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NON-EQUILIBRIUM SURFACE DIFFUSION MEASUREMENTS IN SYSTEMS WITH INTERACTIONS

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Abstract

Diffusion in surface overlayers with adsorbate-adsorbate interactions is described in terms of coverage-dependent diffusion coefficients. The measured phenomenological Arrhenius parameters (activation energy and prefactor) depend on the initial configuration of the system. Since different experimental methods probe the system in different states, the measured diffusion coefficients depend on the method used. Experimental results demonstrating this dependence are presented for O/W(110) - p(2x1) + p(2x2) and Ag/Si(111) - $\sqrt{3} \times \sqrt{3}$ R30°. They were measured during the evolution of the system to attain a new equilibrium state of different symmetry. In addition, simulations on lattice gas models with interactions, modeling other surface diffusion techniques (Laser-Induced-Desorption, fluctuation, non-equilibrium kinetics) support the configuration-dependent results.

Key Words: Surface diffusion, growth, non-equilibrium processes, quantitative Low-Energy-Electron-Diffraction/Reflection-High-Energy-Electron-Diffraction profile analysis, growth under constant deposition rate, growth process modeling.

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Introduction

Surface diffusion has been increasingly studied[6] in recent years, especially experimentally, to understand its role in the growth of atomically controlled structures. The optimization of the final product depends on identifying the basic, underlying parameters that determine surface mass transport. The analysis of growth is usually based on the use of a single particle picture of hopping over a static barrier; in practice, however, more complex analysis is required to account for the multi-body character of the phenomena involved. Growth processes are performed at finite coverage, in almost all cases, with many particles present that mutually interfere in each other's motion both with blocking, but more importantly, with interatomic interactions. The single particle diffusion in a static potential well should be replaced with diffusion in a continuously changing, both spatially and temporally, potential surface. Equivalently, this implies concentration-dependent diffusion coefficients D(c) and an evolving concentration profile described in terms of the non-linear diffusion equation. As the overlayer configuration changes, it modifies the local value of the diffusion coefficient which, in turn, affects the changing configuration.

Very few techniques are currently available to address the problem of concentration-dependent diffusion in systems with interactions. Methods based on small perturbations applied to a system at equilibrium use its relaxation back to equilibrium as a measure of the diffusion coefficient. Small signals and fast time responses are involved which are difficult to measure experimentally and require high amplification techniques. By exploiting the high magnification in field emission electron microscopy, the current fluctuations, induced by the density fluctuations of the number of atoms as they diffuse in and out of a probe area on a field emitter, have been used[6] to measure the decay back to equilibrium. It is difficult to implement experimentally equilibrium methods, especially on the atomic scale, because the deviations from equilibrium are only a few percent from the average value and high spatial resolution is needed to exclude surface defects and non-uniformities. Theoretically, Monte Carlo methods or mean field type approximations on interactive lattice gases have been used to study surface diffusion at equilibrium; as usual, one trades off accuracy with transparency of the results in the two approaches.

Non-equilibrium methods, either in spatially or temporally inhomogeneous systems, have been also used to monitor surface diffusion in overlayers. Because of the large changes involved, a higher experimental signal is available to monitor the evolution of the system back to equilibrium which can be followed easier in the laboratory. However, the

difficulties have been passed on to the theoretical analysis, which becomes highly more complex, because of the non-linear forces involved. The Boltzmann-Matano method[6] uses an initial step-function concentration profile that evolves in time towards uniform concentration. If the evolution of the profile depends only on the scaled variable $\eta = \frac{x}{t^{1/2}}$ (where x is the distance and t the time, an assumption whose physical meaning and range of validity have not been fully explored), then the invariant lineshape of the evolving profile can be used to measure D(c). In temporally non-equilibrium systems, the evolution from an initial to a final state of different symmetry, shown schematically in Fig. 1 (for example, island ordering out of an initial random state, island disordering out of an initial ordered state, adsorption on initially clean surface under constant deposition rate), can be used[23,17] to obtain information about surface diffusion. Theoretically, in analyzing these non-equilibrium techniques, one has to exclusively rely on Monte Carlo methods or analytic solutions to the non-linear diffusion equation because clearly perturbative methods are inapplicable.

The goal of this paper is to present examples where such non-equilibrium experiments on systems with interactions have been performed and surface diffusion coefficients have been extracted. Both experiments on real systems and results with computer simulations on interactive lattice gas models will be presented. As will be seen, the main conclusion is the importance of the overlayer configuration in determining the value of the measured diffusion coefficient, because adsorbate-adsorbate interactions contribute differently in different configurations. However, the use of diffusion to describe non-equilibrium processes poses the question about the meaning of non-equilibrium diffusion and how it is related to the textbook definition of diffusion, which, in general, assumes equilibrium. Although more basic work is required to legitimize the concept of non-equilibrium diffusion, its practical use on several studies so far and the agreement between the non-equilibrium and equilibrium experiments, for the same overlayer configuration, are sufficient proof of its validity.

Experimental Systems

Domain growth kinetics experiments in O/W(110) - p(2x1) + p(2x2)

The O/W(110) system has a well-known phase diagram which can be described[25] in terms of a lattice gas. Nearest-neighbor attractive and next-nearest-neighbor repulsive interactions have been used to model its equilibrium properties. The O mobility in the system was studied[17,20,22] at high coverages, $\theta>0.6$, where interactions are more important with three different techniques. For T<550K the p(2x1) + p(2x2) ordered phases coexist, but for T>550K the p(2x2) phase disorders. These changes can be easily monitored with Low-Energy-Electron-Diffraction (LEED), by measuring the time dependent angular profile S(q,t) of the (1/2, 1/2) spot at different temperatures to extract the non-equilibrium diffusion. Both the ordering[17] out of a random state and the disordering[20] out of an initially ordered state can be used. A LEED video system was used at sufficiently low currents and high magnification so the instrumental resolution was improved to 400Å, a factor of 2 higher than the instrumental limit of a conventional diffractometer. Because of the eight-fold degeneracy of the two phases, the largest sizes formed during ordering or the initial ordered domains during disordering were 2-3 times smaller than the instrumental limit, so resolution effects were less than 10%.

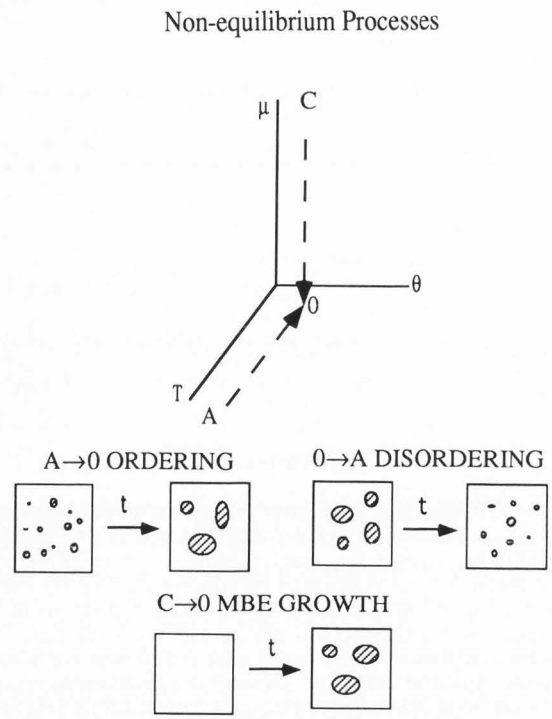

Fig. 1. Schematic illustration of non-equilibrium processes in T-θ-μ parameter space: ordering, disordering, adsorption. The system evolves in time between states of different symmetries.

In addition to these two non-equilibrium experiments with LEED which monitor "catastrophic" changes in the symmetry of the overlayer, a third experiment[22] with the current fluctuation method was also performed at equilibrium. In this experiment, the system is well equilibrated and the decay of the density fluctuations within a probe area at the center of a W(110) oriented field emitter is used to measure the equilibrium diffusion coefficient.

In comparing diffusion coefficients obtained in different experiments, it is easier to compare the measured activation energy than the prefactor. The former requires only a relative measurement of the diffusion length at different temperatures, while the latter can be extracted only if an absolute determination of the length is possible. In the equilibrium experiment, an accurate estimate of the probe area size can be determined from the field emission magnification; in the diffraction experiment, one can easily measure the relative, temperature-dependent change from the peak intensity or Full-Width-Half-Maximum (FWHM), but an accurate spot profile fitting to extract the domain size distribution is needed for absolute measurements. Even if the absolute size of the ordered domains is estimated, other physical parameters like domain line tension, adsorbate molar volume, etc., are involved[23] in the relation between the growing length and the diffusion coefficient, and they should be known from separate experiments.

The ordering kinetics of O/W(110) are studied[17] after depositing oxygen at 120K at a coverage $\theta=0.68$ in a "frozen-in," random configuration. The system is upquenched into the temperature range T=350-384K and the (1/2, 1/2) profiles are measured in time as they grow. They are shown in Fig. 2 for T=384K. The FWHM or the second moment of the

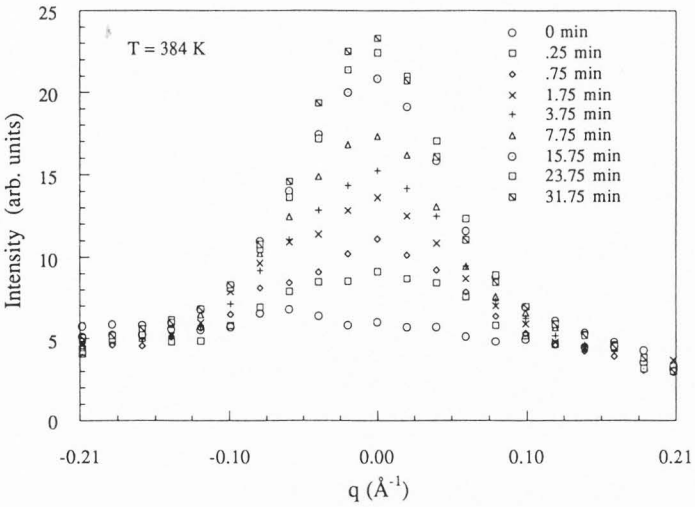

Fig. 2. Ordering profile of the (1/2, 1/2) spot in the O/W(110) - p(2x1) + p(2x2) system after it is upquenched at T=384K from a "frozen" initial configuration deposited at T=120K.

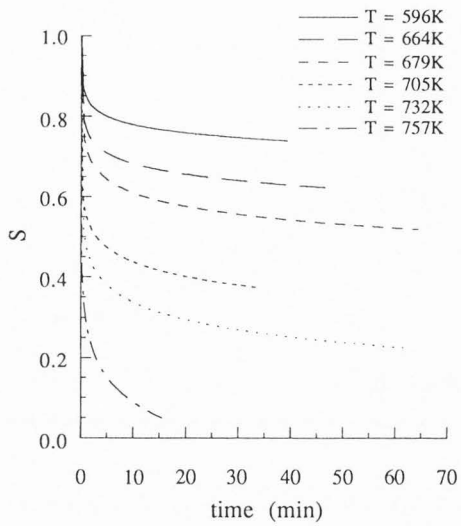

Fig. 3. Decay of the (1/2, 1/2) superstructure spot during the disordering of the p(2x2) phase after an upquench into the range T=596-760K.

profile with respect to its center (when the profile is treated as a probability distribution) can be used as measures of the average domain size. Based on numerous simulations on model systems, it is expected that the domain growth is self-similar in time (i.e., the domain size distribution is time invariant) and the average domain size follows a power law $L=A(T)t^x$. A(T) is the temperature dependent growth rate of the process. We have measured a growth exponent $x=0.31 \pm 0.03$eV and an activation energy $E_A=0.19 \pm 0.02$eV. The diffusion activation energy can be related to the growth rate activation energy with a simple dimensional argument. For the previous equation giving the time dependence of L to be dimensionally consistent, we need to eliminate the time dependence on the right-hand side which implies $A \propto D^x$, since the diffusion coefficient has units of inverse time. Based on this expression, we measure $E_D=E_A/x = 0.6 \pm 0.05$eV for the activation energy of diffusion.

For the disordering experiment,[20] the system is upquenched into the temperature range T=596 - 760K after first heating at T=550K, with the p(2x1) and p(2x2) well developed as measured from the sharpest (1/2, 1/2) spot. The disordering (like the ordering processes) occurs over several minutes, well within the video system acquisition time. A collective response of many atoms is involved in the domain structure change which results in macroscopic measurement times; the finite quench rate has a negligible effect as long as it is faster (few seconds) than the collective response time (minutes). It is surprising that during disordering the FWHM or the second moment of the profile is constant. These measures cannot be used to measure the amount of disorder developed. It is also remarkable that a linear relation is observed between the decaying peak and the 2-D integrated intensity. The non-constant integrated intensity can be understood in terms of the atoms released out of the p(2x2) phase which can either join the p(2x1) or the disordered state and transfer intensity outside the 2-D Brillouin zone of the (1/2, 1/2) spot. The decay of the integrated intensity is shown in Fig. 3 at different final temperatures. As is well known,[8] instrumental limitations do not affect the 2-D integrated intensity. Since the functional form of the decay is still unknown, the initial slope at t=0 is used under the assumption that the intensity is only a function of the unitless combination (Dt) so $I(Dt) = 1-cDt + O(Dt)^2 + \ldots$ The assumption has been previously used[7] in the study of the kinetics of the reconstruction Ir(100) (1x1) → (1x5) and has been theoretically confirmed[4] in studies of one-dimensional disordering. When the initial slope of the intensity decay is plotted vs. 1/T, an activation energy $E=1 \pm 0.05$eV is obtained which is larger by 0.4eV than the activation energy extracted in ordering processes.

Experiments[22] on the O/W(110) system, in the range T=590-715K, were performed at equilibrium with the current fluctuation method. Although the phase diagram has not been mapped out systematically, most likely the system is ordered with the p(2x1) and p(2x2) phases fully developed. The autocorrelation function of the field emission current fluctuations, shown in Fig. 4, is proportional to the density fluctuations and its decay constant is inversely proportional to the diffusion coefficient. The decay constants obtained at different temperatures are plotted in an Arrhenius plot to extract an activation energy of diffusion $E=1 \pm 0.05$eV and a prefactor $D_0 = 10^{-4}$cm^2/sec. The Arrhenius plots in the three experiments are shown in Fig. 5 and as explained before, only activation energies can be compared easily.

We can explain the difference in activation energies obtained in these three experiments in terms of the adsorbate-adsorbate interactions present in this system. The configurations probed by the three experiments are different and the interactions contribute differently to the diffusion barrier. It is important to emphasize that these differences are not related to differences in the coverage, because the three experiments were performed at approximately the same coverage. The ordering experiment probes the random configuration, with an atom having the same number of nearest-neighbors and next-nearest-neighbors. The interactions cancel each other because of their opposite signs. In the disordering and in the equilibrium experiments, the system is probed in a state with ordered p(2x1) and p(2x2) domains. These configurations have higher occupation of nearest-neighbors than next-nearest-neighbors, so the 0.4eV higher activation energy during ordering can be accounted for by the resulting net attractive interaction. It is remarkable that both the disordering and equilibrium experiments, although performed under widely varying conditions, measure the same activation energy.

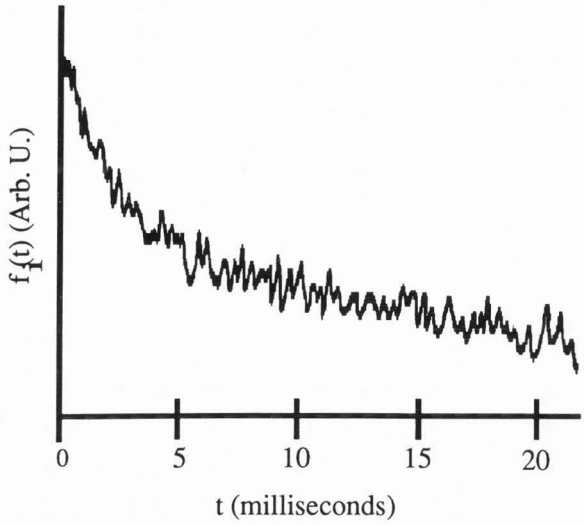

Fig. 4. Autocorrelation function in the O/W(110) - p(2x1) + p(2x2) system, measured from the decay of equilibrium density fluctuations.

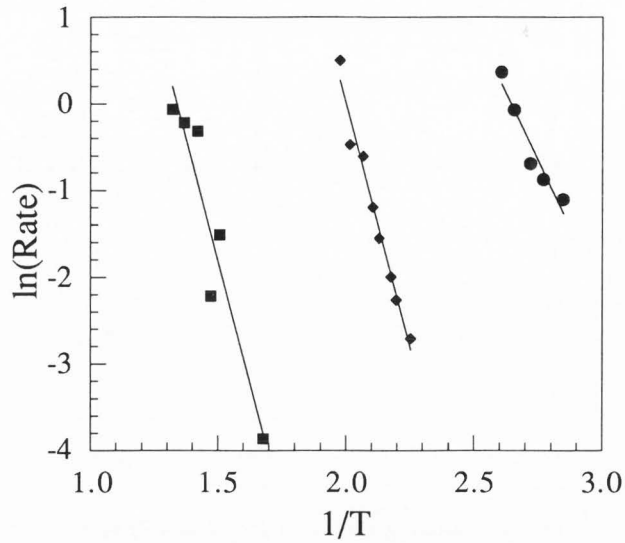

Fig. 5. Arrhenius plots for the three diffusion experiments ordering (●), equilibrium (◆), disordering (■) that measure activation energies of 0.6, 1, 1eV respectively.

Despite the explanation of the measured activation energies in terms of the interactions, it is important to emphasize a conceptual difference between equilibrium and non-equilibrium diffusion. The textbook definition of the diffusion coefficient is given in terms of a small, local variation in the concentration density ($\frac{\delta c}{\bar{c}} << 1$) which approximately transforms[11] the non-linear diffusion equation into a linear equation, D(c) is essentially the same everywhere (unless spatially inhomogeneous phases coexist at equilibrium, with different diffusion coefficients for each phase, so a non-uniform D(c) results). What is the meaning of the diffusion coefficient far from equilibrium? We can define[5] the measured diffusion coefficient as a weighted average over the different local environments present in the overlayer and their corresponding probabilities. During ordering, we can distinguish two types of local environments, one in the interior of the growing domains and the other at the domain boundary. We can define an average diffusion coefficient

$$\overline{D} = D_I P_I + D_B P_B, \tag{1}$$

where D_I, D_B are the diffusion coefficients and P_I, P_B, the probabilities of an atom being inside and at the domain boundary. P_I, P_B scale as the ratio of the area/perimeter of the domains

$$\frac{P_I}{P_B} = \frac{L^2}{L} \sim t^x, \tag{2}$$

assuming self-similarity during ordering and the simple power law time dependence of the average domain size L. This implies that

$$\overline{D} \propto D_B + D_I t^x \tag{3}$$

and since the measurement of the growth rate A(T) was restricted to $t \cong 0$, it is clear that the measured diffusion coefficient corresponds to the random configuration which is similar to the configuration with zero size domains. Is this diffusion coefficient identical to the one obtained when a small perturbation is applied to the same disordered state at equilibrium, i.e., at temperatures well above the transition temperature $T >> T_C$? It is clear that both non-equilibrium and equilibrium experiments in this random state start with the same initial state. In the non-equilibrium experiment the final state, during the short time around t=0 when the growth rate is measured, consists of small domains while in the equilibrium experiment it is the uniform state. The difference in the final states should be irrelevant because the diffusion coefficient defined as a weighted average over the different local configurations is exclusively determined by the initial state. The same activation energy should result in the two experiments since they are in the same initial state. Furthermore, if the ordering experiment growth curves obtained at different temperatures are compared at finite times $t_o > 0$ when the domains have reached a non-zero size, then the activation energy in a mixed state of partially ordered and partially random regions is measured. In this case, the slopes of the growth curve, L(t), at time t_o $\frac{dL}{dt}\Big|_{t_o}$ vs. 1/T can be tested for Arrhenius dependence to extract the effective activation energy of the mixed state.

The issue of non-equilibrium can also be raised for the Boltzmann-Matano method. It is necessary, as pointed out in the introduction, to first establish that the concentration density profile obeys scaling $c(\frac{x}{t^{1/2}})$, which is reminiscent of the self-similarity observed in ordering kinetics. The diffusion coefficient D(c) measured as an integral over the profile $c(\frac{x}{t^{1/2}})$ is not determined by the relaxation of the system back to equilibrium (as in methods which apply small perturbations), but successive intermediate non-equilibrium states are sampled before a uniform state is reached. There is an indirect contribution of the diffusion currents away from the evaluated diffusion coefficient D(c) at a given

concentration c, but they are different from the ones in the uniform state. It is possible to use the same initial state argument to justify at least the legitimacy of the measured activation energy.

Growth during deposition

Non-equilibrium processes, as shown in Fig. 1, also include the growth of overlayer structures by atom deposition at a constant flux rate. When diffraction is used to monitor the deposition, intensity oscillations of the specular beam have been observed[9] which, in general, imply layer-by-layer growth. This requires significant adatom mobility during the growth. Surprisingly, diffraction intensity oscillations have been observed[2] at low temperatures, T=80-150K, for several overlayer/substrate combinations. For most systems with normal diffusion barriers, this temperature range is very low and thermal diffusion is absent, so the origin of the low temperature mobility is not clear.

We have studied[20] the growth of Ag/Si(111) in the range T=150-300K, where we observe 3-4 oscillations at the lower temperatures which disappeared at room temperature. For further identification of the mobility mechanism at 150K, we varied the deposition flux by a factor of 50. If thermal diffusion operates at 150K, then at lower flux rates longer diffusion lengths are expected and a smoother layer should be grown. As the quality of the grown layer improves at lower flux rates, more pronounced oscillations should be observed.

Figure 6 shows that the number and shape of oscillations are independent of flux rate. We have plotted the intensity, testing for scaling: $I/I(o)$ vs. t/τ where τ is the time it takes the intensity to drop to half its original value. It is clear that the data collapse into a single curve for all flux rates. This can be explained if a constant diffusion length R, independent of the flux rate, is the only length characteristic of the growth. In this case the growth is simply determined by the number of atoms available, i.e., the product (Ft), where F is the flux rate and t the deposition time. The diffracted intensity is then described by I(Ft), i.e., scaling is obeyed. Since thermal diffusion (if it operates) results in larger R at the lower flux rates, it follows this is not the mechanism driving the low temperature growth, because it would violate scaling, and produce a more complicated function I(Ft, R(t)). Scaling implies that growth occurs on a time scale faster than the atom arrival plus capture time by the growing islands, so that R is independent of flux. From the flux rates used in the experiment and the expected island separation, we estimate the time scale of the mechanism responsible for low temperature oscillations to be less than 10^{-4} sec. A process faster than 10^{-4}sec is the relaxation of the incoming atoms to the substrate; before an atom gives up its excess energy over the surface potential minimum, it can perform several lateral jumps, if the energy transfer to the substrate is not very efficient. This so-called transient mobility, if present, complicates the simple picture of surface diffusion as a random walk. For the Ag/Si(111) system, it is reasonable to expect such effects because of the strong Si-Si covalent bond. A "stiff" lattice results, which cannot quickly dissipate the extra energy.

At higher temperatures T>473K, the deposited Ag forms the well-known[12] $\sqrt{3}x\sqrt{3}R30°$ structure which can be used to identify further the origin of the Ag mobility. With Reflection-High-Energy-Electron-Diffraction (RHEED), we monitor the evolution of the $\sqrt{3}$ structure at different flux rates and temperatures starting with an initially clean surface. This is a non-equilibrium experiment, similar to the ordering experiment for O/W(110), except it is a constant flux than a constant coverage experiment. The average domain size is measured in real time during the deposition. For a given flux, we use the slope of the I vs. t curve obtained at different temperatures to extract the activation energy of the process. Because the dependence is linear in time, we assume the intensity depends on the dimensionless combination (Dt). For fluxes F > 1/800 ML/sec, an activation energy E=0.25 $\pm$ 0.03eV is obtained which drops to half this value at lower flux rates up to F=1/5000 ML/sec. It is not clear why the activation energy decreases with flux rate; it can be possibly related to the increasing probability of adatoms landing on top of the already formed $\sqrt{3}$. Diffusion on top of the $\sqrt{3}$ is known[13] to be faster than diffusion on the Si substrate. These activation energy values are extremely low when compared[13] to activation energies obtained in other experiments on Ag/Si(111). Although we cannot expect diffusion experiments to measure the same activation energy, in general, (unless they probe the same configuration as emphasized in the O/W(110) experiments), all the measured activation energies for the Ag/Si(111) system are larger than 0.4eV. The growth of the superstructure in our experiment is sensitive not only to single particle diffusion but to other processes like two-dimensional evaporation, clustering, and many-particle effects, which are expected to have higher activation energies. The measured low value of 0.13-0.25eV suggests a weakly temperature-dependent diffusion length. This is consistent with non-thermal mobility: the constant distance traveled independently of growth conditions can lead to a lower activation energy to dissipate laterally the excess condensation energy.

Simulations

Studies on model systems to measure surface diffusion have also demonstrated the importance of interactions and the overlayer configuration. Model systems have well controlled parameters that can be varied independently to isolate the relevant effects. We will present examples where different surface diffusion coefficients are measured with different techniques used on the same model.

Laser-Induced-Desorption vs. Fluctuation Method

Both methods use the same geometry of a circular probe area at the center of the surface. In the fluctuation method, as described before, uniform coverage is present over the entire surface and spontaneous fluctuations are monitored to measure the relaxation of the probe area back to equilibrium. The Laser-Induced-Desorption (LID) method is a spatially inhomogeneous method with the circular probe area initially empty; the diffusion coefficient is obtained from the refilling of the probe area by outside atoms. The measurements are carried out with higher experimental sensitivity when the initial slope of the refilling signal is used, although it has been pointed out that for coverage-dependent diffusion, measuring the refilling signal at late times is necessary, which is a difficult requirement to implement experimentally.

It can be shown[21] for non-interactive systems, the signal measured by the fluctuation method is complementary to the signal measured by the LID method

$$g_{LID}(t) + g_{fl}(t) = 1, \qquad (4)$$

where $g_{fl}(t)$ is the autocorrelation function obtained in the fluctuation experiment and $g_{LID}(t)$ the refilling signal squared. Both $g_{fl}(t)$ and $g_{LID}(t)$ have been normalized to one of their maximum values. This is easily seen if the refilling of the probe area is studied for a given pair (θ_{out}, θ') where θ_{out} is the coverage outside and θ' the coverage inside the

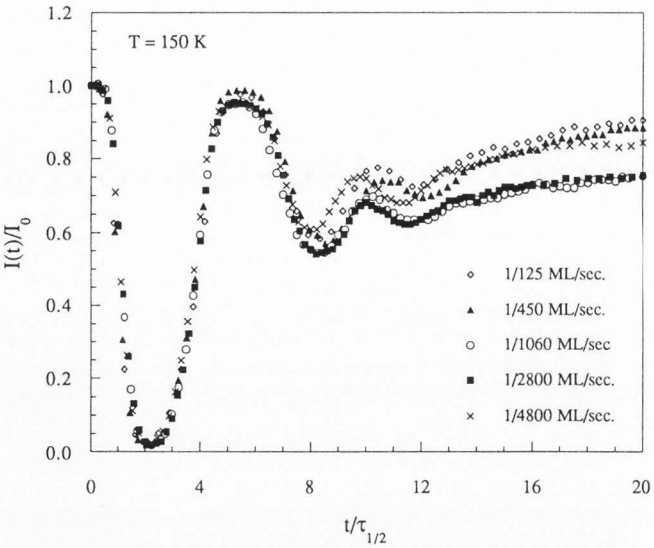

Fig. 6. Reflection-High-Energy-Electron-Diffraction intensity oscillation of Ag/Si(111) at 150K for several deposition rates F. The data are plotted in a scaling form I(t)/I(0) vs. $t/\tau_{1/2}$ where I is the specular beam intensity and $\tau_{1/2}$ the time it takes the intensity to drop to half its value.

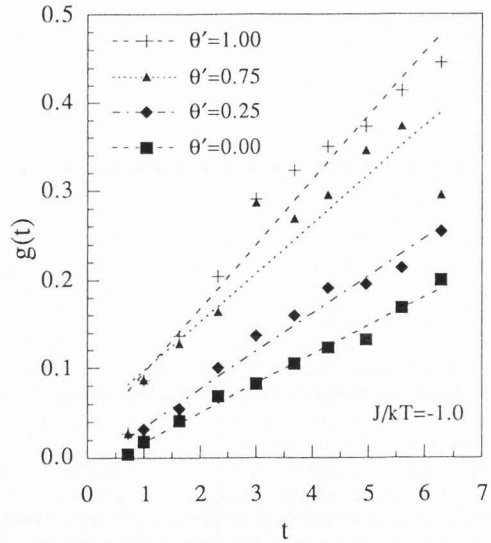

Fig. 7. Refilling signal of the LID method obtained with computer simulations on a model with nearest neighbor repulsive interactions for a given coverage θ_{out}=0.5. The refilling signal depends on the occupation of the probe area θ′, which shows that the diffusion D_{LID} extracted with the Laser-Induced-Desorption method (θ=0) is lower than the one extracted with the fluctuation method D (θ≈θ′).

probe area. The LID method corresponds to the initial condition θ′=0 while the fluctuation method corresponds to $\theta_{out}\approx\theta'$. Simulations on non-interactive lattice gas models (only site exclusion is allowed) clearly show that for a given value of θ_{out} the same refilling signal is obtained irrespective of θ′, thus confirming the same relaxation constant for both the fluctuation and LID geometry. If interactions are present as in Fig. 7, which shows the refilling curves for a model with nearest neighbor repulsive interaction at high temperatures T/T_c=1.86 (T_c is the critical temperature of the transition to c(2x2) ordered phase), different diffusion coefficients are obtained. The slope of the refilling signal is proportional to the diffusion coefficient and it is clear that the slope increases with θ′. It follows that the LID method, which corresponds to the smallest θ′, gives a lower diffusion coefficient than the fluctuation method for the case of repulsive interactions. For attractive interactions, the opposite trend is observed with the fluctuation higher than the LID diffusion coefficient.

More dramatic effects are expected[19] at lower temperatures T/T_c<1 where ordered structures are formed. Simulations are performed both for repulsive and attractive interactions which lead to open c(2x2) and close (1x1) superstructures, respectively. The ratio of the LID to the fluctuation diffusion coefficient was 0.25 - 0.33 for repulsive interactions, while the ratio for attractive interactions was much higher, up to 100 - 200. This is expected because in the (1x1) structure there are more nearest-neighboring sites occupied, interactions are more pronounced, and the relaxation in the probe area depends on the number of atoms present initially.

Non-equilibrium growth of the c(2x2) domains

In the previous simulations,[19] for the case of repulsive interactions, domain growth kinetics of the c(2x2) structure were monitored in time. Repulsive interactions can be easily handled computationally because the domain growth is driven by the excess energy in the domain walls and only local diffusion at the boundary is required for the growth of the domains. The time dependent structure factor $S(q,t)=|\sum c_i(t)e^{i\,x\,q_x + iyq_y}|^2$ is monitored with time, where $c_i(t)$=1, 0 is the occupation of a site, whether full or empty. It was first verified[19] that S(q,t), which is proportional to the average domain size squared L^2, grows linearly with time which implies a growth exponent x=1/2. The exponent x=1/2 does not depend on temperature. The growth rate of S(q,t) at different temperatures is proportional to $A^{2x}(T)\propto D$, since $S(q,t)\propto L^2$. An Arrhenius plot measures an activation energy E=-2.9J in the range -3>J/kT>-4 (with J the nearest-neighbor repulsive interaction) where the (-) sign notes that the diffusion coefficient increases with decreasing temperature, as expected for repulsive interactions. The measured activation energy describes diffusion out of an initially random configuration. Simulations with the LID method with the layer outside the probe area in a random configuration (before equilibration) in the same temperature range -3 > J/kT > -4 measure a similar activation energy E= -2.7J, which agrees well with the result obtained from the domain growth rate. This non-trivial result first confirms explicitly for a specific model the previous conjectured relation between the growth rate and the diffusion coefficient $A\propto D^x$. In addition, it gives further legitimacy to the non-equilibrium diffusion coefficient measured in domain growth kinetics; it has the same activation energy as the coefficient obtained with another technique, the LID method. This is because both methods probe the system in the same initial, random configuration. It is important to note that in using the LID method with the overlayer in an initially random state, the configuration is both spatially (because the probe area is empty initially and the system evolves to a final uniform state) and temporally inhomogeneous (because initially the state is random but the temperature is well below T_c so the

system evolves to form the c(2x2) phase). Apparently the agreement between the activation energy obtained with LID and the domain growth techniques suggest the measurement is controlled by the temporal evolution to form the c(2x2) structure and attain equilibrium.

Equilibrium studies[19] on this system after the overlayer has been prepared in the c(2x2) structure have been also performed. Both the LID and the fluctuation methods were used in the same range -3 > J/kT > -4 and the activation energies obtained were less than 0.7J, much smaller than the values obtained when the system is in the disordered state. The smaller values reflect the open c(2x2) structure that after it is formed, it minimizes interaction effects because of the absence of any nearest-neighbors. It is interesting to note that for predominantly repulsive interactions $E_{eq}<E_{non\ eq}$ holds, as demonstrated with the simulations,[19] while for attractive interactions the opposite is true as shown in the O/W(110) experiments.

Tracer diffusion in non-equilibrium growth

Although the previous differences are related to the chemical diffusion coefficient differences in interactive systems, similar questions can be asked for the tracer diffusion D_t that describes the time dependence of the average mean square displacement $<R^2>$. First, very limited work has been done so far on how interactions determine $<R^2>$ at equilibrium. In general, the expected linear dependence in time has been verified $<R^2>=4D_t t$, except in cases[15] where special one-dimensional "corridor" type structures can lead to sublinear diffusion. Much less work has been performed so far on the tracer diffusion under non-equilibrium conditions, when the system evolves in time out of an initially random state to an ordered state. Figure 8 shows such simulations on the system with nearest-neighbor repulsive interactions. It is clear that for $T/T_c > 1$, $<R^2>$ obeys a linear time dependence as expected, since the system is in a uniform state. ($<R^2>$ is measured as a weighted average over the individual random walks of all the particles in the system.) However, for $T/T_c<1$ it is clear that $<R^2>$ grows slower, with a sublinear dependence $<R^2> \sim t^{1-x}$. This can be related[18] to the temporal inhomogeneity of the system. One can distinguish two types of atoms, those inside the domains with a higher diffusion barrier and those at the boundary, which diffuse more easily. As the domains grow, the relative number of atoms at the boundary decreases with time and their proportional contribution to $<R^2>$ decreases with time. Since these atoms have a higher probability to diffuse and therefore contribute larger diffusion distances in $<R^2>$, sublinear diffusion results. This is analogous to diffusion in a potential with a distribution of activation energies; with time, atoms populate the deepest potential wells out of which an atom has a smaller probability to diffuse which leads to sublinear time dependence, as under non-equilibrium conditions. It is clear that interactions under non-equilibrium conditions not only affect the chemical diffusion and its activation energy, but the simple, linear dependence of $<R^2>$, normally expected for tracer diffusion.

Conclusions

We have presented results for both experimental and model systems that show the dependence of the measured diffusion coefficient on the configuration and the method used to probe the system, if interactions are present. Is the conclusion supported by other experiments reported in the literature on the same overlayer/substrate combination by using different techniques? Table I shows a summary of results which confirms that the measured diffusion

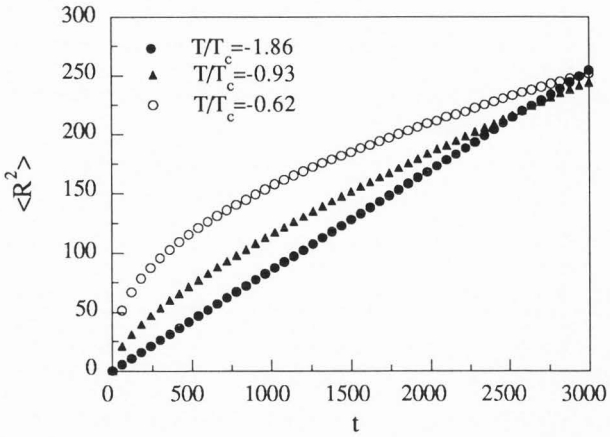

Fig. 8. Mean square displacement of particles at θ=0.5 with attractive nearest neighbors interactions that shows sublinear time dependence during non-equilibrium growth; ordered domains are formed out of a random initial state.

coefficients depend on the method used. For CO/Ni(110), experiments performed on single crystals with the LID method[14] measure the same activation energy as fluctuation experiments[10] on the vicinal planes of (100) - (which are basically (100) terraces), but with the LID prefactor 1000 times larger than the fluctuation prefactor. For Si/Si(100), in diffusion experiments using the density of nucleated islands measured[12] with the STM and grown at different substrate temperatures, E_d=0.67eV is obtained; experiments[16] based on the temperature dependence of the RHEED intensity oscillations recovery (after the shutter of the source is closed) measure E_d=0.9eV. Island density experiments[3] from the evolution of the satellite peak as a function of substrate temperature for Cu/Cu(110) measure E=0.28eV, while the diffusion activation energy extracted[1] in the so-called "step flow" regime from the disappearance of diffraction intensity oscillations is E_d=0.4eV. Finally, the island sizes formed epitaxially during the growth of GaAs(100) at different temperatures and measured[24] with RHEED profile analysis give a very high (for 2-D diffusion) activation energy E_d=4eV, based on single particle diffusion analysis, which is questionable in light of the many-body effects involved. Although it is not clear if the differences between all these experiments can be accounted for by adsorbate-adsorbate interactions, they at least point out the complexity of the diffusion process and potential differences in the results when many particles are present.

It is clear that any tabulation of the surface diffusion coefficients requires more parameters than just listing the overlayer/substrate combination because of the different role played by interactions. Thus, any hope of developing a simple picture for surface diffusion, that depends only on the chemical nature of the atoms involved, most likely is unrealistic. Although this is a pessimistic conclusion when a simple unifying scheme of diffusion is desired, additional analysis can reduce the results to the level of individual atomistic processes, characteristic of a given system that are method independent. Then, the unifying scheme can be presented in terms of these elementary method-invariant processes in different overlayer/substrate combinations. This is a very hopeful possibility, except one rarely can identify a unique set of microscopic processes for a given set of macroscopic measurements because of the information lost in the intervening steps. The alternative, as advocated in the

Table I. Comparison of diffusion coefficients.

Table I summarizes already published results in the literature with the values of surface diffusion measured in the same system showing that different results are obtained if different techniques are used.

System	Method I	Method II
CO/Ni(110)	LID $D_0=2x10^{-2}$ cm^2/sec	Fluctuation $D_0=3x10^{-5}$ cm^2/sec
Si/Si(100)	STM island density $E_d=0.67$ eV	RHEED intensity recovery $E_d=0.9$ eV
Cu/Cu(100)	He diffraction island density $E_d=0.28$ eV	"step flow" regime RHEED $E_d=0.4$ eV
GaAs(100)		RHEED profile fit $E_d=4$ eV

current paper, is to continue using an effective macroscopic diffusion coefficient, which is an average over the many microscopic processes involved in the measurement. The cost of this approach is the apparent discrepancy between results obtained with different techniques, but the corresponding payoff is the usefulness of the information. After all, this is needed in practice, when a real growth experiment is carried out and a practical estimate of its success or failure will be of great help.

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Discussion with Reviewers

R. Gomer: This paper emphasizes the complexity of what is commonly lumped under the single heading, "surface diffusion" and stresses the importance of defining diffusion under non-equilibrium conditions. Based on Onsager's hypothesis it is probably correct to say that a diffusion coefficient can be perfectly well defined locally under non-equilibrium conditions, although it need not be the same everywhere, depending for instance on the local concentration. This is also true in the case of multiphase systems at equilibrium: a local D can be defined for the ordered as well as the disordered phases, and it is not obvious what a given experiment actually measures. The authors point out correctly that this must depend on the experiments, but I am not sure that the emphasis on the distinction between non-equilibrium and equilibrium conditions is the basic one. Even in the latter case, amenable to the field emission fluctuation method, it is not clear how D is averaged if a system is in a two-phase coexistence region of a phase diagram, although this question should be amenable to Monte Carlo simulations. Thus "local conditions" and the type of averaging involved in a given experiment seem to me the paramount factors governing the results, whether the experiment is an equilibrium or a non-equilibrium one.

Authors: We totally agree that non-uniformities in an overlayer complicate the analysis of diffusion, irrespectively of whether the system is at equilibrium or non-equilibrium. The underlying reason of the non-uniformity is the concentration dependence of the diffusion coefficient. Macroscopic techniques, both equilibrium and non-equilibrium, average out different microscopic configurations which results in different effective values for the activation energy and prefactor. In addition to the experimental implications that it is important to avoid the naive expectation of carrying out "the diffusion coefficient" measurement in a system, this complexity poses theoretical challenges to develop general techniques to cross correlate the different results.

S.-C. Ying: I have some reservations concerning the terminology "non-equilibrium diffusion constant" and the implication that at least in some situations they have the same value as the equilibrium diffusion constant. The problem is that there is theoretically no unique way of defining a diffusion constant under non-equilibrium situations. Perhaps a more appropriate focus is on the elementary jump rate from one site to a neighboring site. At low temperatures this certainly will have an activated form with an activation energy. Provided that the activation energy is not a strong function of time, it should correspond to the same value under similar equilibrium configurations. However, the prefactor is entirely a different beast and I can see no simple connection between equilibrium and non-equilibrium results. The dimensional analysis which was used to extract the activation energy could be based on a typical time scale $\tau \simeq \nu^{-1}$ where ν is the elemental jump rate rather than an ill-defined diffusion constant.

Authors: We agree that the usefulness of non-equilibrium experiments so far has been to extract the activation energy of the growth process and not the prefactor. It is an open question how to relate the experimentally measured prefactor in a non-equilibrium experiment (like domain growth) to the prefactor of the diffusion coefficient because there are additional parameters controlling the absolute rate of a growth process (for example, line tension in domain boundaries, density of different phases, etc.). This has been clearly demonstrated in specific models (Lifshitz-Slyozov growth) with an exact relation between the prefactor and the microscopic parameters. However, the activation energy measured, is determined by the relative growth rates at different temperatures and is insensitive to the prefactor so it can be meaningfully related to equilibrium results. Since experimentally non-equilibrium experiments are far easier to carry out because of the larger S/N ratio involved, it is clear that they are important. In addition, since the concept of "non-equilibrium diffusion" has been already used extensively in theoretical studies of growth processes, there is a practical need to further legitimize it by connecting it to the well-developed concept of "equilibrium" diffusion.