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Adsorption and desorption of hydrogen on graphene with dimer conversion

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ABSTRACT

We apply non-equilibrium thermodynamics to describe the adsorption and desorption of molecular hydrogen on graphene. Lateral interactions, precursor states in both adsorption and desorption, and limited dimer conversion are important to explain semi-quantitatively the main features of temperature-programmed desorption spectra. All energy and vibrational parameters are taken from density functional calculations. Deficiencies in previous attempts are discussed. We also point out the need for a multi-dimensional dynamic theory.

1. Introduction

The hydrogenated graphene, as a quasi-2d hydrocarbon system, has attracted extensive interest due to the prospective applications in the field of astrophysics [1,2] and hydrogen storage [3]. It has been reported that hydrogenation is reversible, making this system a candidate for molecular-scale electronics [4]. To further understand the properties of hydrogenated graphene, it is important to investigate the interactions between hydrogen and the graphene surface. Considerable attention has been focused on the chemisorption of atomic hydrogen on graphene [5–13]: hydrogen atoms adsorb at on-top sites with a binding energy of about 0.7–1.0 eV. The necessary transition from sp^2 to sp^3 hybridization leads to a local buckling of the graphene sheet under an adsorbed hydrogen atom. This suggests that the coverage of hydrogen on one side of the graphene sheet is no more than 0.5. As shown convincingly in a series of excellent STM experiments, the hydrogen atoms tend to aggregate at low coverage in small clusters of dimer-like structures [12,13]. This has been confirmed and further elucidated by density functional theory (DFT) calculations, in particular showing that hydrogen dimers are energetically more stable than the monomers [7]. These calculations also found that chemisorption of hydrogen opens a band gap in graphene, which increases with coverage [14,15].

Adsorption of atomic hydrogen is activated, needing a hot beam at about 2000 K. Unfortunately, the sticking probability has not been measured except on the basal plane of graphite where one finds at vanishing coverage $S(\theta = 0) \approx 0.04$ [16]. Such a small value is to be expected as the sticking coefficient is proportional to the mass ratio of hydrogen to carbon $m_H/m_C = 1/12$ due to the fact that energy transfer is less likely for smaller mass ratios. As coverage increases collisions of the incoming atoms with already adsorbed atoms become effective increasing the sticking quickly, initially linearly. This can be viewed as precursor-mediated adsorption.

The desorption kinetics of hydrogen from graphite and graphene has been studied in temperature-programmed desorption (TPD) experiments. Only molecular hydrogen is desorbed. The spectra show two peaks, the main peak accounting for about 90% of the desorbed molecules around 445 (490) K with the remainder desorbing around 560 (580) K for H_2 (D_2), respectively [17,18], see also [12,13]. According to the STM images, there are mostly two kinds of dimers on the surface, the ortho- and para-dimer with two hydrogen atoms adsorbed on nearest neighbor and third nearest neighbor carbon atoms, respectively (Fig. 1). It is argued that the first peak in the TPD spectra corresponds to direct desorption of para-dimers while the second peak is associated with dimer conversion from ortho- to para-dimers and subsequent desorption of the latter. This interpretation of the TPD spectra has been substantiated in Monte Carlo simulations [19,20] and also in model calculations based on rates derived from transition state theory (TST) [21]. There are a number of issues and omissions that need to be addressed in addition to what was done in part in a general theory based on non-equilibrium thermodynamics [22]. With new data

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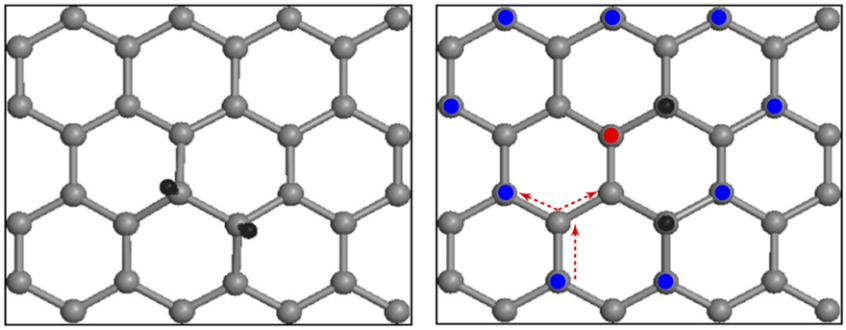

Fig. 1. The configurations of ortho-dimers (left) and para-dimers (right). The gray and black balls correspond to the carbon and hydrogen atoms, respectively. The blue C atoms in the right panel are the nine third neighbors to the red C atom. The dotted red arrows indicate possible migrations.

available a more thorough discussion is now possible, which is essentially the purpose of this paper, such as the role of lateral interactions, precursors, a proper formulation of the conversion mechanism as the rate-limiting step and the implied lack of local equilibrium in the adsorbate during desorption.

Having extensive DFT data available in the literature one is tempted to set up a detailed lattice gas model starting from a Hamiltonian for hydrogen atoms on a graphene surface with multiple lateral interactions such as nearest-neighbor, next-nearest-neighbor etc., two-body as well as many-body interactions with their respective values extracted from the many cluster energies available. This has been shown to give a microscopically well-founded picture of equilibrium and kinetic phenomena for adsorbates [23]. By its very construction such a model would reproduce the abundance of clusters (in equilibrium) as a function of temperature and possible ordered phases. A comparison with experimental data would confirm whether the view of limited diffusion/conversion is unambiguously correct. This project will be pursued elsewhere but the present paper will be based on a minimal set of assumptions, e.g. that dimers dominate the adsorbate.

In the next section we will review the theory and describe the desorption paths for hydrogen. In Section 3 the TPD spectra will be reproduced, with almost all parameters from DFT calculations. In particular we will argue on the basis of a series of refinements to the mechanism of desorption that, contrary to the often cited argument, the spectra are not "typical first order spectra", and that they should not and cannot be regarded as such because of the effects of precursor states, lateral interactions and the lack of local equilibrium. Remaining open questions and future directions will be analyzed. Section 4 is for the summary.

2. Non-equilibrium thermodynamics of adsorption and desorption

To formulate the thermodynamics and kinetics of the adsorption of ortho- and para-dimers on graphene we employ a lattice gas model with lattice sites representing the hexagon cells each of which allows for the adsorption of both species. The Hamiltonian reads

$$H_0 = E_O \sum_i n_i^{(O)} + E_P \sum_i n_i^{(P)} + V^{(lat)}. \tag{1}$$

Here the occupation numbers $n_i^{(O)}$ and $n_i^{(P)}$ are 0 or 1, depending on whether the cell i is empty or occupied by an ortho- or para-dimer, respectively. Both species can be present in any cell. $E_O = -V_O - k_B T \ln Z_O$ is the Helmholtz free energy of an isolated ortho-dimer. V_O is the binding energy of an ortho-dimer relative to a hydrogen molecule at zero kinetic energy far from the surface, and Z_O is the partition function of a single ortho-dimer accounting for the six vibration modes of the constituent hydrogen atoms with respect to the underlying carbon atoms. The analogous terms labeled "P" represent the same quantities but for a para-dimer. Physically a hexagon cell cannot accommodate both the ortho-dimer and para-dimer in the same time. To avoid double occupancy we add a large repulsion $V_0 \sum n_i^{(O)} n_i^{(P)}$ The non-existing double occupation can be excluded by a large on-site energy $V_0 \sum n_i^{(O)} n_i^{(P)}$ which is part of the lateral interaction $V^{(lat)}$ in (1) which also includes the between dimmers in neighboring cells as specified later. At low coverages where lateral interactions are negligible we get for the partial coverages as functions of temperature and the chemical potential $\mu(P,T)$ of molecular hydrogen in the gas phase

$$\theta_O = \frac{\exp[-(E_O-\mu)/k_B T]}{1 + \exp[-(E_O-\mu)/k_B T] + \exp[-(E_P-\mu)/k_B T]}, \tag{2a}$$

$$\theta_P = \frac{\exp[-(E_P-\mu)/k_B T]}{1 + \exp[-(E_O-\mu)/k_B T] + \exp[-(E_P-\mu)/k_B T]}. \tag{2b}$$

Thus the ratio of partial coverages is simply

$$\frac{\theta_O^{(eq)}}{\theta_P^{(eq)}} = \frac{Z_O}{Z_P} \exp[(V_O - V_P)/k_B T]. \tag{3}$$

This ratio is plotted in Fig. 2 for $V_O - V_P = -0.03$ eV. In the temperature range from 210 K to 300 K, the ratio varies from 0.034 to 0.094, which is roughly consistent with the experimental estimate of 0.15 [13]. This ratio is obviously very sensitive to the values of the binding energies. Indeed, if we take the values provided in Ref. [10], namely $V_O - V_P = 0.05$ eV, the ratio will be larger than one, i.e. the ortho-

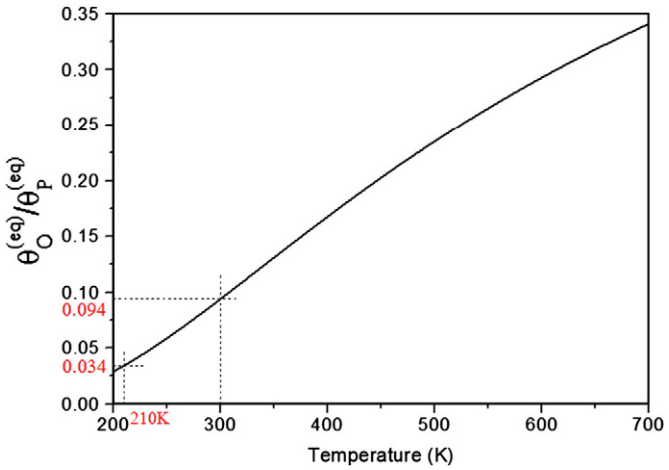

Fig. 2. The coverage ratio of ortho-dimer to para-dimer in equilibrium as a function of temperature. The binding energies relative to two hydrogen atoms far from the surface are 2.89 and 2.92 eV for ortho- and para-dimer respectively (in Ref. [10] they are 2.73 and 2.68 eV). The vibrational frequencies of the hydrogen atoms are ν_P = 1096, 1102, 1112, 1125, 2644, 2661 cm^{-1} and ν_O = 1125, 1168, 1200, 1247, 2734, 2765 cm^{-1}.