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Coverage dependence of finite temperature quantum distribution of hydrogen on nickel(0 0 1) surface

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Abstract

Finite temperature quantum behavior of hydrogen adsorbates on Ni(0 0 1) surface is simulated using path-integral Monte Carlo technique. The adsorbate–surface and adsorbate–adsorbate interactions are described by the many-body alloy potential form, fitted to the adsorption parameters from DFT calculations. Temperatures 100 K and 300 K and coverages from 1/8 to 7/8 are considered. Also quantum and classical adsorbate behavior is compared.

At low temperatures, the quantum delocalization of the adsorbates is considerable with all studied coverages, and therefore, temperature dependence of distributions is weak. At $T = 300$ K, however, the H–H interaction energy has a considerable effect on distributions and energetics. By using a semi-classical description of the hydrogen adsorbates both temperature and coverage dependencies become strong at both temperatures.

Keywords: Monte Carlo simulations; Nickel; Construction and use of effective interatomic interactions; Equilibrium thermodynamics and statistical mechanics; Quantum effects; Hydrogen molecule

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1. Introduction

Hydrogen motion and interactions on metal surfaces are of interest both technologically and fundamentally. Hydrogen interactions are considered to be simple and therefore well suited for fundamental research [1]. In particular, the light mass of hydrogen emphasizes quantum effects [2–5], which are used to explain peculiar adsorbate diffusion [6–12], vibrational observations [6], electron-energy loss spectra [13,14], low-energy electron diffraction [13,14], photoemission [14], helium scattering [15], thermal desorption [7], linear optical diffraction [16] and field emission [16,17]. Furthermore, it has been shown that quantum effects are essential in understanding the phenomena of H interactions on Ni surface [11,13,18], and, H on metal surfaces provides a unique opportunity to observe the crossover from quantum to classical dynamics at elevated temperatures [5]. Finally, combination of the many-body aspect of the interactions and the quantum nature of hydrogen dynamics at low temperatures [2] makes this system even more interesting.

Many of the interesting quantum states relate to Ni(0 0 1) surface, where H adsorbate is known to delocalize and develop a two-dimensional band structure. Thus, the protonic band structure may be important [4,19] in order to understand hydrogen reactions on metal surfaces. Many questions are still open, e.g., to what extent the electronic structure of the surface influences the reaction of atomic H (D) with adsorbed H or D [20]. Also, it is known, that presence of an adsorbate on a surface can profoundly change the surface reactivity [21]. The dissociative adsorption of molecules on surfaces of solids is of central importance in surface catalysis and has been extensively studied both experimentally and theoretically [22].

At low temperatures, the quantum delocalization of the hydrogen adsorbate on a Ni(1 0 0) surface is considerable,

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as we have shown earlier, see Ref. [18], and therefore, temperature dependence of distributions is weak. By using a classical description of the hydrogen adsorbate temperature dependence of the distributions and energetics becomes strong at all temperatures, proving that quantum description is necessary for the correct picture of H/Ni(001) system. At room temperature, $T = 300$ K, the extensive classical distribution is quite similar to that of quantum case and the classical thermal spreading conceals the quantum delocalization. It was found that the classical distributions are more bridge-direction oriented compared with the quantum case, where tunneling allows more circular shape.

Mutual interaction between adsorbed hydrogen atoms may significantly alter the apparent temperature dependence of the diffusion [23], and thus, other properties of the system. Two of the interaction mechanisms are direct, through space, and two are indirect, through substrate [24]: dipole–dipole interaction, direct overlap between adsorbate electronic levels, indirect interaction mediated by the non-rigid substrate ion cores and indirect interaction mediated by the metal electrons. The electrostatic interaction is assumed to be repulsive between hydrogen adatoms at Ni surface [25].

Some Ni surfaces exhibit ordered superstructures for H_n [26], but none is found for (100) surface [1,25]. On some surfaces, a molecular adsorbate is observed, e.g., Ni(510) surface covered with a dense atomic-hydrogen layer [27], but as Mårtensson et al. [27] pointed out, EELS studies of hydrogen adsorption on the flat Ni(100) surface shows that there is no molecular adsorption state populated at 80 K substrate temperature.

We report here fully quantum mechanical and thermally averaged constant temperature path-integral Monte Carlo simulation (PIMC) of hydrogen atoms on a rigid Ni(100) surface. The method is described in detail in Ref. [18] for the case of single H atom. Here we consider the coverages from 1/8 to 7/8. By employing PIMC method, we evaluate the finite temperature many-body density distributions and related energetics for quantum mechanical and classical cases. We compare the results to the semi-classical “atoms at the adsorption sites” picture. We assess the quantum nature and temperature dependencies of the hydrogen distribution and differences with the semi-classical picture. In particular, hydrogen–hydrogen interactions are considered in terms of pair correlation functions and energetics.

In the next chapter, the many-body alloy potential and PIMC are briefly described, chapter 3 gathers the results together and, finally, the last chapter presents the conclusions.

2. Computational methods

For the simulation, we need the full many-dimensional potential-energy hypersurface for several interacting H atoms at the surface. Therefore, we have chosen MBA potential, reviewed in Subsection 2.1, to describe Ni–Ni, Ni–H and H–H interactions. In Subsection 2.2 the path-integral method is described.

2.1. Many-body alloy potential

MBA has been succesfully used for H/Pd systems and for studies of the electronic and structural properties of small clusters [28,29], surfaces of metals, dilute metal alloys, see Ref. [30] and references therein, and the finite temperature quantum distribution of H adsorbate on Ni(001) surface [18].

The total (cohesive) energy of a crystal or a cluster in MBA description is decomposed [30,31] into individual atomic contributions E_i as

$$E_{\mathrm{T}} = \sum_i E_i, \tag{1}$$

where i runs over all atoms in the system and

$$E_i = -\sqrt{\sum_{j\neq i} \xi^2_{\alpha\beta} \exp\left[-2q_{\alpha\beta}\left(\frac{r_{ij}}{r_{0,\alpha\beta}} - 1\right)\right]} + \sum_{j\neq i} \epsilon_{\alpha\beta} \exp\left[-p_{\alpha\beta}\left(\frac{r_{ij}}{r_{0,\alpha\beta}} - 1\right)\right]. \tag{2}$$

The attractive part (first term) is due to the hybridization of orbitals. It is based on a parametrized tight-binding Hamiltonian and the second-moment approximation. The repulsive part (second term) is parametrized as a pair-wise Born–Mayer potential with an exponential distance dependence [31].

We have fitted MBA potential to describe interactions between H adsorbate and Ni atoms [18]. The bulk Ni–Ni parameters were fitted to the lattice constant $a = 3.52$ Å, the nearest neighbour distance $r_0 = 2.49$ Å, cohesive energy $E_{\mathrm{coh}} = -4.44$ eV and bulk modulus $B = 1.17$ eV/Å^3. The H–Ni parameters of MBA potential were fitted to the DFT data given by Mattsson et al. [12]. The fitted quantities are the adsorption energy of the hollow site, $E_{\mathrm{ads}} = 2.8$ eV, the equilibrium distance from the surface at hollow site $r_a = 0.5$ Å and the energy barrier between the hollow sites through the bridge site, $E_{\mathrm{barr}} = 0.14$ eV. For DFT details, see Ref. [12].

For the H_2 dimer in MBA scheme we adopt the parameters from Ref. [31], giving the binding energy as −4.95 eV at bond length 0.9 Å. We note that the parameters are not fitted to describe the free H_2 molecule but the one adsorbing onto on a transition metal surface.

All of the MBA parameters that are used in simulations of this paper are given in Table 1.

Table 1
Many-body alloy (MBA) potential parameters for all atom pairs in Eq. (2)

X_α–X_β	$q_{\alpha\beta}$	$p_{\alpha\beta}$	$r_{0,\alpha\beta}$ [Å]	$\epsilon_{\alpha\beta}$ [eV]	$\xi_{\alpha\beta}$ [eV]
H–H	3.22	5.28	2.30	0.16	0.91
H–Ni	2.87	5.87	1.44	2.70	5.52
Ni–Ni	3.00	8.62	2.49	0.20	1.97