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# Molecular Dynamics Simulations of PVA / Pt(111) Interfaces

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Molecular dynamics simulations are used to study the structure and dynamics of the interfaces between the platinum (111) [Pt(111)] surface and liquid isopropanol or polyvinyl alcohol (PVA) melt oligomers (10 monomers long). The mass and number atoms distributions were found to be very similar. The small discrepancies between isopropanol and PVA are introduced by the chemical bonds between monomers within PVA chains. The differences in orientational structure of O-H and O-C(CH) bond vectors are significantly stronger in immediate proximity to the Pt(111) surface. The chemical bonds between the monomers are also the main reason for such differences. Further from the surface, the orientational structures of Pt(111)/isopropanol or PVA melt are similar. The PVA chains that are directly adsorbed on the surface protrude into the bulk up to 2.25 nm. There exists a region, where adsorbed and non-adsorbed chains mix with each other and, very likely, form hydrogen bonds. One can expect that PVA melt, unlike liquid isopropanol, attaches relatively strongly onto the Pt(111) surface.

## 1 Introduction

Properties of metal/polymer interfaces are crucial to a large number of industrial applications. For instance, coating and adhesion are important in car production, machinery, food packaging, solar power cells, and many others. Thin films with metal nanoparticles distributed in them attract much attention due to their prospective applicability in electronics, optical materials, and sensors.<sup>1</sup> Different polymers, in particular polyvinyl alcohol, are used for stabilizing of metal nanoparticles.<sup>2-5</sup>

Understanding the behaviour of polymers near metal surfaces can provide us with the ability to control necessary interfacial properties in existing applications. This knowledge can also help us to choose components for new uses more effectively. Available experimental techniques can be used to obtain energetic, electronic, and structural information of molecules adsorbed on metal surfaces.<sup>6-9</sup> These techniques are used to study very thin films of molecules (from monolayer to few nanometers) on the surface. Experimental conditions here are usually limited to low temperatures and ultra-high vacuum, as one wants to perform experiments free of any contaminants and in stabilized conformation.

Along with the experimental research molecular simulations have also been used to study interfaces between metals and other organic or inorganic materials. Energetic, electronic, structural, and dynamic properties of interfaces obtained from these theoretical studies can be used to complement experimental results. Molecular simulations can also probe systems and conditions that are inaccessible to experimental techniques. There have been already many attempts to study interfaces of metals with other organic, including polymers, and inorganic molecules by means of quantum calculations (QC)<sup>10-16</sup> and molecular dynamics (MD).<sup>17-24</sup> However, quantum or quantum-hybrid calculations can be used only for a relatively small number of atoms (up to few thousands). Classical MD simulations

cannot be used unmodified for simulations of metal/organic interfaces, and especially for transition metals. The complications in MD simulations are caused by the complex chemical and electrostatic interactions between metals and organic matter, for which there are no simple physical laws. Metal/organic interfaces cannot, therefore, be easily (and systematically) parameterized and simulated in a way as it is done, for instance, in the case of purely organic systems. One has to introduce and parameterize a specific (state-of-the-art) treatment of the interactions between organic matter and transition metal surface.

Delle Site et al. have already studied bisphenol-A-polycarbonate melt near a Ni(111) surface via coarse-grained molecular dynamics simulations.<sup>25</sup> In their system, only ends of polymer chains could be adsorbed on the metal surface chemically. This specific adsorption was found to influence the structure and dynamics of the interface, which are quite different from the interface where no chemical bonding occurs. Schravendijk et al. studied hydrated amino acids at the nickel metal surface using MD simulations, where chemical binding was fitted to the reference quantum calculations.<sup>26</sup>

In our previous contribution we studied Pt(111)/isopropanol (2-propanol) interface,<sup>27</sup> where isopropanol molecules bind to the platinum surface through a weak chemical bond between the hydroxyl oxygen and one of platinum atoms. The purpose of the current work is to make the next step and to study the properties of the interface between the Pt(111) surface and polyvinyl alcohol (PVA) oligomers of different length and at different temperatures. It is also of interest to see how the properties of the interface change depending on the tacticity of oligomers and regular appearance of hydroxyl group in the chains.

## 2 Motivation for Usage of High Performance Computers

In order to estimate properties of interfaces between organic polymers and metal surfaces using molecular dynamics simulations, one must build a molecular model that represents the real system of interest. For this, it is necessary to create a large enough system that contains not only the immediate interface, but also the *bulk* region of the polymer above the metal surface (Fig. 1). This must be done, since one is interested in the properties of the interfacial region that is located between the metal surface and the polymer bulk.

To determine if the simulated interface contains the bulk region, one has to calculate certain properties of the bulk that are then compared to those properties of the interface in regions at different distance to the surface. A match between the properties of the bulk and the chosen region must be found. These properties can be static, dynamic, or both. In our previous studies, in which interfaces between liquid isopropanol or PVA melt and platinum (111) [Pt(111)] surface were studied, we have used the profile of the density as a function of the distance from the surface to confirm the presence of the bulk region.<sup>27,28</sup> Ideally, the choice of properties, which are used to determine the bulk region in the simulated system and, therefore, the size of this system, should depend on the properties of the interface that one wants to investigate. However, in the case of polymeric materials near a solid surface, the relaxation times of the polymer can be extremely long<sup>22,27</sup> and, therefore, can pose very high computational demands.

Interactions in coarse-grained simulations are usually short ranged and, thus, can be parallelized using the distributed-memory model and the Domain Decomposition (DD) approach. In atomistic simulations, long range (electrostatic) interactions may be present, which basically ban the usage of the DD strategy for parallelization. In such situation,

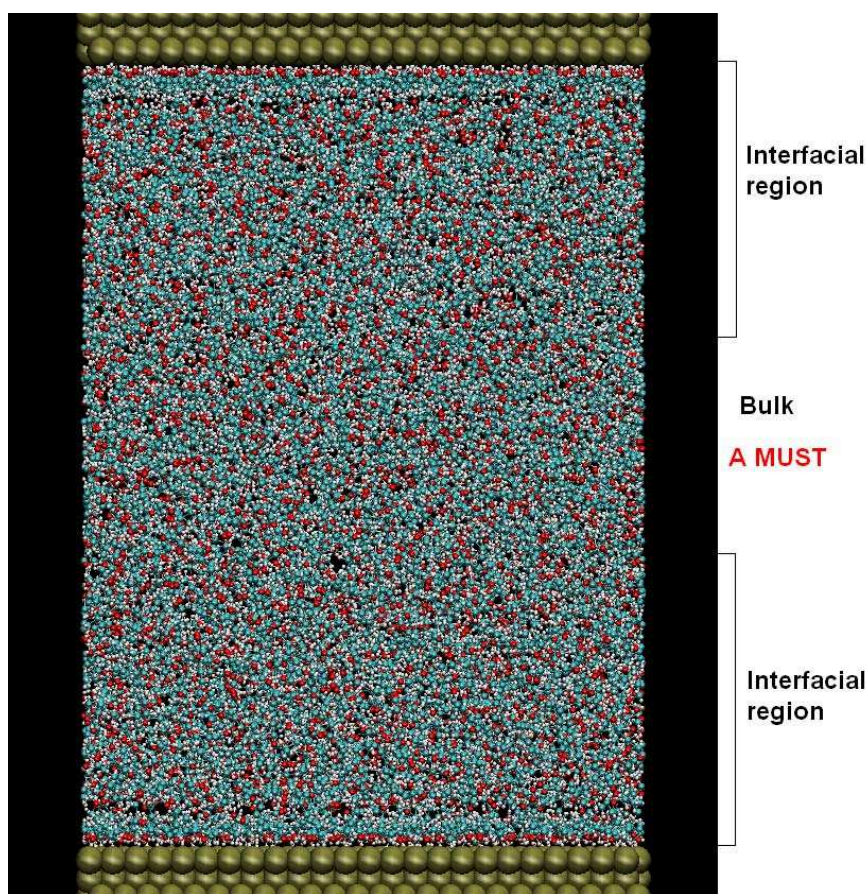


Figure 1. A screenshot of the simulated PVA/Pt(111) interface. The bulk region, which is identified via structural and dynamic properties, **must** be present in any polymer/metal interface system.

the use of shared-memory high performance computers (like ones located at Jülich) for atomistic simulations of interfaces between polymer melts and metal surfaces becomes a very attractive option.

### 3 Current Work and Results

The interfaces between the Pt(111) surface and liquid isopropanol and melt of PVA oligomers with chain length  $N=10$  have been investigated.<sup>27,28</sup> It was found from the comparison of various structural properties that the structure of the Pt(111)/PVA-melt interface at 400K is similar to that of the Pt(111)/liquid-isopropanol interface at 300K<sup>28</sup>. The distributions of mass density (Fig. 2) and of number density of different atom types (Fig. 3) in PVA melt correspond, generally, to those of liquid isopropanol. The differences in

these distributions can be traced to the chemical bonds between monomers in PVA chains that are absent in the case of isopropanol.

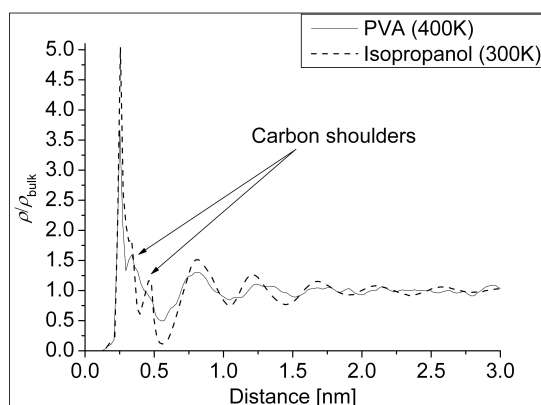


Figure 2. The mass density distribution of PVA melt at 400K and liquid isopropanol at 300K along the surface normal normalized by the corresponding bulk density. The 0 value of the distance axis corresponds to the position of the surface atoms of the platinum slab.

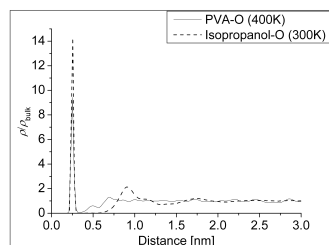


Figure 3a

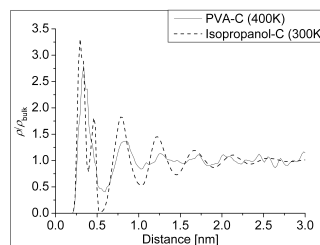


Figure 3b

Figure 3. The number density distribution of hydroxyl oxygen (a) and carbon (b) of PVA melt at 400K and liquid isopropanol at 300K along the surface normal normalized by the corresponding bulk number densities. The 0 value of the distance axis corresponds to the position of the surface atoms of the platinum slab.

This connectivity has substantially stronger impact on the orientational structure. A small change in the distribution of methine carbene atoms (Fig. 4) causes a strong change in the preferred orientation of the O-C(CH) molecular vector (Fig. 5). In the case of isopropanol one can consider that each hydroxyl-methine couple has only methyl groups

as neighbours. For PVA, each of hydroxyl-methine couple (except at the ends of chains) is connected over a methylene bridge to two other hydroxyl-methine couples. It is clear that these hydroxyl-methine couples are larger than methyl groups. Therefore, they introduce additional sterical constraints that result in the sign change of the order parameter  $S^2$  of the O-C(CH) bond vector directly at the surface (Fig. 5).

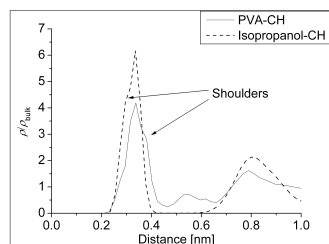


Figure 4a

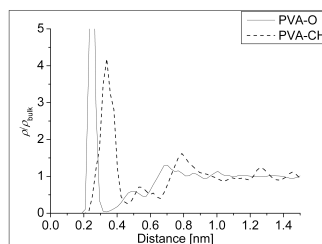


Figure 4b

Figure 4. The number density distribution of the methine carbons for PVA and isopropanol (a), and the hydroxyl oxygens and methine carbons of PVA melt at 400K (b) along the surface normal normalized by the corresponding bulk densities. The 0 value of the distance axis corresponds to the position of the surface atoms of the platinum slab.

The PVA chains adsorbed onto the Pt(111) surface were found to extend into the bulk for up to a few nanometers. There is also an overlap region, where both adsorbed and nonadsorbed chains co-exist and mix with each other (Fig. 6). Hydrogen bonds are very likely formed between adsorbed and nonadsorbed chains in this region. For the Pt(111)/isopropanol interface, interactions between molecules that adsorb directly on the surface (and create hydrophobic methyl brush) and the next layer are weak (Fig. 7). Unlike

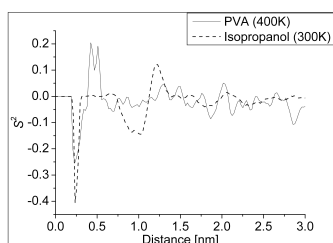


Figure 5a

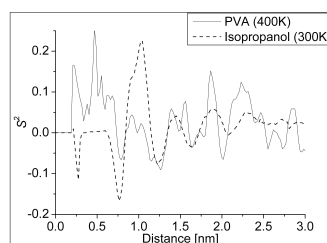


Figure 5b

Figure 5. The order parameter  $S^2 = 1/2 \langle 3\cos^2\theta - 1 \rangle$  as a function of distance of molecular vectors O-H (a) and O-C(CH) (b) for melt PVA oligomers at 400K and liquid isopropanol at 300K. The position of the oxygen atom was used to calculate the distance.  $\theta$  is the angle between the vector being analyzed and the surface normal.  $S^2 < 0$  signifies a preferential orientation in the surface plane,  $S^2 > 0$  an orientation perpendicular to the surface, and  $S^2 = 0$  a random orientation. The 0 value of the distance axis corresponds to the position of the surface atoms of the platinum slab.

in the case of Pt(111)/liquid isopropanol, mixing between adsorbed and non-adsorbed PVA chains will cause stronger attachment of PVA bulk to the adsorbed chains and, therefore, to the Pt(111) surface. However, to quantify this, the non-equilibrium shear molecular dynamics should be carried out.

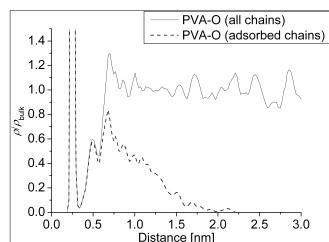


Figure 6a

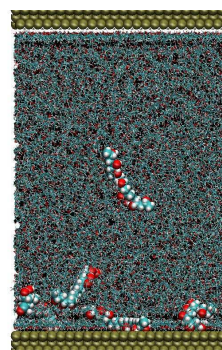


Figure 6b

Figure 6. The number density distribution of hydroxyl oxygen atoms along the surface normal for all chains and only those that have at least one oxygen atom adsorbed onto the Pt(111) surface (PVA melt at 400K) (a). An oxygen atom was considered as adsorbed if its distance was the first minimum of the oxygen density distribution ( $< 0.32$  nm). Both distributions are normalized by the oxygen bulk density in melt of PVA oligomers at 400K. The 0 value of the distance axis corresponds to the position of the surface atoms of the platinum slab. A snapshot of PVA chains adsorbed on the surface and in the mixing region above the surface (b).

## 4 Future Work

Currently the bulk properties of PVA oligomers with chain length  $N=2,3,5$ , and 7 are being investigated. These studies can be considered as the preliminary step towards the investigation of the properties of interfaces between the Pt(111) surface and mono- and bi-dispersed PVA melts.<sup>29</sup> The obtained properties of the bulk will then be used to build molecular systems with the required bulk region present. These systems will then be used to study the properties of PVA/Pt(111) interfaces and the influence of chain length and mixture composition on these properties.

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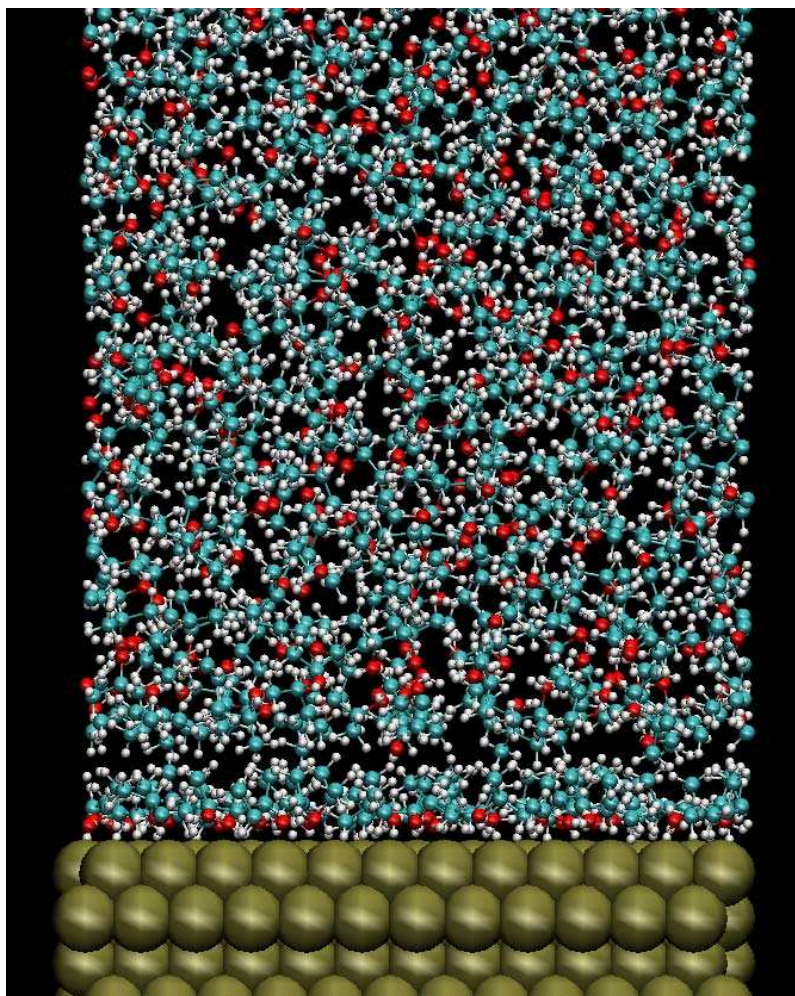


Figure 7. A snapshot of liquid isopropanol adsorbed on the surface. The molecules that are adsorbed directly on the surface create a hydrophobic brush of methyl groups.

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