

The Self-Assembly of Nano-Objects code (SANO-Grid) using Grid Interpolation technique: Application to epitaxial organic monolayers adsorbed on metal surfaces

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ABSTRACT

The self-assembly of nano-objects onto surfaces is one step toward bottom-up technique for the miniaturization of electronic devices with tunable physical properties. Finding the optimal conditions to position precisely the molecular building blocks on surfaces remains very challenging. Statistical mechanics and numerical approaches on large scales are essential to understand and eventually predict their equilibrium nanostructures, their thermodynamic properties, nucleation and growth mechanisms, which occur at sub-micrometric scalings. Atomistic simulations of thousands of these large flat organic molecules require computational efforts that become rapidly unaffordable. However, assuming the intramolecular degrees of freedom play a minor role on the resulting nanostructures, and taking advantage of grid interpolation techniques, we overcome this challenging issue and have implemented a Grand Canonical Monte-Carlo code, transferable to many transition metal surfaces and organic molecules.

Keywords: monte carlo, adsorption, phthalocyanines, self-assembly, metal surface, ombe

1 INTRODUCTION

One of the main challenges is to precisely position the first molecular building blocks in the first layer of thin films in order to tune their hetero-epitaxial properties, or else, to adjust the substrates for further steps of growth.

Phthalocyanines (Pc) molecules have a large extended π -conjugated often implying a flat-lying adsorbed molecules on the metal surfaces. These molecules are composed of 57 atoms, and the metal located in their center of mass, and can be substituted; by changing the nature of the metal, we can tune their optical (Zn, Cu), electronic (As, Ge) or magnetic (Fe, Co) properties. These molecules are ideal systems since we can enhance and modify their adsorption potential energy and also their intermolecular interactions by functionalizing or substituting their peripheral atoms. This latter modification can imply substrate-imposed stress on the overlayer which can have a significant influence on the resulting molecular self-assembly [1,2].

We have implemented a Grand Canonical Monte-Carlo code capable to simulate the entropically driven formation of (hetero-)epitaxial monolayers. For the seek of reliable statistics, we freeze the atoms of the metal surface and assume the molecules rigid, and use a grid interpolation techniques to reduce dramatically the computational time consumption [3]. Therefore, the intermolecular potential energy becomes a pairwise interaction, since it is reduced to only three variables: the intermolecular distances, and the two azimuthal orientations of each molecule. It allows simulations of thousands of molecules keeping the same precision than atomistic simulations.

To evaluate the transferability of our approach, we are studying the adsorption of copper-phthalocyanines-fluorinated adsorbed on gold ($\text{CuPcF}_{16}/\text{Au}_{111}$) or else Diindenoperylene (DIP) molecules adsorbed on Cu_{111} and Au_{111} [4], and bimolecular systems of interest for their composition dependent symmetry and crystallinity [4-6]. Herein, we present first results on zinc-phthalocyanines-chlorinated adsorbed on a dense silver surface ($\text{ZnPcCl}_8/\text{Ag}_{111}$).

2 COMPUTATIONAL METHODS

2.1 Generating a realistic transition metal surfaces

The metal structures are built as slabs of 12-dense layers stacked along the $\langle 111 \rangle$ orientation of the crystalline face-centered cubic (*fcc*). We then relax the surface performing a quenched molecular dynamics. The metallic interaction energy is modeled by a semi-empirical many-body potential derived from the tight binding scheme in its second moment approximation (TB-SMA). The latter model from Rosato *et al.* [7] is suitable for several transition-metal elements and implies that the band energy term of each atom is proportional to the square root of the second moment of the density of states, after that a pairwise Born-Mayer repulsive term is added to ensure core-repulsion. The total energy of a system of N atoms is then written as:

$$E_{\text{cohesion}} = \sum_i^{N_{\text{at}}} \left(\sqrt{\sum_{j \neq i}^{N_{\text{at}}} \xi^2 \left(-\exp^{2q \left(\frac{r_{ij}-1}{r_o} \right)} \right)} + A \exp^{p \left(\frac{r_{ij}-1}{r_o} \right)} \right) \quad (1)$$

where ξ in the attractive term is an effective hopping integral, summed over all the interatomic distances r_{ij} (when $r_{ij} < r_c$) for a pair of atoms at sites i and j . The set of parameters (A , ξ , p , q) are adjusted on the bulk modulus, elastic constants and cohesive energies of the given metal. Sets of parameters were originally provided by Rosato and more specifically by Mottet *et al.* [8] for silver structures.

Gupta [9] has shown that the based-on Friedel's high binding model yields physical contraction of face-centered-cubic (100), (110) and (111) surfaces, proper to the square root function of the atomic coordination number, while a simple pairwise potential yields intrinsically to a non-physical expansion of the interlayer distances at the metal surface. This latter realistic expansion would prejudice the adsorption potential energy calculation.

2.2 SANO-grid scheme:

Potential energy calculations for sub-micrometric of organic overlayers on crystalline substrates are computationally very demanding with rather large molecules (50 to 100 atoms) due to the colossal number of atoms to be considered. The grid-interpolation technique used already by Mannsfeld *et al.* [3] enables the calculation of both the molecule-substrate interactions and the molecule-molecule interactions in a very fast way. Hence, the potential energy calculation of a pair of molecule indexed i and j is reduced to three variables: the intermolecular distance (d_{ij}) joining their center of mass; their two orientations (θ_i and θ_j) relatively to the axis \mathbf{d}_{ij} and respectively extracted from their two azimuthal orientations (ϕ_i and ϕ_j).

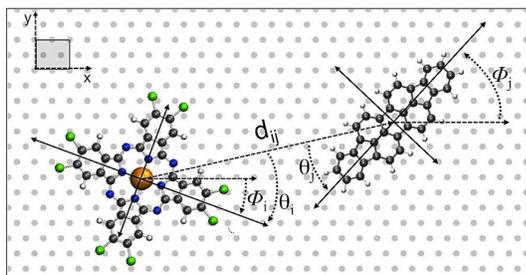


Figure 1: 2D schematic representation of the grid interpolation technique..

Three former steps are necessary to prepare and perform Grand Canonical Monte-Carlo simulations. The optimization of the molecular structure and their partial charge distribution; the prestoring of the potential energy between the molecule and the surface, and then, between two molecules.

2.2.1. Molecule-Surface interactions:

The interactions between the metal surface and the organic molecules are described atomically within a

pairwise 12-6 Lennard-Jones potential (LJ). A recent set of parameters has been reported by Heinz *et al.* [10] for several face-centered cubic metals (Ag, Al, Au, Cu, Ni, Pb, Pd, Pt), which reproduces accurately surface tensions and interface properties with water and (bio)organic molecules, within a good quantitative and qualitative agreement with experiment under ambient conditions. We pre-calculate and store in a (2D+1)-grid the molecule-surface interaction energy as a function of the radial (x_r^I, y_r^I) and angular (ϕ_I) points corresponding respectively to the molecule center of mass and the azimuthal orientation. The orthorhombic surface unit cell is split in a mesh with a lattice spacing of 0.1 Å and 1 degree of revolution spacing. We store the minimized potential energy for each point after adjusting the distance, z_o , between the molecule center of mass and the surface.

Hence, the potential energy is calculated atomically as:

$$V^{MS}(x_r^I, y_r^I, \phi_I)_{z_o} = \sum_{i=1}^{N_{atom}^{Molecule}} \sum_{j=1}^{N_{atom}^{Metal}} \left[4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right]_{OPLS-AA} + \dots \quad (2)$$

$$+ \left(\frac{1}{4\pi\epsilon} \sum_{i=1}^{N_{charges}} \left[\frac{-q_i^2}{2|z_i - z_M|} + \sum_{j \neq i}^{N_{charges}} \frac{-q_i q_j}{\sqrt{(x_j - x_i)^2 + (y_j - y_i)^2 + (z_i + z_j - 2z_M)^2}} \right] \right)_{z_o}$$

where the first dispersive term (LJ) for the interatomic distances r_{ij} between an the i^{th} atom site of the molecule and the j^{th} atom site of the surface; The second term described by Mannsfeld [11] represents the Coulombic interactions between the partial charges localized on the atomic nuclei of the molecule and their respective mirror charges seen through free metal electrons considered as a gelium. This latter term is a function of the bi-dimensional coordinates of the molecule nuclei (x_i, y_i) (parallel to the surface) where the partial charge is localized, and z_i is the azimuthal distance when the molecule is distant at z_o from the surface; z_M designates the mirror plane position which is reported for several transition metals by Chulkov [12], and for the (100) and (111) crystalline orientations surfaces. The atomic parameters (σ and ϵ) are the OPLS All-Atom Force Field (OPLS-AA) parameters [13] for the organic molecule, and the ones reported by Heinz *et al* for the metal. The geometric mixing rule is applied to define the crossed-parameters.

2.2.2. Intermolecular interactions:

In this work, the intermolecular interactions are simply derived from the same terms, and for computational efficiency issue with the coulombic interactions evaluated only in its real part. The cutoff range is taken large enough to ensure that more than 99% of its contribution is taken into account (*e.g.* 5 nm in this work). The intermolecular interactions when performing Monte-Carlo simulations are then derived from the following term:

$$V^{MM}(\theta_I, \theta_J, d_{IJ}) = \sum_{i=1}^{N_{\text{atom}}^{\text{Molecule I}}} \sum_{j=1}^{N_{\text{atom}}^{\text{Molecule J}}} \left(4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right) + \dots \quad (3)$$

$$\sum_{i=1}^{N_{\text{charges}}^{\text{Molecule I}}} \sum_{j=1}^{N_{\text{charges}}^{\text{Molecule J}}} \left(\frac{1}{4\pi\epsilon} \left[\frac{q_i q_j}{r_{ij}} \right] \right)$$

Simulations of multi-components systems require one grid for each type of intermolecular interaction (*i.e.* three in the case of a bi-molecular system, six for a ternary, ...).

2.3 The Grand-Canonical Monte-Carlo

The phase equilibria in the experimental syntheses and the phase transitions observed occur in general for over ten-minute to several hours [1]. Such time scale phenomena are unaffordable within a classical molecular dynamics approach. Hence, Monte-Carlo is more appropriate to provide microscopic properties at equilibrium. We implemented a standard Grand Canonical Monte Carlo (GCMC) simulations consisting in at least 10^5 Monte-Carlo attempts (insertions, extractions, translations/rotations) per molecule to reach an equilibrium. Simulations are performed on (2D) periodic simulation boxes containing ($n \times m$) orthorhombic unit cells of the substrate (*e.g.* Ag_{111} : $5.78 \text{ \AA} \times 5.009 \text{ \AA}$); typically a simulation box size is made of 120×120 unit cells for the silver surface (*e.g.* $693.6 \times 601.08 \text{ \AA}^2$). Therefore, simulations of adsorption isotherms allow the exploration of the accessible configurations space of the system, varying the average density of the organic layer respectively to the incrementing chemical potential excess, with the vacuum as referential state.

3 FISRT RESULTS AND DISCUSSION

The adsorption of ZnPcCl_8 molecules on Ag_{111} surface have been reported by means of combined experimental and *ab initio* theoretical studies, showing compact arrangements governed by the activation of hydrogen-chlorine bonds network [1]. Three different phases which evolve with time were observed experimentally [1,2]; first, a rhombic phase (P1) where no hydrogen bonds are formed and presumed to be stabilized by permanent dipoles from the molecule; an asymmetric phases with four (P2) and finally square-phase stabilized with the formation of eight hydrogen-chlorine bonds (P3). A theoretical study based on first-principle density functional theory calculations has described the nature of these contacts, and detailed accurately the structural properties of the molecules, partial charges distribution, and the cohesive energy for the respective phases due to the hydrogen-chlorine [14]. However, the Van der Waals interactions are missing to give a full description of the intermolecular interactions involved in the system. In this work, we will provide this counterpart without including these already known

effects [1] to measure their contributions in the self-ordering.

The figure below illustrates the self-assembly of ZnPcCl_8 on Ag_{111} and the annealing effects of the temperature, and the incrementing chemical potential on the resulting nanostructures.

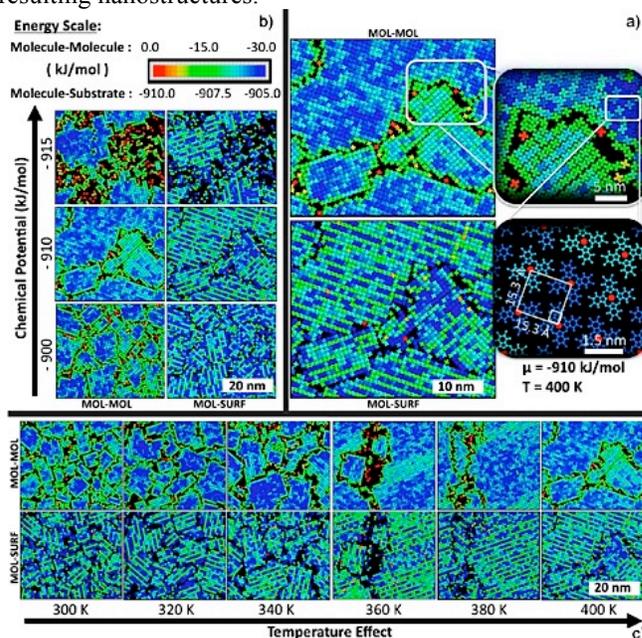


Figure 2: Simulations of ZnPcCl_8 molecules self-assembled on Ag_{111} : a) is a snapshot obtained at 400K $\mu = -910$ kJ/mol. The colours are scaled on the potential energy (kJ/mol) of the molecule-molecule (MOL-MOL) and molecule-surface (MOL-SURF); the substrate is not represented. Figure b) three simulations at 400K at different chemical potential -915, -910 and -900 kJ/mol. Figure c) shows the annealing temperature effect on the island-size distribution at the transition.

When occurs the first order transition in the adsorption isotherms (Fig. 3), we observe large-domain clusters of ZnPcCl_8 (several hundreds of molecule per cluster) ordered in the square phase (P3) with preferential orientations relatively to the substrate and an average lattice spacing of 15.3 \AA . In agreement with the experimental observation and *DFT* calculations [1], the representation of the substrate-molecule potential energy with a color scale highlights the 'point-on-line coincidence' (coincidence-I [11]) of the overlayer with the substrate. It means that the overlayer is orientated in a way that its two lattice vectors starts and ends on one class of the primitive substrate lattice lines. The closest matching supercell of the silver surface is about 14.5 per 15 \AA , respectively along the $[1\bar{1}0]$ and $[110]$ directions. The averaged overlayer square-lattice spacing presents a higher mismatch with the former direction. Also, the higher is the chemical potential, or the lower is the temperature, smaller size are the clusters with different alignments, more boundaries and defects. We can observe graphically the competitive alignment of each

cluster along one of the three [110] equivalent directions of the silver (111) surface.

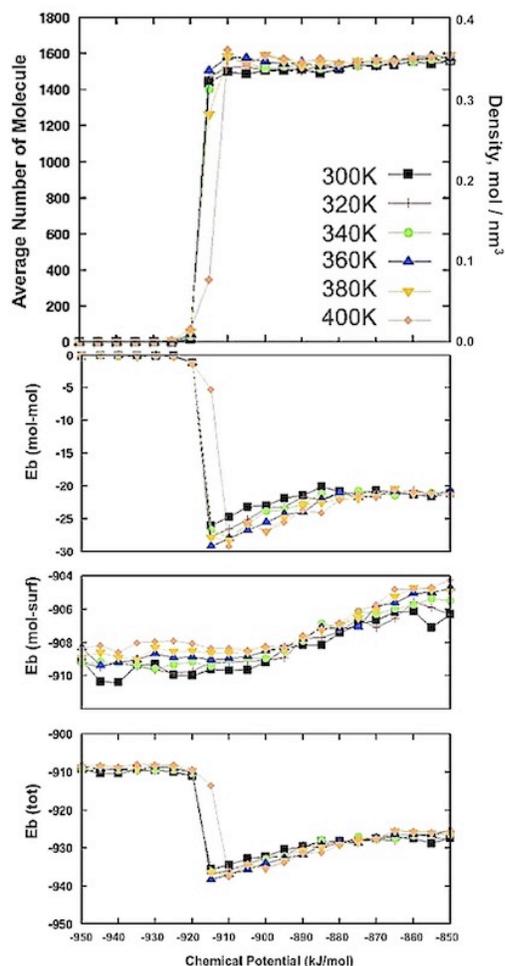


Figure 3: (from top to bottom): Adsorption isotherms as a function of the chemical potential of ZnPcCl_8 on Ag_{111} at different temperatures, and the corresponding molecular density (molecules/ nm^2); the intermolecular, molecule-substrate and total potential energies (in kJ/mol).

The first order transition is mainly driven by the intermolecular interactions. When the temperature is raised of 100K, the loss observed in the molecule-substrate interaction is about 2 kJ/mol while the system gains about 5 kJ/mol from the intermolecular contribution, reaching local densities around $\rho_o = 0.37 \text{ mol/nm}^2$. Therefore, this thermodynamic approach provides qualitative and quantitative insights on the annealing role played by the temperature in the competitive energy balance in favor of the overlayer organic film cohesive energy and to the detriment of the molecule-substrate interaction. An ultimate point within this preliminary work is that the intermolecular

This work is supported by the Spanish Government under NANOSELECT CONSOLIDER project CSD2007-00041, project and under projects CTQ2008-05370/PPQ.

interactions are around 20-25 kJ/mol, which are above the hydrogen bonds binding energies reported for a square phase [1].

CONCLUSION

Taking advantage of the grid-interpolation technique, we have implemented a transferable and versatile (off-lattice) GCMC code which demonstrates the capacity of simulating the adsorption of several hundreds to thousands of large flat ZnPcC_8 molecules adsorbed on a dense metal surface. Adsorption isotherms of organic molecules were performed at the typical sub-micrometric scales where phase transitions occurs experimentally and coexisting phases are observed.

The empirical approach reveals its potential to overcome the computational effort requirements, and to render efficiently the substrate roughness and stress cumulated in the organic layer, annealing effects of the temperature, or else, his capacity to search the optimized commensurate superstructure between a given molecule network with crystalline metal surfaces. Further works are focusing on the self-assembly of modified phthalocyanines on different surfaces, or else their mixtures co-adsorption with molecules of different symmetries.

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