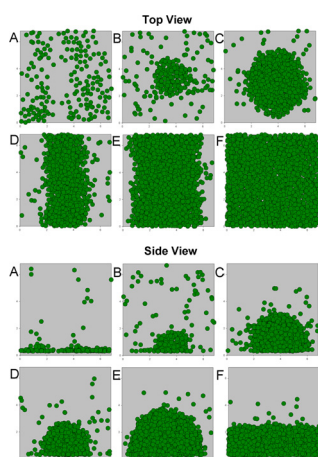# Cluster growth and coalescence of argon on weakly adsorbing substrates The origin of the thin-to-thick film transition

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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

We have studied argon adsorption on weakly adsorbing substrates using Monte Carlo simulation in both the canonical and grand canonical ensembles in order to determine the microscopic mechanism of the non-wetting/wetting/pre-wetting transitions, and have compared the results with adsorption on graphite (a strong adsorbent). To characterize the affinity of a substrate for a given adsorbate, we used the ratio $D*$, of the depth of the solid-fluid potential energy of a single molecule to the depth of the pairwise fluid-fluid potential energy. The range of $D*$ investigated for argon is from 1.7 to 9, where 1.7 represents a very weak substrate and 9 represents a very strong substrate (graphite). Argon adsorption on graphite ($D* = 9$) exhibits a mechanism of wetting (molecular layering) of the first adsorbate layer while non-wetting is the mechanism for the weak substrate with $D* = 1.7$ at all temperatures. For the intermediate substrate, with $D* = 4$, the mechanism switches from non-wetting at low temperatures to wetting/pre-wetting at higher temperatures, with a so-called thin-to-thick film transition occurring at temperatures falling between the wetting temperature and the critical pre-wetting temperature. At the wetting temperature the isotherm exhibits a transition from non-wetting to an infinitely thick adsorbed film at P_0, and at the critical pre-wetting temperature the "thin to thick" transition disappears. Below the wetting temperature the adsorption is non-wetting and above the critical pre-wetting temperature, adsorption follows a continuous wetting process. Analysis of the microscopic details of the canonical and grand canonical simulation results, reveals that the origin of the "thin-to-thick film" transition, is in fact a sequence of

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processes of cluster growth, coalescence and molecular layering. It is the coalescence of clusters to form molecular layers that is responsible for the sharp jump in the adsorbed density.

1. Introduction

Adsorption of noble gases on strongly adsorbing solids such as graphitized thermal carbon black, which has a very high surface density of carbon atoms, has been extensively reported in the literature, and it is well-established that the mechanism of adsorption is molecular layering [1–9]. However, the physics of adsorption of gases on weakly adsorbing adsorbents that have been found to exhibit wetting transitions is not well understood, despite numerous experimental and simulation studies (*e.g.* inert gases on alkali metals: xenon on Cs, xenon on Li, neon on Mg [10–12], argon on solid CO_2 [13], and many other systems [14–20]). In Fig. 1 we illustrate schematic plots of the adsorbed density *versus* the reduced pressure for a range of temperatures from below the wetting temperature, T_W, to above the critical pre-wetting temperature, $T_{C,Pw}$. An interesting feature that is not often recognized is that, for a given reduced pressure, the adsorbed density decreases with temperature in the wetting region (after the vertical jump in the density) but increases with temperature in the non-wetting region (before the vertical jump).

The definitions of the various types of wetting transition are [21–23]:

1 *Non-wetting*: the adsorption isotherm crosses the saturation vapour pressure ($P/P_0 = 1$), at which only a "thin film" is formed on the surface. This occurs at temperatures below the wetting temperature T_W. We will show later that the term "thin film" is not an appropriate description of the microscopic configurations, since the adsorbate is in fact a collection of delocalised clusters on a sparsely covered surface, rather than a coherent continuous film as the description suggests.
2 *Wetting*: at the wetting temperature T_W, a first order wetting transition is manifested in the grand canonical isotherm as a sharp jump from a "thin film" to a film of infinite thickness at P_0.
3 *Pre-wetting*: The so-called pre-wetting region occurs at temperatures between T_W and the critical pre-wetting temperature ($T_{C,Pw}$). In this region, the grand canonical isotherm shows a sharp increase in the adsorbate density at a threshold pressure $P^* < P_0$. This phenomenon is referred to as a thin-to-thick film transition, and the density difference across this transition is called the pre-wetting transition line, which decreases with temperature and disappears at $T_{C,Pw}$. The threshold reduced pressure (P^*/P_0) also decreases with temperature.
4 *Continuous wetting*: At temperatures greater than $T_{C,Pw}$, continuous layering (wetting) occurs and the adsorbate density diverges as the pressure approaches the saturation vapour pressure (P_0).

There are many open questions concerning the physics of the thin-to-thick film transitions, which occur mainly in systems where the depth of the solid-fluid (*SF*) interaction energy of a single molecule (D_{SF}) is comparable to the depth of the pairwise fluid-fluid (*FF*) interaction energy (D_{FF}). Although simulation studies have confirmed the occurrence of this transition [10–12,24], the sharp change in the adsorbate density does not bring out the microscopic mechanism of the transition. To probe the underlying physics, we have investigated argon adsorption on homogeneous surfaces of different affinities over a range of temperatures using Monte Carlo simulation in the canonical and grand canonical ensembles. Graphite, which is a strong adsorbent for argon because of its very high carbon density, is used as a reference. The affinity of an adsorbent may be characterized by the parameter $D^* = D_{SF}/D_{FF}$. The values of D^* in this paper range from 1.7, representing a very weak adsorbent for argon, to 9 for a graphite (strong) adsorbent. The following questions are raised: (1) what is the microscopic mechanism of the thin-to-thick film transition and (2) what is the

relationship between the temperature and the wetting behaviour? To address these questions, we analysed in detail the canonical and grand canonical isotherms and the isosteric heats, supplemented by snapshots, local density distributions, radial density distributions and histograms of the number of molecules as functions of the solid-fluid energy and the fluid-fluid energy.

2. Theory

2.1. Simulation methods

2.1.1. Volumetric method (2V-NVT)

Simulations in the canonical ensemble were carried out using the *2V NVT* scheme of Nguyen et al. [25], which is based on the gauge cell method proposed by Neimark and Vishnyakov [26]. The simulation set-up comprises two boxes: one containing the adsorption system and the other a gas reservoir whose size is large enough to control the fluctuations, and molecules are allowed to exchange between these two boxes. We used at least 150,000 cycles in both the equilibration and sampling stages, and each cycle consists of 1000 attempted displacements and/or exchanges between the boxes. We found that a cubic gas reservoir with a linear dimension of 7 nm was suitable to trace the canonical isotherms [25]. In the adsorption box, the surface dimensions were $20\sigma_{ff} \times 20\sigma_{ff}$ and the box height was 10 nm. The pressure of the gas reservoir was determined from the virial equation.

2.1.2. Grand Canonical Monte Carlo (GCMC)

In the *GCMC* simulations, we used 100,000 cycles in both the equilibration and sampling stages for low loadings and 800,000 cycles for loadings across the transitions in order to ensure the accuracy of the simulation. Each cycle consists of 1000 attempted displacements, insertions and deletions with equal probability. For a given pressure, the chemical potential was calculated from the equation of state of Johnson et al. [27], and was used as the input in the simulation. In the equilibration stage, the maximum displacement length was initially set as 2 nm
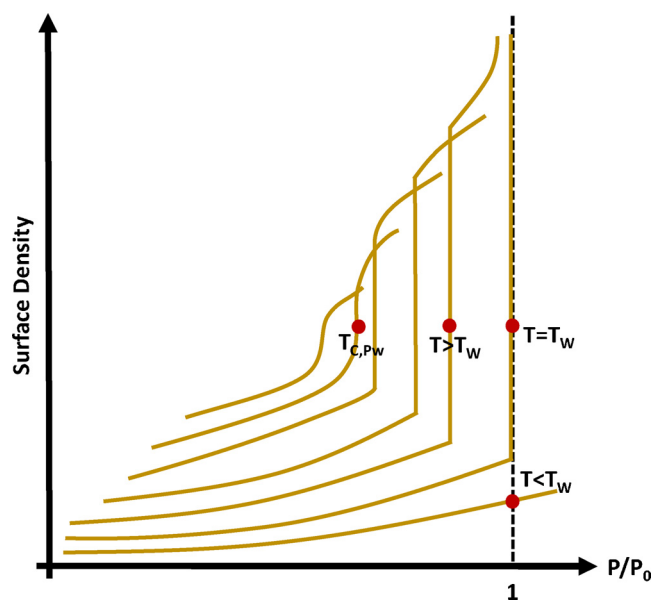
Fig. 1. Schematic plot of adsorbate density *versus* the reduced pressure over a range of temperatures, illustrating non-wetting to wetting behaviour. T_W is the wetting temperature and $T_{C,Pw}$ is the critical pre-wetting temperature.