

# Supporting information for: Observation of uncorrelated microscopic motion in a strongly interacting adsorbate system

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# 1 Signatures of pairwise interaction in the intermediate scattering function

The ISF can be defined directly in  $\Delta K$  and  $t$  space as,  $I(\Delta K, t) = \langle \sum_{i,j} \exp\{i\Delta K [R_i(t) - R_j(0)]\} \rangle$ , where the double summation is performed for all the pairs of particles,  $R_i$ , is the time dependent position of the  $i$ 'th particle within the surface plane, and the brackets denote an ensemble average.<sup>1</sup>

At elevated temperatures, random motion will take place on a surface. After a time,  $t$ , this motion will lead to some loss of spatial and temporal correlation both when considering the same particle ( $i = j$ ) and for any pair of different particles ( $i \neq j$ ). Thus, the  $R_i(t) - R_j(0)$ , term will evolve randomly with time, leading to a dephasing of the complex exponent and a decay with time of the ISF. When the interaction between particles is negligible, the position of different particles is uncorrelated in time and space so that the time and momentum transfer dependency of the ISF will be dictated by the  $i = j$  term, which will not change as a function of coverage.

In the presence of pairwise interactions certain 'optimal' adsorbate structures that minimize these interactions become energetically favorable. At any non zero-temperature the system will continuously vary from one structure to another, and both the energetically preferred structure as well as any other random structure may be present on some part of the surface at a given time. The effect of increasing the strength of the pairwise interactions or increasing the coverage (decreasing the separation distance) will be to increase the lifetime of the preferred structures and correspondingly reduce

the relative lifetime of any other random structure.

The different lifetimes of optimal and non-optimal structures, in real space, will necessarily lead to a similar effect in reciprocal space. The result is a different time dependence of the ISF at different momentum transfer values leading to peaks and dips in  $\alpha(\Delta K)$ . Figure S1 illustrates the origin of the peaks and dips for the simple case of a one dimensional adsorbate system with pairwise repulsive forces. In the presence of pairwise repulsion, the optimal structure will be the equally spaced structure illustrated in the left side of figure S1, we will denote the mean spacing between neighboring particles as  $R_{NN}$ . When we perform an experiment with a particular momentum transfer value,  $\Delta K_1$ , which satisfies  $R_{nn} \cdot \Delta K_1 = \pi$ , the scattering contribution from the optimal structure is in anti phase, making this structure practically invisible to the experiment. Thus for  $\Delta K_1$  only the non-optimal structures contribute to the ISF. The reduced lifetime of these structures mentioned above will lead to an increase in the inverse lifetime,  $\alpha$ , seen as a peak on the right side of figure S1. In contrast for  $\Delta K_2$ , which satisfies  $R_{nn} \cdot \Delta K_2 = 2\pi$ , the optimal structure is in perfect phase making it the leading term in the ISF. The increased lifetime of this structure leads to a stable  $R_i(t) - R_j(0)$  term and the corresponding dip shown in the figure. This minimum of the inverse lifetime, which coincides with a peak in the static structure factor,<sup>2</sup> is the 2D analog of the DeGennes narrowing observed in neutron measurements of liquids.<sup>3</sup>

## 2 Experimental and numerical details

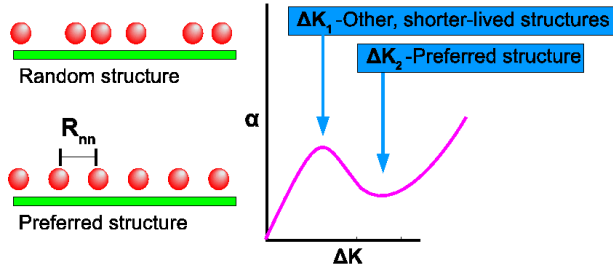


Figure 1: Fig. S1 - Illustrating the relation between adsorbate structures and  $\alpha(\Delta K)$  modulations. A random and an equally spaced 1D adsorbate structure are illustrated on the left. In the presence of repulsive forces, the equally spaced structure will be energetically preferred and will have a longer lifetime than any other random structure. The peak and dip features seen in the  $\alpha(\Delta K)$  illustration on the right correspond to two scattering condition where the ISF is dominated by either the random short-lived structures or the more stable preferred structure, respectively.

The Pt(111) crystal used in this study was mounted in a UHV chamber with a base pressure of  $3 \times 10^{-11}$  mbar and cleaned by repeated cycling of argon ion sputtering (800eV, 450K) and annealing (1100K). Polarization curves were measured for sample temperatures between 280K-450K and CO coverages of 0.065ML to 0.3ML, (1ML = one CO molecule for each Pt atom on the surface). Within the experimental temperature and coverage range of this study, the static structure factor measured was featureless indicating a disordered phase of the adsorbate over-layer, in agreement with previous observations.<sup>4</sup> The CO coverage was calculated using the sticking coefficients measured by Yeo et al.<sup>5</sup> A different sticking model has been given in,<sup>6</sup> this model results in coverage estimates up to 20% higher than the values we used. These higher coverage estimates do not have a significant effect on any of our conclusions. For temperatures and coverages where desorption occurs, the required coverage was achieved by maintaining a constant CO pressure, the value of which is set to give the appropriate attenuation of the specular helium beam.<sup>7</sup>

The following procedure was used to construct the PES described in the text. This PES allows for both top and bridge site adsorption and has only two free parameters. We will denote the distance between the origin and the first diffraction peaks of the 111 surface as  $\zeta$ , where  $\zeta = \frac{4\pi\sqrt{2}}{\sqrt{3}a}$  and  $a$  is the bulk lattice constant. For a basic 6 fold PES we only need three vectors which we chose as  $\vec{g}_1 = (\zeta, 0)$ ,  $\vec{g}_2 = (\zeta \cos(\pi/3), \zeta \sin(\pi/3))$  and  $\vec{g}_3 = (-\zeta \cos(\pi/3), \zeta \sin(\pi/3))$ . To introduce more than one kind of adsorption site we add 3

more vectors  $\vec{g}_4 = 2\vec{g}_1$ ,  $\vec{g}_5 = 2\vec{g}_2$  and  $\vec{g}_6 = 2\vec{g}_3$ . The basic shape of the PES,  $U(x, y)$  is then calculated using  $U(x, y) = -\sum_{i=1}^6 A_i \cos(\vec{g}_i \cdot \vec{r})$ . The amplitude of the first 3  $g$  vectors,  $A_{1,2,3}$ , are set to 1. The amplitudes of the last 3  $g$  vectors are kept equal to each other and are used as a variable parameter which allows us to set the difference in energy between the bridge and top sites. For the case of  $A_{4,5,6} = 0$ , we obtain a PES with no minimum in energy at the bridge site, in contrast, the other extreme case  $A_{4,5,6} \Rightarrow \infty$ , leads to equal energies at the top and bridge site,  $E_t = E_b$ . The second variable parameter we use is a simple scaling factor multiplying the PES to obtain a particular energy barrier along the line which connects two top-sites, this value is denoted as  $U_{tt}$ . For example, a PES which satisfies  $\frac{U_{tt}-E_b}{U_{tt}-E_t} = \frac{1}{2}$  is obtained using  $A_{4,5,6} = 1.5$ , thus, if  $U_{tt} = 100meV$  we obtain  $E_t - E_b = 50meV$ .

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