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Adsorption-Desorption Kinetics of H_2 Molecules on Graphite: a Molecular Dynamics Study

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1. Introduction

In a vison of the hydrogen society, hydrogen is crucial as an energy carrier. The gas plays, for instance, a key role in fuel cells, to be used in the transport sector in this scenario. However, under ambient conditions hydrogen is volatile and difficult to manipulate. It is necessary to store it and to have an efficient kinetic cycle for its discharge to the electrodes where it is being used. The most common storage material is activated carbon because of its low cost. Carbon materials are also used as catalyst support for the electrodes in the polymer electrolyte fuel cell where hydrogen is oxidized at the anode. The kinetics of adsorption and desorption of H_2 molecules on carbon surface are key steps of these processes. We shall show using molecular dynamics (MD) simulations that the adsorption process follows a Langmuir isotherm, as is well known, but that the adsorption kinetics deviate from a Langmuir model.

2. Model and Simulation Details

The system was composed of two infinite planes of graphite separated by about 160 Å, and in contact with different amounts of hydrogen molecules. The surface was in the plane of the hexagonal structure. A rectangular simulation box, 44 Å long and 34 Å wide was extended to infinity by the use of periodic boundary conditions. The graphite and the hydrogen were simulated using an atomic model. The atoms were allowed to interact through inter- and intra molecular potentials. Their movement was determined by integrating the Newton`s equations of motion.

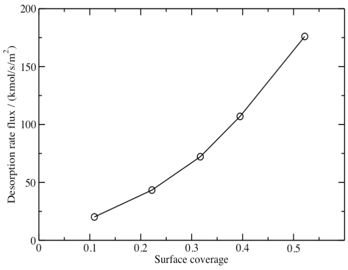

Fig. 1: Desorption rate J_d as a function of the surface coverage θ, at 110 K. The Langmuir's kinetics predicts a linear trend contrary to what is observed.

Systems with 50, 100, 150, 200 and 300 molecules of hydrogen were simulated at different temperatures ranging from 70 K to 300 K. Adsorption isotherms were computed under equilibrium conditions and the influx and outflux of hydrogen to the surface were calculated.

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3. Results and Discussion

The adsorptions isotherms until 170 K were well fitted using Langmuir's isotherm, while at higher temperatures the isotherms obeyed Henry's law. Such results have been found by other investigators also.

The adsorption and desorption fluxes, however, could not be fitted using the classical Langmuir's kinetics, see figure 1. The adsorption rate flux J_a was, according to the simulation results, simply proportional to the gas pressure, P, while the desorption flux J_d was proportional both to the surface coverage θ and to the inverse of the free space on the surface $1-\theta$:

$$J_a = k_a P/P^0, \qquad J_d = k_d \theta/(1-\theta), \qquad (1)$$

Here k_a and k_d are the adsorption and desorption rate constants, and P^0 is the standard pressure, 1 bar. These results are not in agreement with the view of the Langmuir's kinetics model, indicating that the adsorption rate depends also on the available space at the surface and that the desorption rate is only proportional to the surface coverage, see figure 1.

The adsorption rate constant, eq. 1, decreases as the temperature rises, while the desorption rate constant increases. While the amount of hydrogen molecules adsorbed on the graphite surface is small under ambient conditions, the equilibrium exchange fluxes for adsorption and desorption are large. The activation energies calculated from the dependence of these rate constants with temperature were smaller than the hydrogen binding energies to the surface.

4. Conclusion

Using molecular dynamics simulation of hydrogen molecules adsorbed on graphite we have shown that the kinetics of adsorption-desorption do not follow the Langmuir kinetics while the adsorption isotherm is still Langmurian. This surprising observation may be linked to the state of the hydrogen at the surface. It is important for the transport normal to the surface, and might play a role for the transport along the surface.