SIMULATION OF ADSORPTION AND PHASE TRANSITIONS OF GASES ON METAL SURFACES

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ABSTRACT

A general procedure will be described how to obtain thermodynamic properties and phase diagrams of adsorbed gases on metal surfaces by first-principles computational methods. Starting from DFT calculation on rather small unit cells one obtains effective interaction energies, which will be used in a lattice-gas Hamiltonian to find thermodynamic properties by means of Monte Carlo calculations. The Metropolis Monte Carlo and the Wang-Landau algorithm will be employed in the canonical ensembles.

Keywords: phase diagram, Monte Carlo, density functional theory.

INTRODUCTION

Understanding the elementary reaction steps in detail is a major goal in heterogeneous catalysis. For this purpose one has to describe the surface structure of the transition metal catalyst, the reactants and their reaction steps like adsorption, dissociation, diffusion, association and desorption. The development of first-principles approaches like density functional theory (DFT) [1-3] and periodic Hartree-Fock (HF) [4] up to high-level ab initio methods [5] allow calculating reactions and other molecular properties with increasing realism and accuracy. In DFT the electronic density is the basis variable. Hohenberg and Kohn [6] showed that all the observable ground state properties of a system of interacting electrons moving in an external potential $\nu_{ext}(\mathbf{r})$ are uniquely dependent on the charge density $\rho(\mathbf{r})$ that minimizes the systems total energy. In other words, there exists a one-to-one correspondence between the electron density of a system and its energy. Unfortunately, there is no formula available yet to calculate the total energy of many electrons moving in a general potential from the charge density. A general DFT energy expression can be written as

$$E_{DFT}[\rho] = T_{S}[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \tag{1}$$

Here $T_{S}[\rho]$ is the kinetic energy functional calculated from a Slater determinant, $E_{ne}[\rho]$ the nuclei-electron attraction functional, $J[\rho]$ the Coulomb electron-electron repulsion functional, and $E_{xc}[\rho]$ is the exchange correlation term. By equating $E_{DFT}$ with the exact energy eq. (1) can be considered as the definition of $E_{xc}[\rho]:$

$$E_{xc}[\rho] = (T[\rho] - T_{S}[\rho]) + (E_{ee}[\rho] - J[\rho]) \tag{2}$$

where $T[\rho]$ is the kinetic energy functional and $E_{ee}[\rho]$ the electron-electron repulsion functional, which
consists of a Coulomb and an exchange part $K[\rho]$. Therefore, the first term in eq. (2) represents the kinetic correlation energy while the second contains both exchange and potential correlation energy. The exchange energy is by far the largest contribution to $E_x[\rho]$. The advantage of DFT is that only charge density needs to be considered. In order to calculate the kinetic energy one has to introduce orbitals again to obtain a sufficient accuracy. But the computational effort of DFT is similar to a HF calculation. The most difficult problem with DFT is the derivation of suitable expressions for the exchange-correlation term. If the exact $E_x[\rho]$ was known, DFT would provide the exact total energy of the system, including correlation energy. In fact, one has to employ approximate functionals, in particular, the local density approximation (LDA) or various generalized-gradient approximations (GGAs), for which explicit formulas are available. One eventually obtains the Kohn-Sham pseudo-eigenvalue equations [7]:

$$h_{KS} \phi_i = \varepsilon_i \phi_i$$

(3)

with

$$h_{KS} = -\frac{1}{2} \nabla^2 + V_{eff}$$

(4)

They are a set of Schrödinger-like independent-particle equations, which must be solved iteratively subject to the condition that the effective potential $V_{eff}$ and the electron density are consistent. The iterative procedure successively changes $V_{eff}$ and the electron density to approach the self-consistent solution. DFT is now the most used first-principles method. Unfortunately, at present it cannot calculate dispersion forces with a high accuracy. Tuned functionals for this purpose are only useful for some special applications.

Having obtained the electronic energies by DFT, one has to proceed with statistical thermodynamics [8-10]. Statistical thermodynamics provides the link between the microscopic properties of matter and its bulk properties. Thermodynamic properties of real systems can in most cases only be obtained by appropriate numerical techniques like Monte Carlo approaches [11,12] or Molecular Dynamics [13]. An introduction to both methods is given by Frenkel and Smit [14]. A very short overview of these approaches can be found in the book by Leach [15]. DFT calculations lead to results at zero Kelvin. One has to employ statistical thermodynamics so as to calculate phase stability, for example, at constant temperature by means of the free energy which can be obtained from the partition function of the system. If the partition function of a system is known, any thermodynamic equilibrium property can be calculated.

In the following paragraphs the general procedure for calculating phase diagrams and other thermodynamic properties from first principles will be described. Some examples from a thesis by Lazo [16] on hydrogen on Pd(111) will be given.

**DENSITY FUNCTIONAL THEORY CALCULATIONS**

The metal adsorbent is modeled as a repeated slab with vacuum in between, which is called the supercell approach (see Fig. 1). Through an infinite array of slabs, the surface is cast into a three-dimensional periodicity, which e.g. allows to exploit 3D periodicity (periodic boundary conditions) and to make efficient use of plane waves and fast Fourier Transforms in the solution of the DFT equations. In other words, we model the surface in all three dimensions. The semi-infinite slabs consist of several layers in one direction. The necessary minimum number of layers has to be found out by test calculations. The same holds for the vacuum thickness. Having two surfaces at the top and the bottom of the slab, the number of layers has to be large enough to avoid interactions between these two surfaces. Atoms in the center of the slab should adequately model the crystal bulk atoms. In some calculations, in order to enforce a continuous transition from the surface to the bulk region within the slab, atoms at the bottom layers of the slab are fixed in their bulk positions and only atoms in the upper layers are allowed to relax. Periodic boundary conditions can only be used if every cell is neutral and also does not have appreciable higher order charge moments.

The plane waves (wave functions) are written as the product of a cell periodic part and a wavelike part

$$\phi_i(\mathbf{r}) = \rho_i(\mathbf{r}) \cdot e^{i(\mathbf{k} \cdot \mathbf{r})}$$

(5)

The cell periodic part, $\rho_i(\mathbf{r})$, which represents the periodicity of the crystalline solid, is described by lin-
ear combination of a finite number of basis functions in the reciprocal space. According to Bloch’s theorem the electronic wave function is periodic in space, with the periodicity of the primitive cell:

\[ \rho_{n,k}(\mathbf{r} + \mathbf{R}) = \rho_{n,k}(\mathbf{r}) \]  

(6)

whereby \( \mathbf{k} \) is the wave vector, \( n \) the band index, and \( \mathbf{R} \) the lattice vector. In general, the cell periodic part of the wave functions is represented as a linear combination of a finite number of basis functions in the reciprocal space. To a large extent, the choice of the basis determines the achievable accuracy. The most used types of basis sets are localized functions, e.g. linearized muffin tin orbitals (LMTOs), extended plane waves (PWs), mixed basis sets posed of localized orbitals and plane waves, e.g. augmented plane waves (APWs) or linearized augmented plane waves (LAPWs) [17]. Schemes that avoid any kind of shape approximation for the potential and electronic density are called full-potential, e.g. full potential LAPW (FP-LAPW). This method is, for example, used in the WIEN2k program [18].

A further important factor, besides the choice of proper basis functions, is the integration over the Brillouin zone. This integration also determines the accuracy of the results and computational cost. To evaluate physical properties of the solid, like the electron density, a summation over all occupied states has to be executed. For the electron density we obtain:

\[ \rho(\mathbf{r}) = 2 \sum_{n,k} \left| \phi_{n,k}(\mathbf{r}) \right|^2 \]  

(7)

where \( n \) is the band index, \( \mathbf{k} \) the wave vector, and the \( \phi_{n,k} \) are occupied orbitals. The choice of \( \mathbf{k} \) points needed to represent \( \rho(\mathbf{r}) \) is extremely important in calculations on periodic systems and is known as the \( \mathbf{k} \)-point sampling or Brillouin zone sampling. It depends on the size of the unit cell used in the calculations and on the system point symmetry (crystal class). In general, the bigger the cell, the smaller the number of \( \mathbf{k} \) points is needed. The reason for this is because the Brillouin cell becomes smaller in the reciprocal space when a bigger unit cell (a supercell) is used so that \( \mathbf{k} \) points appear closer to each other and fewer of them are needed. There are several approaches for efficient summations over the \( \mathbf{k} \) points available. We will use the approach by Monkhorst and Pack [19]. Other methods were developed by Chadi and Cohen [20], and Evarestov and Smirnov [21]. In order to obtain accurate results from calculations carried out in cells of different size, the \( \mathbf{k} \) points sampling has to be equivalent in all the cells.

Since in metals the bands are crossing the Fermi level, the occupation and consequently the integration over the Fermi level surface is discontinuous. A possible solution to this problem is the introduction of a Fermi distribution at a finite temperature to broaden the Fermi surface.

The DFT results presented below were obtained by the WIEN2k software package [18], whereas all the statistical mechanics results were obtained by software prepared in our institute [16].

**RESULTS FROM DFT CALCULATIONS**

The most important output of DFT calculations is the total electronic energy of the system. In order to compare different adsorbed structures with each other on the same basis, one often calculates the gain of energy of the adsorbate-substrate system with respect to
the clean surface and the free molecule, which corresponds to the adsorption energy:

\[ E_{ads} = \frac{1}{n} \left[ E_{total}^{slab} - E_{total}^{clean} - \frac{n}{2} E_{total}^{molec} \right] \]  

(8)

where \( E_{ads} \) is the adsorption energy per ad-atom, \( E_{total}^{slab} \) is the total energy for a specific adsorbate configuration, \( E_{total}^{clean} \) is the total energy of the clean surface, \( E_{total}^{molec} \) is the energy of the free molecule formed by its respective ad-atoms, and \( n \) is the number of ad-atoms in the surface unit cell. \( E_{ads} \) is a negative value which corresponds to zero Kelvin. From adsorption energy data one can derive lateral interaction parameters. Understanding phase stabilities, it is often more useful calculating formation energies according to:

\[ \Delta E_f^\theta = \theta \left( E_{ads}^\theta - E_{ML}^{1ML} \right) \]  

(9)

where \( E_{ads}^\theta \) is the adsorption energy for a specific coverage, \( E_{ML}^{1ML} \) is the adsorption energy at full coverage, and \( \theta \) represents the coverage. The formation energy allows for determining the ground state structures by drawing a convex line in a \( \Delta E_f^\theta \) vs. \( \theta \)-graph connecting the lowest energy points.

Phase transitions occur because all systems in thermodynamic equilibrium are in the minimum of their free energy:

\[ F = U - TS \]  

(10)

where \( U \) is the inner energy, \( T \) the absolute temperature, and \( S \) the entropy. The chemisorbed overlayers are essentially incompressible. Highly ordered phases are typically present at low temperatures, where the term \( U \) is dominant in eq. (10). At higher temperatures, the entropic term in eq. (10) becomes more important which results in phases with a higher degree of disorder (see Fig. 2). The free energy is related to the partition function, \( Z \), in the following way:

\[ F = -k_B T \ln Z \]  

(11)

where \( k_B \) is the Boltzmann constant. The canonical partition function is given by:

\[ Z = \sum_i \exp \left( -E_i / (k_B T) \right) \]  

(12)

where \( i \) runs over all microstates. In practice the partition function cannot be calculated exactly for most systems as the number of microstates \( i \) is too large. One can numerically evaluate \( Z \) by means of Monte Carlo methods. But even then one needs a very large number of energy evaluations (> 10⁶) in order to calculate thermodynamic properties close to the thermodynamic limit. DFT calculations can be executed only for small cells (about 3 x 3) because the computing time is tremendous. Therefore, one calculates the energy and energy of formation of many configurations of adsorbed atoms on a small cell by means of DFT. For chemisorbed adsorbates one finds well-defined adsorption sites. This allows for the introduction of the lattice gas model, for which the complex many-body interactions in the adsorbate/adsorbents system are coarse grained to lateral interactions among the adsorbates on defined surface sites. The energy is then given by an Ising-like Hamiltonian:

\[ H(n) = E(n) = \sum_i V_0 n_i + \sum_{i,j} V_{ij} n_i n_j + \sum_{i,j,k} V_{ijk} n_i n_j n_k + ... \]  

(13)

where \( V_0 \) is the energy of an isolated atom, \( V_{ij} = V_{ji} \), \( V_{ijk} \) is the energy of nearest next nearest, third nearest neighbors, and so on, respectively; \( V_{ij} \) rep-
represents the energy of trio interactions. Higher order terms are also possible in the expansion, but it is assumed that the series converges rapidly. The terms \( n_i \) are so-called point variables, which are either \( n = 1 \) (occupied site) or \( n = 0 \) (vacant site). Owing to their correspondence to spin variables \( (\sigma = +1 \) (occupied), \( \sigma = -1 \) (vacant)), these variables can also be used \( (n_i = 0.5(1 + \sigma)) \).

The point variables, \( n_i \), lead to lateral interactions, \( V \), between adsorbed atoms on the metal surface that have a physical meaning [22]. It can be shown [23] that when all lateral interactions are taken into account in eq. (13), the expansion can represent any function \( E(n) \) of configuration \( n \) by appropriate interaction parameters, \( V \).

The formalism employed in eq. (13) is called cluster expansion method (CE) [24], and the lateral interaction parameters, \( V \), are known as effective cluster interactions (ECI). The unknown parameters of the cluster expansion, \( V_p \), are determined by fitting them to the energy of a relatively small number of configurations obtained by DFT computations. This approach was introduced by Connolly and Williams [25]. The procedure is summed up in Fig. 3, where some configurations of adsorbed atoms are presented. For each of these configurations the energy is calculated, such that one obtains a system of equations with energies from the DFT calculations on the lhs and a matrix having the corresponding point variables times the vector of the unknown interaction parameters, \( V \):

\[
\begin{pmatrix}
E_1 \\
E_2 \\
\vdots \\
E_m
\end{pmatrix} = 
\begin{pmatrix}
\sum_{i \sigma j}^{n(1)} n_i^{(1)} n_j^{(1)} \\
\vdots \\
\sum_{i \sigma j k}^{n(m)} n_i^{(m)} n_j^{(m)} n_k^{(m)}
\end{pmatrix} \begin{pmatrix}
V_0 \\
V_1 \\
\vdots
\end{pmatrix}
\]

\[ (14) \]

The main criterion to select structures for the CE is the ground state search, which means, the CE has to reproduce the same ground state configurations as predicted by the first-principles calculations. For this purpose one computes more DFT energies than the ECIs, \( V \). These ECIs can be interpreted as lattice averages of the interatomic potentials [26]. Even though they have a well defined physical meaning, their value can only be obtained as a statistical average. Various methods taken from statistics can be used to determine the unknown ECIs, besides singular value decomposition. A result of such a ground state search for hydrogen on Pd(111) is given in Fig. 4 [16]. DFT formation energies vs. coverages are plotted. The ground state configurations for three coverages are also presented.

Once the ECI have been determined, the Hamiltonian in eq. (13) will be employed for Monte Carlo simulations of adsorbed layers of rather large cells.

**MONTE CARLO SIMULATIONS**

After having obtained the interaction parameters, \( V \), one can execute Monte Carlo simulations. The canonical ensemble (temperature, \( T \), and coverage, \( \theta \), are constant) has been used as it mimics the experimental
conditions, for example, LEED experiments. It is also possible to carry out Monte Carlo simulations of chemisorbed systems in the grand canonical ensemble (μ, V, T are constant). Both ensembles should lead to the same results. If the Hamiltonian of a system is known, the internal energy of the system can be calculated from

$$ U = \langle E \rangle = \frac{1}{M} \sum_{i=1}^{M} E_i $$  \hspace{1cm} (15) $$

Within the frame of a Metropolis Monte Carlo simulation, the algorithm works in principle like this:
1. Start with an arbitrary configuration \( a_{i} = \{ n_1, n_2, \ldots, n_n \} \).
2. To generate a new configuration \( a_{k+1} \):
   a. Pick a particle randomly,
   b. move the particle to a free site to create a trial configuration \( n_{r} \),
   c. calculate the energy, \( E_n \), of the trial configuration.
   d. If \( E_n < E_{a_{i}} \), accept the trial; that means, set \( a_{k+1} = a_{n_{r}} \).
   e. If \( E_n > E_{a_{i}} \), accept with the probability
      \( P = \exp(-\beta(E_n - E_{a_{i}})) \); \( \beta = 1/(k_B T) \).
      i. Choose a uniform random number \( 0 \leq r \leq 1 \).
      ii. Let \( a_{k+1} = \begin{cases} a_{n_{r}} & \text{if } P \geq r \text{ accept} \\ a_{k} & \text{if } P < r \text{ reject} \end{cases} \)
3. Repeat the above procedure until equilibrium has been achieved (average energy is constant).
4. Calculate properties.

Thermodynamic properties can now be calculated, for example, the heat capacity, \( C_v \):

$$ C_v = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2} $$ \hspace{1cm} (16) $$

With

$$ \langle E^2 \rangle = \frac{1}{M} \sum_{i=1}^{M} E_i^2 $$ \hspace{1cm} (17) $$

The entropy may be found by thermodynamic integration

$$ S(T) = S(T_0) + \int_{T_0}^{T} \frac{dU}{T} $$ \hspace{1cm} (18) $$

In practice \( U(T) \) is spline-fitted and numerically integrated.

Now we can calculate the Helmholtz free energy:

$$ F = U - TS $$ \hspace{1cm} (19) $$

Even though the Metropolis algorithm is simple and powerful, it has some limitations, in particular close to phase transitions.

In a first order phase transition, the canonical distribution shows a double peak structure at the phase transition owing to the two-phase coexistence. In general, the degree of freedom that changes dramatically in a phase transition is called the order parameter. For example, for a first order phase transition the free energy vs. order parameter shows two minima separated by a hill. An order parameter of zero indicates disorder, whereas a value of one represents an ordered state. In case of order-disorder phase transitions of adsorbates on metal surfaces, order parameters are defined according to the symmetry broken during the transitions. The criterion to determine the critical temperature, \( T_c \), of the transition is the inflection point of the \( \psi(T) \) curve, where \( \psi \) is the order parameter (see Fig. 5). It indicates the transition from an ordered phase to a disordered phase. Therefore, the \( \psi(T) \) data from the Metropolis Monte Carlo simulations are conveniently fitted to a sigmoidal curve:

$$ \psi(T) = \frac{A_1 - A_2}{1 + e^{(T - T_c)/A_3}} + A_2 $$ \hspace{1cm} (20) $$

Where the \( A_1, A_2, A_3 \) and \( T_c \) are fitting parameters. Analogous to the energy and heat capacity, the phase transition can also be determined from the fluctuations in the order parameter \( \psi \):

$$ \chi(T) = \frac{\langle \psi^2 \rangle - \langle \psi \rangle^2}{Nk_B T} $$ \hspace{1cm} (21) $$

Where the susceptibility peaks at the order-disorder phase transition, \( N \) is the total number of atoms.

The problems with the Metropolis Monte Carlo simulations of first order phase transitions are the following:
- It takes an extremely long time to tunnel from one peak to the other in energy space.
- The algorithm easily gets trapped in metastable states.
- Second order phase transitions lead to a so-called "critical slowing down". This problem arises from the fact that the long-range critical correlations of the adsorbates correspond to the occurrence of large clusters of correlated adsorbates. It takes a very long time until such a cluster disintegrates and finally disappears by many subsequent trials in the Metropolis algorithm.

- The Metropolis algorithm suffers from inefficient sampling at low temperatures.

To overcome the drawbacks of the standard Monte Carlo method, several algorithms have been developed to compute the density of states (DOS). The histogram method [27] and the multiple histogram method [28] can be regarded from this point of view. The multicanonical method [29] in some sense is also a computation of the density of states. The same applies to the transition matrix Monte Carlo method [30]. If the density of states can be computed with sufficient accuracy, then most equilibrium thermodynamic quantities can be obtained with little further effort. We have used the recently published Wang-Landau-algorithm [31-33] which turned out to be very efficient for calculating the DOS of large systems. We recognize that the classical partition function can be written either as a sum over all states or over all energies

$$Z = \sum_i \exp(E_i / (k_B T)) = \sum_E g(E) \exp(-E / (k_B T)) \tag{22}$$

where $g(E)$ is the density of states. Since $g(E)$ is independent of temperature, it can be used to find all thermodynamic properties of the system at all temperatures without executing further Monte Carlo simulations. One begins with some simple guess for the density of states, namely all entries are reset $g(E) = 1$. Then, for example, spins are flipped (or adsorbates are moved to another site) according to the probability

$$p(E_i \rightarrow E_j) = \min \left( \frac{g(E_i)}{g(E_j)}, 1 \right) \tag{23}$$

where $E_i$ is the energy before flipping (or before moving the particle) and $E_j$ is the energy that would result if the spin were flipped (or the particle moved).
Following each spin-flip (move) trial the density of states is updated:

\[ g(E) \rightarrow g(E) \times f_i \]  \hspace{1cm} (24)

where \( E \) is the energy of the resultant state (i.e. whether the spin is flipped or not) and \( f_i \) is a modification factor that is initially greater than 1, e.g. \( f_0 \sim e^1 \). A histogram of energies visited is maintained, and when it is “flat”, the process is interrupted, \( f \) is reduced, e.g. \( f_{i+1} = f_i^{0.5} \), all histogram entries are reset to zero, and the random walk continues using the existing \( g(E) \) as the starting point. This is repeated until \( f = f_{\text{min}} = \exp(10^{-4}) \). The Wang-Landau algorithm is able to probe extremely complicated energy landscapes. The Wang-Landau simulations were also carried out in the canonical ensemble. An example of typical results of the configurational density of states (\( \ln(\Omega(E)) \)) for a system of H/Pd(111) at a coverage of \( \theta = 0.333 \) is presented in Fig. 6. The insets show characteristic snapshots of H/Pd(111) configurations for a \( (15 \times 15) \) unit cell.

The configurations correspond to the ground state, a random configuration and the highest energy configuration. Since the highest energy configuration corresponds to a clustering (i.e. the most unfavourable configuration) of atoms in the nearest neighbour positions. The repulsive energy is then maximized.
RESULTS FROM MONTE CARLO SIMULATIONS

Some results of Metropolis Monte Carlo and Wang-Landau simulations in the canonical ensemble will be presented [16]. The system is H/Pd(111) in (60 x 60) unit cells with periodic boundary conditions. Convergence studies of the phase diagram with respect to a larger unit cell size lead essentially to the same results. The thermodynamic properties for a coverage of $\theta = 0.333$ is shown in Fig. 7. Results of H/Pd(111) calculated from Metropolis Monte Carlo and Wang-Landau simulations are presented. The internal energy $U(T)$, the specific heat $C_v(T)$, the order parameter $\varphi(T)$, the susceptibility of the order parameter $\chi(T)$, the free energy $F(T)$ and the entropy $S(T)$ all indicate a phase transition at $T_c$ of about 96 [K] in good agreement with the experimental value of 85 [K] [34]. One should keep in mind that the experimental value has some variance. There is essentially no difference between the Metropolis Monte Carlo and the Wang-Landau results. The phase transition at $\theta = 0.333$ is continuous as can be seen by examining the free energy $F(T)$ curve in Fig. 7. The first derivative of the free energy is a continuous function of temperature. There are no steep jumps in either the internal energy or the entropy. The canonical distribution at $T_c$ is single peaked (not shown here) and, therefore, indicates a continuous phase transition. Fig. 8 shows phase diagrams obtained from Monte Carlo simulations [16] and LEED experiments [34]. The results are in good agreement with the experimental results.

CONCLUSIONS

A general procedure was described how to obtain phase diagrams of adsorbed gases on metal surfaces by computational methods without referring to any experimental data. Minor deviations from experimental findings are mostly due to some inherent inaccuracies of the DFT calculations which, as yet, cannot describe dispersion forces properly. Starting from DFT calculations on rather small unit cells one obtains effective interaction energies which are then applied in Monte Carlo simulations in the canonical ensemble on larger unit cells to obtain thermodynamic properties and phase diagrams.

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