from an impurity. In other words, we want to determine whether or not the shape of the spectral density or the correlation function is affected by island formation, for example, which may be occurring several lattice spacings away. When the correlation function is measured at a substantial

Figure 4.20: Image of the surface after the spectra were taken. In A, agglomeration was observed (seen as the bright region); none was observed in B.
Figure 4.21: Spectrum taken with the tip positioned above a pinning site (dashed line), compared with spectrum taken in the middle of the terrace where no agglomeration of adsorbates was observed (discrete symbols). While the expected form, $E_i(f)$ (shown as a continuous line), accurately represents the spectrum taken in the middle of the terrace, indicating no pinning effects, the same is not true for the one taken above a pinning site (dashed line).

distance away from a pinning site, where the potential is now symmetric, no effect is observed. Of course a very simple picture has been used here: very low coverage and no ad–ad interactions. Nevertheless, this implies that the fluctuation method is a highly local probe which could potentially, under the proper conditions, be used to determine effects of individual perturbations on the surface which may affect adatom mobility.

What we have just discussed are what seem to be the most obvious factors that
need to be considered. For sure there are other factors that we have not addressed here that may have an impact on the measurement process or an effect on the measured value. (An example would be what happens at higher coverage when adsorbate-adsorbate interactions may not be negligible.) We hope that these neglected factors are, at worst, minimal, or are tractable enough for further experiments to reveal and are reasonably easy to compensate for.
5. CONCLUSION

The method we have introduced here of utilizing the scanning tunneling microscope is an addition to the very few existing microscopic surface diffusion measurement techniques. From an instrumentation point of view there are only few additional requirements to a normally operating STM in order to employ this technique. It only requires the availability of a spectrum analyser with low enough $f_t$, and a mechanism to suspend the feedback while tunneling, such as the sample-and-hold circuitry. Numerous analysers are available that could be sufficient for this task as are data acquisition boards that may be configured for autocorrelation. STMs which are able to do spectroscopy should also be equipped with a sample-and-hold circuit. One only needs to check that the droop rate is slow enough for the correction voltage to practically remain constant while data is collected. If necessary, this can be easily corrected by attaching an external capacitor in parallel to the already existing hold capacitor. Necessarily, the ability to attain ultra high vacuum, a method of mounting and cleaning the substrate, and a way of depositing adsorbates on the substrate are implicitly assumed. The technique can be employed over a rather wide range of temperatures, limited only by the highest temperature at which the substrate surface or tip is destroyed.

To recapitulate, the technique involves monitoring the time dependence of fluctu-
ations in the tunneling current, believed to be caused by mobile adsorbates diffusing into or out of a probe region defined by the projection of the solid angle subtended by the tip onto the substrate. For a given system, the diffusion barrier can be simply extracted from the decay of either the correlation function, $c(t)$, or the power spectrum, $W(f)$. Another advantage of this technique is the ease by which pure diffusive motion may be judged. For pure diffusion, $c(t)$ or $W(f)$ are represented by their expected forms, (3.5) and (3.6), respectively. Effects caused by the electric field underneath the tip, those caused by impurities, or even the presence of simultaneous diffusion on the substrate and tip cause a deviation of the measured $c(t)$ and $W(f)$ from their theoretical forms.

The case of simultaneous diffusion is particularly easy to detect because it produces a power-law dependence for the power spectrum and a two-segment correlation function. And even when the data indicates simultaneous diffusion, if $c(t)$ was measured, by calculating part of the area underneath the normalized $c(t)/c(0)$ curve, we should be able to determine the ratio of diffusion coefficients. If the diffusion barrier of an adatom on the tip is known, for example, that for the substrate is likewise determined. Alternatively, we can decouple the data by fitting the initial decay of $c(t)$ to the theoretical form and extracting an activation energy—that for the faster process. From the difference in diffusion barriers, the other activation energy may also be extracted. Of course it is also possible to fit both segments of the two-segment correlation function to separate theoretical curves but in most cases it may happen that a substantial drop in $c(t)$ has already occurred due to the faster process by the time the segment due to the slower process is evident so that the signals may already be too small. The determination of which barrier belongs to the tip or the
substrate will have to rely on additional, extraneous information about the system being investigated.

The effect of the electric field should be a concern in this technique when using adsorbates of high permanent dipole moment and/or polarizability, but much less so when weakly polarizable ones are used. Nevertheless, it is still advisable that the influence of the field should be checked for each individual system. Unlike the case of data indicating simultaneous diffusion which may be analysed to extract the activation energies, the same may not be true here because the measurement itself changes the physical quantity. The use of O/Si(111) to test the viability of this technique was fortunate because the low polarizability of oxygen prevented a strong coupling with the electric field, hence allowing us to measure spectra unaffected by the field. Results may likewise be generated and parameters extracted from field-influenced data although their interpretation may not be simple. Still the use of this technique will not exclude many systems because of their possible coupling with the electric field.

Perhaps a big drawback of using the decay of the spectral density (i.e., the low frequency or long time) to measure diffusion parameters is that the prefactor, $D_0$, cannot be known because we only measure a quantity proportional to the diffusion coefficient, $D$. On the other hand, constructing the time autocorrelation function could afford an estimate of the prefactor (to within a factor of 10) because the decay time, $\tau$, is equal to $r_0^2/4D$. Although a different configuration for data acquisition should be set up, this should not pose as a problem. For studies where only a map of the diffusion barrier is needed, measuring the power spectra, $W(f)$, at different locations on the surface and at different temperatures should be sufficient.
The limitations of this technique are not unlike those of the existing microscopic techniques but it does open up the possibility of studying substrates other than refractory metals. Because of its highly local character it has the potential to shed light on basic questions that have remained elusive. For example, a controversial question is how the surface potential deforms near a step edge. We have illustrated earlier how the shape of $c(t)$ is sensitive to any deformations of the surface potential within the probe region but virtually unaffected if the probe region is distant from the deformation. By taking the spectra or the correlation function at different distances from a perturbation (a step edge, an impurity, etc.), in principle the range of the perturbation and the relative diffusion barriers may be ascertained.

We estimate that diffusion coefficients as high as $\sim 10^{-8}$ cm$^2$/sec may be measured with this technique. On the other hand, $D$ as low as $\sim 10^{-15}$ cm$^2$/sec should also be accessible so long as $f_i$ is low enough (i.e., $\tau f_i < 10^{-2}$). Basically a wide range of diffusion coefficients can be measured so that a small overlap with the range measurable by other techniques, especially the macroscopic ones, exists. Finally, although it was indeed fortunate (for reasons mentioned) that we used O/Si(111) to test the viability of this technique, it also did not allow a better verification of $E_d = 0.92$ eV for O/Si(111) because although O/Si is one of the most studied systems, diffusion of oxygen on silicon has never been directly investigated until now. Two other independent studies corroborate our extracted value but these studies were not directly measuring the diffusion barrier of O/Si(111). Only one other study using silicon as a substrate (but using hydrogen as adsorbate) has attempted to measure the diffusion coefficient directly. Nevertheless the overlap of this technique with some macroscopic techniques should now allow better comparative studies.


[33] S. M. George, private communication.


APPENDIX A: DERIVATION OF $c(t)$ FOR THE STM GEOMETRY

The time autocorrelation function

$$c(t) \equiv \langle \delta i(0) \delta i(t) \rangle$$  \hspace{1cm} (5.1)

can be constructed as follows.

$$\langle \delta i(0) \delta i(t) \rangle = \int_0^\infty d\vec{\tau} \int d\vec{\tau}' \langle \delta j(\vec{\tau}, 0) \delta j(\vec{\tau}', t) \rangle$$  \hspace{1cm} (5.2)

$$= \int_0^\infty d\vec{\tau} \int d\vec{\tau}' \langle \delta j(\vec{\tau}) \delta j(\vec{\tau}') \rangle \langle \delta n(0) \delta n(t) \rangle$$

$$= \int_0^\infty d\vec{\tau} \int d\vec{\tau}' \langle \delta j(\vec{\tau}) \delta j(\vec{\tau}') \rangle B^2 \langle \delta n(0) \delta n(t) \rangle$$  \hspace{1cm} (5.3)

using

$$\langle \delta n(0) \delta n(t) \rangle = S(\vec{r} - \vec{r}', t) = S_0 e^{-|\vec{r} - \vec{r}'|^2 / 4Dt}$$  \hspace{1cm} (5.4)

by (2.3), (2.8), and (2.21) where

$$S_0 = \frac{\langle (\delta N)^2 \rangle}{A} = k_B T K \langle n \rangle^2$$  \hspace{1cm} (5.5)

and $K$ is the adlayer compressibility. Equation (5.3) then becomes

$$\langle \delta i(0) \delta i(t) \rangle = \frac{B^2}{4\pi Dt} S_0 \int_0^\infty d\vec{\tau} \int_0^\infty d\vec{\tau}' \int_0^2 \int_0^2 \int_0^2 \exp \left( -\frac{3\alpha}{2} \left[ \frac{r^2}{z_0^2} + \frac{r'^2}{z_0'^2} \right] \right) \times \exp \left( -\frac{|\vec{r} - \vec{r}'|^2}{4Dt} \right)$$  \hspace{1cm} (5.6)
if we use

\[ j(r) = j_0 \exp \left( -\frac{3\alpha}{2} \left( \frac{r^2}{z_0^2} \right) \right) \]  

(5.7)

where \( j_0 \equiv \text{mean current density at } r = 0 \) and \( \alpha \) is a constant with dimensions \( \text{volt}^{1/2}/\text{length} \).

We now make the substitution

\[ \beta^2 = \left( \frac{3\alpha}{2z_0^2} \right)^{-1} \]  

(5.8)

and equation (5.6) can be written as

\[
\langle \delta i(0) \delta i(t) \rangle = \frac{B^2 S_0}{4\pi D} \int_0^\infty d\tau \int_0^\infty d^2 \tau' \exp \left( -\frac{r^2 + r'^2}{\beta^2} - \left| \vec{r} - \vec{r}' \right|^2 \right) \times
\exp \left( -\frac{\left| \vec{r} - \vec{r}' \right|^2}{\beta^2 \tau} \right)
\]  

(5.9)

\[
= \frac{B^2 S_0}{\pi \beta^2 \tau} \int_0^\infty d\rho d\rho' \int_0^\infty d\rho' d\theta \times
\exp \left[ -(\rho^2 + \rho'^2) \right] \exp \left( -\frac{\rho^2 + \rho'^2 - 2\rho \rho' \cos(\theta - \theta')}{\tau} \right)
\]  

(5.10)

where we have made another substitution, \( 4Dt = \beta^2 \tau \), going into equation (5.9) and shifted to circular cylindrical coordinates with a change of variable to \( \rho = r/\beta \), going into equation (5.10). The integration over angles can be easily accomplished with the use of the relation

\[
\int_0^{2\pi} d\theta d\theta' \exp \left( \frac{2\rho \rho'}{\tau} \cos(\theta - \theta') \right) \rightarrow 2 \int_0^\pi d\phi \exp \left( \frac{2\rho \rho'}{\tau} \cos \phi \right) = 2\pi I_0 \left( \frac{2\rho \rho'}{\tau} \right),
\]  

(5.11)

where \( I_0(x) \) is the Bessel function, \( J_0(x) \), with imaginary arguments. Then

\[
\langle \delta i(0) \delta i(t) \rangle = \frac{B^2 S_0}{\pi \beta^2 \tau} \int_0^\infty d\rho \int_0^\infty d\rho' \exp \left( -[\rho^2 + \rho'^2] \right) \times
\]  

...
\[ \exp \left( -\frac{\rho^2 + \rho'^2}{\tau} \right) 2\pi I_0 \left( \frac{2\rho\rho'}{\tau} \right) \]

\[
= \frac{B^2 S_0}{\pi \beta^{-2\tau-1} J_0^2} \int_0^\infty \int_0^\infty d^2 x' I_0(2xx') e^{-(x^2+x'^2)(1+\tau)}
\]

by a further change of variable: \( \rho^2 = \tau x^2 \). If we now multiply both sides of the equation by \( J_0(\gamma x') \) and take the limit as \( \gamma \to 0 \), we get

\[ \langle \delta i(0) \delta i(t) \rangle = \lim_{\gamma \to 0} \frac{B^2 S_0}{\pi \beta^{-2\tau-1} J_0^2} \int_0^\infty \int_0^\infty d^2 x' I_0(2xx') J_0(\gamma x') e^{-(x^2+x'^2)(1+\tau)} \]

\[
= \frac{B^2 S_0}{\pi \beta^{-2\tau-1} J_0^2} \int_0^\infty d^2 x \exp \left( -x^2(1+\tau) \right) x \lim_{\gamma \to 0} \int_0^\infty d^2 x' \exp \left( -x'^2(1+\tau) \right) I_0(2xx') J_0(\gamma x').
\]

Equation (5.13) then becomes

\[ \langle \delta i(0) \delta i(t) \rangle = \lim_{\gamma \to 0} \int_0^\infty d^2 x \exp \left( -x^2(1+\tau) \right) I_0(2xx') J_0(\gamma x') \]

identifying \( \xi = 1 + \tau \),  \( \nu = 0 \), and \( \eta = 2x \). Then

\[ \lim_{\gamma \to 0} \int_0^\infty d^2 x \exp \left( -x^2(1+\tau) \right) I_0(2xx') J_0(\gamma x') \]

\[
= \lim_{\gamma \to 0} \left\{ \frac{1}{2(1+\tau)} \exp \left[ \frac{4x^2 - \gamma^2}{4(1+\tau)} \right] J_0 \left( \frac{2x\gamma}{2(1+\tau)} \right) \right\}
\]

\[ = \frac{1}{2(1+\tau)} \exp \left[ \frac{x^2}{1+\tau} \right].
\]

Equation (5.13) then becomes

\[ \langle \delta i(0) \delta i(t) \rangle = \frac{B^2 S_0}{\pi \beta^{-2\tau-1} J_0^2} \int_0^\infty d^2 x \exp \left( -x^2(1+\tau) \right) \frac{1}{2(1+\tau)} e^{x^2/(1+\tau)} e^{x^2/(1+\tau)} \]

\[
= \frac{B^2 S_0}{\pi \beta^{-2\tau-1} J_0^2} \frac{1}{2(1+\tau)} \int_0^\infty d^2 x \exp \left( -x^2 \left[ \frac{2 + \tau}{1 + \tau} \right] \right)
\]

\[ = \frac{B^2 S_0}{\pi \beta^{-2\tau-1} J_0^2} \frac{1}{4(2 + \tau)}.
\]
By lumping all extraneous constants to $M$, the time autocorrelation function takes the form

$$c(t) = \frac{M}{D(t + t_0)}.$$  \hspace{1cm} (5.15)

Maybe it is worth mentioning at this point that a slight “adjustment” was made in performing the integrations. Whereas the limits of integration should strictly have been the probe region of area $A$ the actual limits used encompassed the entire surface. This should be a good approximation since the integrand drops off as $e^{-r^2}$ and contributions for large $r$ are thus negligible. Besides, it tremendously simplifies the calculations.
APPENDIX B: MONTE CARLO SIMULATION ROUTINES

SUBROUTINE PATCH

C THIS SUBROUTINE EXECUTES THE MAIN TIME LOOP OF DIFFUSING
C PARTICLES WITH NO AD-AD INTERACTIONS ON A SQUARE LATTICE

integer coord(1861,2),lsize,time,dir,x,y,t,chooser
integer occupancy,value,master(1000000),idum,xtip,ytip
integer xcoord,ycoord,latt(61,61),xnew,ynew,iwidth
real yes,cov,chance,prob,next,rsquared
character*20 filename
dimension char(2)
data char/_'_','x'/

C THIS PORTION CONSTRUCTS A SQUARE LATTICE OF SIZE lsize AND
C FILLS IT WITH PARTICLES WITH COVERAGE cov. THE OUTPUT IS AN
C (lsize x lsize) ARRAY, latt(x,y), WHICH REPRESENTS THE LATTICE,
C AND coord(x,y) WHICH IS A RECORD OF THE POSITIONS OF THE
C PARTICLES IN latt(x,y).

C THE FOLLOWING WAS INTENDED TO BE A SEPARATE SUBROUTINE BUT THE
C INITIALIZATION OF THE RANDOM NUMBER GENERATOR GETS LOST
C WHEN GOING FROM ONE SUBROUTINE TO THE NEXT. HENCE THE
C ROUTINE IS INSERTED HERE.

print *, 'size of lattice?'
read *, lsize

print *, 'enter a desired coverage (0<cov<1):'
read *, cov
print *, 'enter a value for the seed (negative integer):'
read *, idum
start = ran2(idum)

p = 0
do x = 1,lsize
doi y = 1,lsize
   next = ran2(idum)
   if (cov.ge.next) then
      latt(x,y) = 1
      p = p + 1
      coord(p,1) = x
      coord(p,2) = y
   else
      latt(x,y) = 0
   endif
endo
endo

print *, p,'particles laid down'

C THIS PORTION ASKS FOR AND READS PARAMETERS THAT WILL BE
C NECESSARY IN THE CALCULATIONS OF THE PARAMETERS

print *, 'how many monte carlo steps to execute?'
read *, time

print *, 'name of file to store data in?'
read (*, '(a20)') filename

print *, 'what is the x-position of the tip?'
read *, ytip

print *, 'what is the y-position of the tip?'
read *, xtip

C THIS PROBABILITY TAKES VALUES 1.LE.prob.GE 0 WHERE prob=1
C MEANS THAT A JUMP WILL OCCUR UNLESS THE PROSPECTIVE SITE IS
C OCCUPIED.
print *, 'value for diffusion probability?'
read *, prob

C THIS IS THE EFFECTIVE RADIUS OF A CIRCULAR PROBE AREA,
C IMITATING THAT OF AN IDEAL TIP WHICH WOULD HAVE CYLINDRICAL
C SYMMETRY. A VALUE OF 1 IS EQUIVALENT TO 5 SITES IN THE
C PROBE REGION.

print *, 'enter width-radius of probe area:'
read *, iwidth

C THIS IS THE START OF THE MAIN TIME LOOP

do t = 1, time

C THIS IS THE MAIN TIME LOOP EQUIVALENT TO ONE MONTE CARLO
C STEP (MCS). p PARTICLES ARE CHOSEN AT RANDOM AND EACH ONE
C ATTEMPTS TO JUMP TO A RANDOM SITE ADJACENT TO IT.

    do n = 1, p
        chooser = 1 + (p*ran2(idum))
        xcoord = coord(chooser,1)
        ycoord = coord(chooser,2)

    C THIS CHOOSES A RANDOM DIRECTION (1,2,3,4) CORRESPONDING TO
    C (N,W,S,E)

        yes = ran2(idum)
        dir = 1 + 4*yes

    C THIS CHECKS WHETHER OR NOT THE PROSPECTIVE SITE IS OCCUPIED.
    C IF IT IS, THE NEXT PARTICLE IS CHOSEN.

        if (dir.eq.1) then
            if (xcoord.gt.1) then
                xnew = xcoord - 1
                ynew = ycoord
            endif

            if (xcoord.eq.1) then
xnew = lsize
ynew = ycoord
endif

elseif (dir.eq.2) then
  if (ycoord.gt.1) then
    ynew = ycoord -1
    xnew = xcoord
  endif

  if (ycoord.eq.1) then
    ynew = lsize
    xnew = xcoord
  endif

elseif (dir.eq.3) then
  if (xcoord.lt.lsize) then
    xnew = xcoord +1
    ynew = ycoord
  endif

  if (xcoord.eq.lsize) then
    xnew = 1
    ynew = ycoord
  endif

elseif (dir.eq.4) then
  if (ycoord.lt.lsize) then
    ynew = ycoord +1
    xnew = xcoord
  endif

  if (ycoord.eq.lsize) then
    ynew = 1
    xnew = xcoord
  endif

C THE FOLLOWING IS TO TERMINATE THE PROGRAM IF WRONG VALUES FOR dir ARE DETECTED
else
    print *, 't,n:'
    write (*,'(2I10)') t,n
    stop
endif

C IF THE NEW SITE IS UNOCCUPIED, A JUMP OCCURS WITH
C PROBABILITY prob. OTHERWISE A NEW PARTICLE IS CHOSEN.

if (latt(xnew,ynew).eq.0) then
    chance = ran2(idum)
    if (prob.gt.chance) then
        if ((dir.eq.1).or.(dir.eq.3)) then
            coord(chooser,1) = xnew
            latt(xcoord,ycoord) = 0
            latt(xnew,ynew) = 1
        elseif ((dir.eq.2).or.(dir.eq.4)) then
            coord(chooser,2) = ynew
            latt(xcoord,ycoord) = 0
            latt(xnew,ynew) = 1
        endif
    endif
endif

enddo

C THIS IS THE END OF ONE MCS

C THE FF COUNTS THE NUMBER OF PARTICLES WITHIN THE PROBE AREA
C BOUNDED BY xtip+/iwidth AND ytip+/iwidth

    occupancy = 0
    do x = xtip - iwidth, xtip + iwidth
        do y = ytip-iwidth, ytip+iwidth
            rsquared=(x-xtip)**2 + (y-ytip)**2
            if (rsquared.le.iwidth**2) then
                occupancy = occupancy + latt(x,y)
            endif
        enddo
    enddo
endo
endo
master(t) = occupancy
endo

C THIS IS THE END OF THE TIME LOOP

C THE FF RECORDS THE ARRAY IN A FILE filename.

open (unit = 105, file = filename, status = 'unknown')
do t = 1,time
   value = master(t)
   write (105,'

endo
close (unit = 105)

end
SUBROUTINE ROUND

C THIS SUBROUTINE INCORPORATES THE EFFECT OF SURFACE POTENTIAL
C ASSYMETRIES WHICH MAY BE CAUSED BY NON-UNIFORM ELECTRIC FIELD
C ON THE SURFACE DUE TO THE TIP OR SUCH THINGS AS IMPURITIES OR
C STEP EDGES. THIS IS ACCOMPLISHED BY PRODUCING A PROBABILITY
C MATRIX WHICH IS POSITION-DEPENDENT. THIS DEPENDENCE MIMICS
C THE EFFECT IN THE FOLLOWING WAY. THE PROBABILITY IS TAKEN AS
C EXP(-a) AT INFINITY. AT LOCATIONS PROXIMAL TO THE CENTER OF
C THE SOURCE (THE TIP FOR THE CASE OF FIELD-EFFECTS), THE
C ACTIVATION ENERGY, a, IS MODULATED BY A FACTOR b. THE NEW
C PROBABILITY NOW BECOMES EXP(-(a+b)). b COULD BE POSITIVE OR
C NEGATIVE.

C FOR FIELD EFFECTS, THE EFFECT INDUCED IS THE RAISING OR
C LOWERING OF THE BARRIER HEIGHT (SADDLE POINT) WHILE TO
C SIMULATE PINNING SITES (OR REPULSION SITES), THE TROUGH
C IS RAISED OR LOWERED.

integer coord(l861,2),p,lsize,time,dir,x,y,t,chooser
integer occupeincy,value,master(4000000),idum,xtip,ytip
integer xcoord,ycoord,latt(61,61),xnew,ynew,iwidth
real yes,cov,chance,prob,next,const.numer,denom
real polar,fzero,sep,temp,rsquared,factor1,factor2,a,b
real sign, newprob(61,61)
character*20 filename
dimension char(2)
data char/_','x'/

C THIS PORTION CONSTRUCTS A SQUARE LATTICE OF SIZE lsize AND
C FILLS IT WITH PARTICLES WITH COVERAGE cov. THE OUTPUT IS AN
C (lsize x lsize) ARRAY, latt(x,y), WHICH REPRESENTS THE LATTICE
C AND coord(x,y) WHICH IS A RECORD OF THE POSITIONS OF THE
C PARTICLES IN latt(x,y).

print *, 'size of lattice?'
read *, lsize

print *, 'enter a desired coverage (0<cov<1):'
read *, cov
print *, 'enter a value for the seed (negative integer):'
read *, idum
start = ran2(idum)

p = 0
do x = 1,lsize
   do y = 1,lsize
      next = ran2(idum)
      if (cov.ge.next) then
         latt(x,y) = 1
         p = p + 1
         coord(p,1) = x
         coord(p,2) = y
      else
         latt(x,y) = 0
      endif
   enddo
endo
do x = 1,lsize
   do y = 1,lsize
      next = ran2(idum)
      if (cov.ge.next) then
         latt(x,y) = 1
         p = p + 1
         coord(p,1) = x
         coord(p,2) = y
      else
         latt(x,y) = 0
      endif
   enddo
endo

print *, p,'particles laid down'

C THIS STORES THE INITIAL LAYOUT IN 'init.fig'

open (unit = 10, file = 'init.fig', status = 'unknown')
do x = 1,lsize
   write (10,'(lx,61a2)') (char(1+latt(x,y)), y = 1,lsize)
endo
close (unit = 10)

print *, 'how many monte carlo steps to execute?'
read *, time

print *, 'name of file to store data in'
read (*,'(a20)') filename

print *, 'what is the x-position of the tip?'
read *, ytip

print *, 'what is the y-position of the tip?'
read *, xtip

print *, 'what is the tip-sample separation (in units of z0)?'
read *, sep

print *, 'enter value for Ea'
read *, a

print *, 'enter value for deltaE'
read *, b

print *, 'input -1 for away, +1 for toward'
read *, sign

print *, 'enter width-radius of probe area:'
read *, iwidth

C THIS PORTION CALCULATES THE PROBABILITY MATRIX, newprob.
C JUMPING PROBABILITIES ARE HENCEFORWARD DERIVED FROM THIS MATRIX

do x = 1,lsize
  do y = 1,lsize
    rsquared = (x-xtip)**2 + (y-ytip)**2
    factor2 = (1 + rsquared/sep**2)**(-3)
    numer=b*factor2
    newprob(x,y)= exp(-(a+(sign*numer)))
  enddo
endo
do x = 1,lsize
  do y = 1,lsize
    rsquared = (x-xtip)**2 + (y-ytip)**2
    factor2 = (1 + rsquared/sep**2)**(-3)
    numer=b*factor2
    newprob(x,y)= exp(-(a+(sign*numer)))
  enddo
endo

C THIS WRITE THE PROBABILITY MATRIX IN A FILE

open(unit = 320, file = 'probmatrix',status = 'unknown')
do x = 1,lsize
  write(320,'(2x,61F7.3)') (newprob(x,y), y = 1,lsize)
endo
close(unit = 320)
print *, 'probmatrix done.'

C THIS IS THE START OF THE MAIN TIME LOOP
do t = 1, time
C THIS IS THE MAIN TIME LOOP EQUIVALENT TO ONE MONTE CARLO
C STEP (MCS). p PARTICLES ARE CHOSEN AT RANDOM AND EACH ONE
C ATTEMPTS TO JUMP TO A RANDOM SITE ADJACENT TO IT.

   do n = 1, p
      chooser = 1 + (p*ran2(idum))
      xcoord = coord(chooser,1)
      ycoord = coord(chooser,2)

C THIS Chooses A RANDOM DIRECTION (1,2,3,4) CORRESPONDING TO
C (N,W,S,E)

      yes = ran2(idum)
      dir = 1 + 4*yes

C THIS Checks WHETHER OR NOT THE PROSPECTIVE SITE IS OCCUPIED.
C IF IT IS, THE NEXT PARTICLE IS CHOSEN.

      if (dir.eq.1) then
         if (xcoord.gt.1) then
            xnew = xcoord - 1
            ynew = ycoord
         endif

         if (xcoord.eq.1) then
            xnew = lsize
            ynew = ycoord
         endif

      elseif (dir.eq.2) then
         if (ycoord.gt.1) then
            ynew = ycoord -1
            xnew = xcoord
         endif

         if (ycoord.eq.1) then
            ynew = lsize
         endif
xnew = xcoord
endif

elseif (dir.eq.3) then
  if (xcoord.lt.lsize) then
    xnew = xcoord + 1
    ynew = ycoord
  endif
  if (xcoord.eq.lsize) then
    xnew = 1
    ynew = ycoord
  endif
elseif (dir.eq.4) then
  if (ycoord.lt.lsize) then
    ynew = ycoord + 1
    xnew = xcoord
  endif
  if (ycoord.eq.lsize) then
    ynew = 1
    xnew = xcoord
  endif
else
  print *, 't,n:'
  write (*,'(2I10)') t,n
  stop
endif

C IF THE NEW SITE IS UNOCCUPIED, A JUMP OCCURS WITH PROBABILITY
C prob. FOR FIELD EFFECTS, prob = newprob(xnew,ynew) WHILE FOR
C PINNING SITES, prob = newprob(xcoord,ycoord).

if (latt(xnew,ynew).eq.0) then
  prob = newprob(xnew,ynew)
C prob = newprob(xcoord,ycoord)
  chance = ran2(idum)
if (prob.gt.chance) then
  if ((dir.eq.1).or.(dir.eq.3)) then
    coord(chooser,1) = xnew
    latt(xcoord,ycoord) = 0
    latt(xnew,ynew) = 1
  elseif ((dir.eq.2).or.(dir.eq.4)) then
    coord(chooser,2) = ynew
    latt(xcoord,ycoord) = 0
    latt(xnew,ynew) = 1
  endif
endif
endif
enddo

C THIS IS THE END OF ONE MCS

C THE FF COUNTS THE NUMBER OF PARTICLES WITHIN THE PROBE AREA
C BOUNDED BY xtip+/-iwidth AND ytip+/-iwidth

occupancy = 0
do x = xtip - iwidth, xtip + iwidth
  do y = ytip-iwidth, ytip+iwidth
    rsquared=(x-xtip)**2 + (y-ytip)**2
    if (rsquared.le.iwidth**2) then
      occupancy = occupancy + latt(x,y)
    endif
  enddo
enddo
master(t) = occupancy

C THIS RECORDS THE FINAL LAYOUT IN final.fig

if (t.eq.time) then
  open (unit = 20, file = 'final.fig', status = 'unknown')
  do x = 1, lsize
    write (20, '(lx,61a2)') (char(i+latt(x,y)), y = 1,lsize)
  enddo
C THIS IS THE END OF THE TIME LOOP

C THE FF RECORDS THE ARRAY IN A FILE filename.

open (unit = 105, file = filename, status = 'unknown')
do t = 1,time
    value = master(t)
    write (105,'(I3)') value
endo
close (unit = 105)

end
PROGRAM AUTOCORRELATE

C THIS PROGRAM IS AN AUTOCORRELATION ROUTINE PERFORMED ON
C FILE name1. THE CORRELATED FILE IS STORED IN FILE result.
C IN THE CORRELATION PROGRAM, THE MEAN NUMBER, avg, IS
C SUBTRACTED.

integer time,t,j,corlt,r,ii,jj
real avg,newval,value,nought,reg(5000000),sum,what,ac(16384)
character*20 namel

C THE TOTAL NUMBER OF MCS IS THE LENGTH OF EACH FILE

print *, 'total number of MCS?'
read *, time

print *, 'length of correlation function?'
read *, corlt

C THE FF INITIALIZES THE ARRAY ac TO ZERO. THIS ARRAY IS
C USED TO STORE THE CORRELATED VALUES

do j = 1, corlt
   ac(j) = 0
endo

C THE FF STARTS THE MAIN CORRELATION ROUTINE.

print *, 'name of time file?'
read(*,'(a20)') namel

open(unit = 30, file = namel, status = 'unknown')
sum = 0

do t = 1, time
   read(30,*) value
   reg(t) = value
   sum = sum + value
endo

avg = sum/time
close(unit = 30)
print *, avg

C THE ACTUAL CORRELATION FUNCTION IS CALCULATED HERE.
C THE LIMIT IN THE FIRST DO--LOOP (time - corlt + 1) DETERMINES
C THE NUMBER OF MULTIPLICATIONS SUMMED INTO EACH TERM.
C THE LIMIT IN THE SECOND DO--LOOP (corlt + ii - 1)
C DETERMINES THE LENGTH OF THE CORRELATION FUNCTION.
C A BASELINE avg IS SUBTRACTED FROM THE VALUE IN reg(t).

    do ii = 1, time - corlt+1
       do jj = ii, corlt + ii - 1
          ac(jj-ii+1) = ac(jj-ii+1) + (reg(jj)-avg)*(reg(ii)-avg)
       enddo
    enddo

C AFTER HAVING CORRELATED ALL THE FILES, THE CORRELATION
C MAY BE NORMALIZED BY DIVIDING THE VALUES BY ac(1).
C THIS WRITES THE CORRELATION FUNCTION TO A FILE NAMED result

open(unit = 40, file = 'result', status = 'unknown')
    do j = 1,corlt
       write(40,*) ac(j)
    enddo
close(unit=40)
end
PROGRAM CORNOAV

C THIS PROGRAM IS AN AUTOCORRELATION ROUTINE PERFORMED ON
C FILE namel. NO SUBTRACTION OF THE MEAN NUMBER IS DONE.
C THE OUTPUT IS STORED IN FILE result.

integer time, t, j, corlt, r, ii, jj
real avg, newval, nought, reg(5000000), sum, what, value, ac(16384)
character*10 name1

C THE TOTAL NUMBER OF MCS IS THE LENGTH OF EACH FILE

print *, 'total number of MCS?'
read *, time

print *, 'length of correlation function?'
read *, corlt

C THE FF INITIALIZES THE ARRAY ac TO ZERO. THIS ARRAY IS
C USED TO STORE THE CORRELATED VALUES

do j = 1, corlt
   ac(j) = 0
enddo

print *, 'name of time file?'
read(*,'(a10)') name1

open(unit = 30, file = name1, status = 'unknown')
sum = 0

do t = 1, time
   read(30,*) value
   reg(t) = value
   sum = sum + value
endo
davg = sum/time

close(unit = 30)

C THE ACTUAL CORRELATION FUNCTION IS CALCULATED HERE.
THE LIMIT IN THE FIRST DO--LOOP (time - corlt) DETERMINES
THE NUMBER OF MULTIPLICATIONS SUMMED INTO EACH TERM.
THE LIMIT IN THE SECOND DO--LOOP (corlt + ii - 1)
DETERMINES THE LENGTH OF THE CORRELATION FUNCTION.

\[
\begin{align*}
\text{do } & ii = 1, \text{ time } - \text{ corlt}+1 \\
& \text{do } jj = ii, \text{ corlt} + ii - 1 \\
& \quad ac(jj-ii+1) = ac(jj-ii+1) + \text{reg}(jj)\times\text{reg}(ii) \\
& \quad \text{enddo} \\
& \text{enddo}
\end{align*}
\]

AFTER HAVING CORRELATED ALL THE FILES, THE CORRELATION
MAY BE NORMALIZED BY DIVIDING THE VALUES BY ac(1).

THIS WRITES THE CORRELATION FUNCTION OF THE ENSEMBLE
(both time and space) TO A FILE NAMED result

\[
\begin{align*}
\text{open(unit = 40, file = 'result', status = 'unknown')} \\
& \text{do } j = 1, \text{corlt} \\
& \quad \text{write(40,* ) ac(j)} \\
& \quad \text{enddo} \\
\text{close(unit=40)}
\end{align*}
\]

end
PROGRAM DOBLE

C THIS PROGRAM ATTEMPTS TO SIMULATE SIMULTANEOUS DIFFUSION ON THE
C SURFACE AND ON THE TIP OF THE STM. BASICALLY, IT IS ASSUMED
C THAT THE TIP AND THE SUBSTRATE ARE INDEPENDENT OF EACH OTHER,
C OR AT LEAST THE MOTION OF THE ADATOMS ON EACH SURFACE DOES NOT,
C IN ANY WAY, AFFECT THE DIFFUSION OF THE OTHER. TO ACHIEVE THIS,
C THE NUMBER OF PARTICLES IN THE PROBE REGIONS OF THE TIP AND THE
C SUBSTRATE ARE COUNTED AND THEN CORRELATED. IN PRINCIPLE,
C SITUATIONS WHERE TWO PARTICLE ARE 'ON TOP' OF EACH OTHER ARE
C NOT EXCLUDED.

integer comb,i,total,j,time,ii,jj,r,corlt,t
real reg(4000000), ac(16390), sum, avg,nought,newval,val1,val2
character*20 namel, name2

C THE TOTAL NUMBER OF MCS IS THE LENGTH OF EACH FILE

print *, 'total number of MCS?
read *, time

print *, 'name of first file?
read (*,'(a20)') namel

print *, 'name of second file?
read (*,'(a20)') name2

C THE LENGTH OF THE FUNCTION IS EQUAL TO THE NUMBER OF TERMS
C IN THE CORRELATION FUNCTION

print *, 'length of correlation function?
read *, corlt

C THE FF INITIALIZES THE ARRAY ac TO ZERO. THIS ARRAY IS
C USED TO STORE THE CORRELATED VALUES

open(unit = 30, file = namel, status = 'unknown')
open(unit = 40, file = name2, status = 'unknown')

sum = 0
do t= 1, time
   read (30,*), vail
   read (40,*), val2
   comb = (vail + val2)
   sum = sum + comb
   reg(t) = comb
endo
dxo = sum/time
print *, avg

close(unit = 30)
close(unit = 40)

C THE ACTUAL CORRELATION FUNCTION IS CALCULATED HERE.
C THE LIMIT IN THE FIRST DO--LOOP (time - corlt) DETERMINES
C THE NUMBER OF MULTIPLICATIONS SUMMED INTO EACH TERM.
C THE LIMIT IN THE SECOND DO--LOOP (corlt + ii - 1)
C DETERMINES THE LENGTH OF THE CORRELATION FUNCTION.

do j = 1, corlt
   ac(j) = 0
endo
do ii = 1, time - corlt+1
   do jj = ii, corlt + ii - 1
      ac(jj-ii+1) = ac(jj-ii+1) + (reg(jj)-avg)*(reg(ii)-avg)
   enddo
endo

C AFTER HAVING CORRELATED ALL THE FILES, THE CORRELATION
C MAY BE NORMALIZED BY DIVIDING THE VALUES BY ac(1)
C
nought = ac(1)

open(unit = 50, file = 'result', status = 'unknown')
do j = 1,corlt
   write(50,*), ac(j)
endo
close(unit=50)
end
FUNCTION RAN2(idum)

C THIS RANDOM NUMBER GENERATOR IS TAKEN FROM
C 'NUMERICAL RECIPES IN FORTRAN, 2ED.' BY PRESS, ET. AL.

integer idum, IM1,IM2,IMM1,IA1,IA2,IQ1,IQ2,IR1,IR2,NTAB,NDIV
real ran2,AM,EPS,RNMX
parameter (IM1=2147483563,IM2=2147483399,AM=1./IM1,IMM1=IM1-1,
+ IA1=40014,IA2=40692,IQ1=53668,IQ2=52774,IR1=12211,
+ IR2=3791,NTAB=32,NDIV=1+IMM1/NTAB,EPS=1.2e-7,RNMX=1.-EPS)
integer idum2,j,k,iv(NTAB),iy
save iv,iy,idum2
data idum2/123456789/,iv/NTAB*0/,iy/0/
if (idum.le.0) then
  idum = max(-idum,1)
idum2 = idum
  do j = NTAB+8,1,-1
    k = idum/IQ1
    idum = IA1*(idum-k*IQ1)-k*IR1
    if (idum.lt.0) idum = idum + IM1
    if (j.le.NTAB) iv(j) = idum
  enddo
  iy = iv(1)
endif
k = idum/IQ1
idum = IA1*(idum-k*IQ1) - k*IR1
if (idum.lt.0) idum = idum + IM1
k = idum2/IQ2
idum2 = IA2*(idum2-k*IQ2) - k*IR2
if (idum2.lt.0) idum2 = idum2 + IM2
j = 1 + iy/NDIV
iy = iv(j) - idum2
iv(j) = idum
if (iy.lt.1) iy = iy + IMM1
ran2 = min(AM*iy, RNMX)
return
end