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SOME RECENT RESULTS IN SURFACE DIFFUSION

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Résumé L'extension de la méthode de fluctuations à la détermination des tenseurs de diffusion bi-dimensionnelle des couches adsorbées est esquissée. Les résultats obtenus pour O/W(110), $^1\text{H}/\text{W}(110)$, et $^2\text{H}/\text{W}(110)$ sont présentés, ainsi qu'un début d'interprétation. La diffusion par l'effet tunnel de ^1H , ^2H et ^3H sur W(110) est décrite et discutée.

Abstract Extension of the fluctuation method to the determination of 2-dimensional diffusion tensors of adsorbates is sketched and results for O/W(110), $^1\text{H}/\text{W}(110)$, and $^2\text{H}/\text{W}(110)$ are presented and tentatively interpreted. Results for the tunneling diffusion of all three hydrogen isotopes on W(110) are presented and discussed.

The field emission fluctuation method for studying surface mobility makes it possible to determine chemical (i.e. Fick's law) diffusion coefficients on the virtually perfect microscopic single crystal surfaces encountered on field emitters under conditions of effectively constant coverage, which however, can be varied widely /1/. The method has recently been extended to a determination of anisotropy, i.e. the full 2-dimensional diffusion tensor /2/. This paper reports some results recently obtained by these methods.

I - DIFFUSION ANISOTROPY

The fluctuation method is based on the fact that even very small changes in adsorbate concentration on a field emitter surface lead to appreciable emission current changes because of its high sensitivity to work function. By means of a probehole emission from regions 50-100 Å in radius can be examined, since the magnification of the field emission microscope is $10^5 - 10^6$. Under conditions of adsorbate mobility appreciable number and hence current fluctuations occur on such small regions because of adsorbate diffusion into and out of the probed region. For a circular probe area a relaxation time τ_0

$$\tau_0 = r_0^2/4D \quad (1)$$

is associated with the buildup and decay of fluctuations, Here r_0 is the radius of

the probed region and D the chemical diffusion coefficient. It turns out that the time autocorrelation function of the number fluctuations can be expressed as a function of t/τ_0 . The field emission current correlation function is nearly proportional to the number fluctuation function, although slightly more complicated, since dipoles outside the probed region also contribute to the local work function within it and hence affect emission, but this is a technical detail. In any case it is possible to obtain τ_0 and hence D (since r_0 can be estimated from the emitter radius and the probehole size) from a comparison of theoretical and experimental correlation functions.

If the probehole is constructed in the form of a long narrow slit, it can be shown /2/ that the correlation function decomposes into a product of two one-dimensional functions, if the slit is lined up along one of the principal axes of the diffusion tensor. Each of these functions has its own relaxation time

$$\tau_x = a^2/D_{xx} \quad (2a)$$

$$\tau_y = b^2/D_{yy} \quad (2b)$$

if the slit dimension $2a$ is orthogonal to the x and the dimension $2b$ orthogonal to the y direction, x and y being principal axes. If $b/a \gg 1$ it is clear that $\tau_x \ll \tau_y$ even if $D_{xx} < D_{yy}$ so that the decay of the experimental correlation function is determined by τ_x only, unless very long times are used. Thus D_{xx} can be found. If the slit is then rotated 90° so that $\tau_x = b^2/D_{xx}$, $\tau_y = a^2/D_{yy}$, τ_y and hence D_{yy} will be determined from the experimental correlation function.

A tube with $b/a = 10$ and a magnetically rotatable slit has been used by M. Tringides and the author to look at the anisotropy of diffusion on a W(110) plane. The principal axes, which can be determined from symmetry (i.e. the requirement that D remain invariant under the symmetry operations of the surface) are (110) and (100) (y and x in Fig. 1, respectively). If diffusion occurs along the axes labelled x_1 and x_2 in Fig. 1 (i.e. (111) directions), it can be shown /2/ that the ratio of tracer diffusion coefficients $D_{yy}^*/D_{xx}^* = 2$. No predictions can be made a priori about the ratio of chemical diffusion coefficients, but as long as the substrate symmetry is not broken it is probable that adsorbate-adsorbate interactions will not modify the ratio 2. A definitive answer will have to await Monte Carlo simulations. A more detailed discussion of this point is given in a forthcoming paper by M. Tringides and R. Gomer.

The results for oxygen adsorption show that $D_{yy}/D_{xx} = 2$ under nearly all conditions of coverage and temperature, although for $O/W = 0.6$ the ratio is less except at high temperature. Very surprisingly for hydrogen and deuterium $D_{yy}/D_{xx} \approx 1$ under all conditions, including tunneling diffusion at 27 K. In view of the oxygen

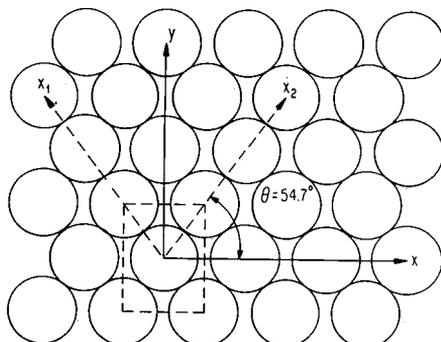


Fig. 1 - Schematic diagram of bcc (110) plane. Non-primitive unit cell shown as dashed rectangle. x and y are principal axes and correspond to (100) and (110) directions. x_1 and x_2 are (111) directions and probably correspond to physical jump directions for most adsorbates.

results it seems most unlikely that H-H interactions can be directly responsible for this result. The explanation must therefore be sought in a symmetry breaking for, or resulting from H adsorption. For instance H might be adsorbed in the asymmetric bridge sites at either end of the "hourglass" regions in Fig. 1 with a barrier in the middle. However, this would require the barrier to be of the same height (and opacity in tunneling) as those between hourglasses, and this seems unlikely. A more reasonable explanation is suggested by a recent finding of P. Estrup, namely that H adsorption causes surface reconstruction, consisting of a shift of the top W layer parallel to the (110) direction. Such a shift amounts to a Jahn-Teller lifting of the degeneracy of the 2 asymmetric bridge sites at each end of the hourglass, making one such site more, and the other less tightly binding for H. It can be shown that this can lead to jumps by H atoms with no or less projection on the y axis but with normal projections on the x axis, thus reducing the ratio D_{yy}/D_{xx} .

The fact that ^1H and ^2H show virtually the same lack of anisotropy also militates against the chain propagation mechanism invoked previously /1/ to explain the anomalously high prefactors in activated diffusion for ^2H at high coverage.

II - MEAN SQUARE FLUCTUATION ANISOTROPY

The diffusion measurements just discussed also give, in the form of the correlation function at $t = 0$ mean square fluctuations. For sufficiently large probed areas, embedded in a sufficiently large (i.e. infinite in principle) plane these are proportional to the 2-dimensional compressibility K of the adlayer /3/:

$$\langle (\delta n)^2 \rangle / \langle n \rangle = ckTK \quad (3)$$

where c is adsorbate concentration in atoms/cm² and $\langle n \rangle$ the mean number of atoms. It was therefore surprising to find considerable anisotropy with slit orientation in $\langle (\delta n)^2 \rangle$. For O/W(110) an anisotropy of ~ 2 almost independent of T and θ was found, the fluctuation being larger for the long dimension of the slit parallel to (100). Anisotropies from ~ 3 to < 1 , depending on temperature and θ were found for ^1H and ^2H . It turns out, however, that this behavior is to be expected for sufficiently small rectangular probe areas if the correlation lengths of the fluctuations in the x and y directions differ and if at least one of the correlation lengths is comparable to the short probe dimension. It is not possible to assign unique sets of correlation lengths to explain the observed anisotropies, but the article by Tringides and Gomer already referred to shows that reasonable values, giving the observed anisotropies, can be calculated by mean field theory, using the oxygen-oxygen nearest, next-nearest, and next-next nearest neighbor interaction energies which are invoked to explain the phase diagram of this system /4/ and which have also been used to explain almost quantitatively the increase in activation energies of diffusion with coverage /5/. The larger anisotropies, and their more dramatic variation with T and θ , seen for ^1H and ^2H suggest more complex interactions and possibly the inadequacy of a lattice gas model for these systems.

III - TUNNELING DIFFUSION OF HYDROGEN, DEUTERIUM, AND TRITIUM

The diffusion of ^1H and ^2H was studied by the fluctuation method by DiFoggio and Gomer /1/, who noted in addition to thermally activated also temperature independent diffusion at $T \leq 140\text{-}160$ K, depending on isotope and coverage. These measurements, have been verified and extended by S. C. Wang and the author. Only the tunneling results will be discussed here, although the thermally activated ones also present a number of interesting features. Log D values at 27 K plotted against θ are shown in Fig. 2. The agreement with Ref. 1 is very good, where overlap exists, except for a general shift downward of the ^1H curve. This probably results from errors in r_0 , which must be determined from emission data rather indirectly and can depend markedly on local magnification. Several features of Fig. 2 are quite striking. First, tunneling still occurs for ^3H and as $\theta \rightarrow 0$ the value of $D(^3\text{H})$ is only 1/15 of that for ^1H . Second, the θ dependence of ^1H and ^3H is virtually identical, while that for ^2H differs for $\theta > 0.7$. Finally all curves show an initial minimum followed by a maximum at $\theta = 0.3$. Straightforward application of the WKB tunneling probability would require the barriers to be extremely transparent in order to explain the small mass effect, but then the observed absolute values of D would be many orders of magnitude too small for any reasonable model. The qualitative explanation lies in the fact that there is mass renormalization, in the form of additive mass corrections, as explained in a forthcoming paper by K. A. Muttalib and J. Sethna. The effect arises

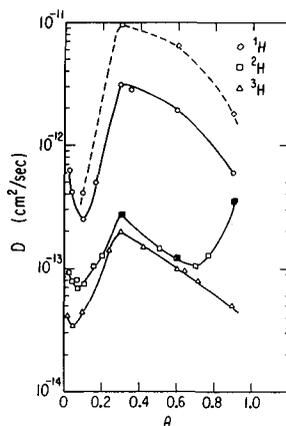


Fig. 2 - Log D vs. relative coverage θ for ^1H , ^2H , and ^3H on W(110) at 27 K. Dashed curve for ^1H from Ref. 1. Points for ^2H from Ref. 1 shown as full squares.

because the adsorbate distorts the substrate. In tunneling this distortion is carried along and gives rise to phonon generation, which translates into effective mass corrections. As θ increases the substrate distortion for a given adatom is counteracted by other adatom-substrate interactions; the lattice is thus stiffened, and the mass decreased, resulting in increased D . At even higher θ site blocking, or equivalently, lattice softening for hole diffusion again reduces D . At very low θ , however, it appears that 2 body (ad-ad) interactions result either in some substrate softening or in more blocking than stiffening. This could result from the preferred 2 body sitings at low θ .

The increase in D for $\theta > 0.7$ and the generally lower than expected D values for ^2H pose a puzzle. It is quite likely that the difference between ^1H and ^3H on the one hand and ^2H on the other arises from nuclear statistics. If electrons hop on and off the adsorbate rapidly, only nuclear statistics matter and ^2H then behaves like a spin = 1 boson. For this case a Fermi hole is absent in 2/3 of encounters between two ^2H atoms while it is present in 3/4 of encounters for ^1H or ^3H atoms. At low θ this is a disadvantage, leading to unproductive configurations for subsequent jumps, but at high θ where hole diffusion predominates it facilitates the latter.

IV - CONCLUSION

The results described here give a sampling of the phenomena being uncovered by the fluctuation technique. Surface diffusion is turning out to be far more complex, but also far more interesting than one might have imagined, its ramifications leading deeply into the statistical and quantum mechanics of two-dimensional systems.

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