

Report

On the doctoral thesis of Alena Habartová

The doctoral thesis of Alena Habartová entitled as “Investigation of monomolecular organic layers and their interaction with atmospheric oxidants and pollutants” describes a nice piece of scientific work, based on two published and another two submitted scientific papers. (I wonder if the two submitted papers have already accepted since the completion of the thesis). The main part of the thesis is 44 pages long, and consists of four main chapters. Copies of the two published papers and of the manuscripts of the two submitted papers are added as attachments, to complete the dissertation. The thesis also consists of a brief Introduction and Conclusion sections, a dedication, lists of the figures, tables, and used abbreviations, and a list of references. The English of the thesis is fairly good, and the number of typos, misspells are well below the disturbing limit.

The first main chapter follows a brief introduction of the problems studied, and it concerns the methodological issues related to the work done. I found this chapter being probably the weakest point of the thesis. First, to my opinion, this 8 pages long chapter is far too brief, even if the thesis is organized in such a way that the scientific papers of the Candidate are attached to it. Furthermore, the work done by the Candidate is purely computer simulation, hence, I find it completely useless to waste almost 3 of these 8 pages to describe experimental methods used by the collaborators. This thesis should primarily describe the work of the Candidate, and hence summarize the methods employed by herself. On the other hand, I severely miss a detailed description of the methodology of molecular dynamics simulations. Only a two-pages, long brief description of it is given in the Thesis, even less than what is said about the (non-used) experimental methods. The Candidate should have provided equations-of-motion, described integrating algorithms, given details how force field parameters should be determined, provided equations of the constraining and thermostating algorithms used etc. In a broader context, she should have even describe the role of computer simulation

methods in science, and give a brief overview of other methods (e.g., Monte Carlo), and their relation with the used molecular dynamics method. Furthermore, in this brief section the Candidate mixed the description of the principles of the methodology used and details of the calculations performed. This is again rather disturbing.

The same comments hold for the (only half pages long !) description of free energy calculation methods, which does not contain any equation. At least the basic equations of the field (relation of the free energy with the partition function and configurational integral) and details of the used methods (umbrella sampling and weighed histogram analysis) should have been given. The role of such a chapter in a doctoral thesis is to demonstrate that the Candidate really masters the methods used and not just "pushes the buttons" on the computer. Based on this methodological section, this cannot be done.

The second main chapter presents the results concerning adsorption of six different halocarbon molecules at the surface of amorphous ice (or, as a reference, on clusters of argon) and at the surface of liquid water. The choice of the studied molecules is nice, they include small aliphatic chlorinated hydrocarbons of different size, an aromatic chlorinated hydrocarbon, and also the corresponding non-halogenated molecules (methane and benzene) for reference. The chapter describes very extensive simulation work: only the simulations on amorphous ice consist of 60 different simulations of 50 ns each. The chapter also includes orientational analysis of the adsorbed molecules, and free energy profile calculation of six different chlorinated or brominated hydrocarbon molecules at the water surface. The results corresponding to CHCl_3 are in a nice agreement with former literature data (Pártay et al., JPC/C 111, 9407, 2007, not cited), but the results concerning CH_2Cl_2 show considerable differences from these former data, the origin of which should have been discussed.

This chapter describes an extensive and interesting work, however, two weak points of this has to be mentioned, as well. First, fluid interfaces, such as the liquid-vapor interface is corrugated by capillary waves. The neglect of these waves in interfacial analyses leads to a systematic error of unknown magnitude, due to the fact that not necessarily the truly interfacial molecules (i.e., the ones being at the boundary of the two phases) are regarded as the ones forming the interface. To overcome this problem, one should detect the so-

called intrinsic (i.e., capillary wave corrugated, real) interface and perform all the analyses with respect to this interface rather than to one of the faces of the rectangular basic box. Several such intrinsic algorithms (e.g., ISM, ITIM, GIP, GITIM, etc.) have been described, the code of most of which being freely available. so such intrinsic surface detection should have been done prior to the analyses.

The other problem concerns the orientational description of the adsorbed molecules. Clearly, the orientation of a rigid body (molecule) relative to an external direction or plane (macroscopic surface) can be done by two independent orientational variables, and hence the orientational statistics needs the bivariate distribution of these independent variable pair. (JCP 117, 2271, 2002; PCCP 6, 1874, 2004). Monovariate distributions are always averages of this full bivariate distribution along one of the variables, and hence contain less information. In some lucky cases this information might be enough to catch at least the most probable orientation, but it cannot be known without having the full bivariate distribution whether we have such a lucky case or not. The problem becomes more severe when the molecules have multiple orientational preferences, these preferences can easily be missed by averaging over one of the relevant orientational variables. Clearly this is the case for CH_2X_2 and CHX_3 species on ice (panels b and e, and c and f, respectively, of Fig. 2.14), where the dual orientational preference is already seen on the monovariate distributions. The Candidate (mis)interprets the two-peak structure as different peaks coming from different CH bonds in the same molecular alignment. Recent simulations of the adsorption of CH_2Cl_2 and CH_2F_2 on ice revealed that at least the dihalomethane molecules indeed have a dual orientational preference at the ice surface (JPC/C 119, 17243, 2015). The inappropriate statistical tool used in the thesis questions all the results concerning the orientational preferences of the adsorbed molecules.

The third main chapter describes works on a palmitic acid monolayer at the water surface at different lateral pressures (surface compressions). Again, this chapter reports a very extensive simulation work, as the system was simulated at 10 different surface pressures, and 3 different force fields of palmitic acid were tested, which makes a total number of 30 simulations, 100 ns long each, of a rather large system that are described in this chapter. A very important point here is that before structural analyses would have

been performed, the Candidate tested several force fields, and detected the one that is in a best agreement with the experimental data. Such a validation of the force field used is a very important (and often forgotten) point of computer simulation studies, especially in the case of complex systems. The results are interpreted in terms of chain length and tilt angle distributions, density profiles, and order parameters. I have only one small critical remark here. Thus, when discarding force field C, the Candidate states that it results in unrealistically broad tilt angle distribution. However, this is simply the sign that at the temperature of the simulation model C is in a different phase than models A and B (and, apparently, the real system). Namely, systems A and B are in the gel (L_{β}), system C is in the liquid crystalline (L_{α}) phase, the transition between which is usually close to room temperature. The Candidate is certainly right to exclude model C for her own work, as this model is in an incorrect phase, but the model, in general, cannot be ruled out without having a detailed comparison with the experimental phase diagram.

To my opinion, far the best part of the thesis is the fourth main chapter. This chapter connects the seemingly different subjects of chapters 2 and 3, as it describes interaction of a palmitic acid monolayer at the water surface with haloalkane molecules. I find this approach really nice, and the work described in this chapter is not only (once again) very extensive (altogether results of 27 simulations 100 ns long each are given in this chapter), but it is also excellent in a scientific sense. Further, while the adsorption of small molecules, including halocarbons, and surfactant monolayers at the surface of water and ice have been reported numerous times in the past two decades, I am not aware of any simulation work of an analogous system of this ternary one. I also like the approach of starting the study with the simple case and approach towards more complicated ones. Further, the analysis of the water/PA/haloalkane systems is divided to two parts: short chain and long chain haloalkanes are discussed separately. This treatment nicely takes into account the fact that short chain haloalkanes adsorb at the water/surfactant or surfactant/air interface, while long chain haloalkanes can mix with PA in the surfactant layer. A very important part of this chapter is the calculation of the free energy profile of chloromethane across the water/PA/air system.

The four main chapters are followed by a short Conclusions section, in which the main scientific results of the work are summarized in five thesis points

Summarizing, to my opinion the scientific content of the doctoral thesis of Alena Habartová is sufficient for getting the doctoral degree. I accept all the results described in the Thesis, and summarized in the five thesis points of the Conclusions section as new and original scientific results. Therefore, independently from the answers to my subsequent questions, I support Ms. Habartová to be provided with the doctoral degree.

I have the following comments and questions concerning the thesis. (Questions are typed by bold characters, the Candidate should only respond to them.)

- **In what sense are, to the opinion of the Candidate, halomethanes and haloethanes the “most relevant” atmospheric pollutants? (First paragraph of Introduction.) They are certainly not the most abundant or the most dangerous ones (these are acetone and methane, and probably sulphure and nitrogen oxides, respectively).**
- The first intermolecular term of eq. 1.1 (page 8) represents not only the van der Waals interaction, (as stated in the text, after the equation), but also steric repulsion (LJ attraction and repulsion, respectively).
- Assuming canonical ensemble, the measure of the stability of a system is the Helmholtz rather than Gibbs free energy (as stated in page 11). Gibbs free energy is the measure of stability on the isothermal-isobaric ensemble.
- It is not explained in eq. 1.5 (page 10) what is the “ α th molecular axis”.
- The title of chapter 2 is a bit misleading, as this chapter describes also work concerning the surface of amorphous ice.

- **What is m_{\max} (2nd paragraph of page 13)? The meaning of this quantity is not explained.**
- The Candidate states (bottom of page 14) that the picked-up molecules generally remained at the position of first contact at the amorphous ice surface. Some evidence of this statement should have been added.
- **The Candidate states (top of page 16) that the strong self-association behavior of benzene can be explained by the π -stacking interaction of the benzene ring. How was the aromatic character (π -electron sextet) of the benzene ring taken into account in the molecular model used in the simulation?**
- **The Candidate states (end of sec. 2.1) that the “average maximal cluster sizes” were, in general, in a good agreement with experimental data. Does she mean average or maximal cluster sizes?**
- **How does finite size effect affects the results in sec. 2? This concerns average/maximal cluster sizes (given that only 12 adsorbed molecules were taken into account, this value cannot exceed 12, and its error increases as its value approaches 12), and also the water surface residence times of several molecules (e.g., for C_3H_7Cl it resulted in 1 ns in a 2 ns long simulation).**
- In describing the definition of angle ϑ (middle of page 18) it is not specified how the z axis of the basic box (macroscopic interface normal) was directed.
- Given that the average energy of a H-bond is around 20-25 kJ/mol, the energetic results given in Table 2.3 could have also been interpreted in terms of (typical) number of H-bonds between an adsorbed molecule and the ice surface.

- **One of the most important conclusions of sec. 2 is that halocarbon molecules self-associate at the surface of amorphous ice, but they do not show such self-association behavior at the surface of an argon nanocluster (see also the first point in Conclusions). To the opinion of the Candidate, what can be the reason of this difference?**

- Relevant works of the field of surfactant monolayer simulation should have been mentioned at several points of Chapter 3. Thus, although a PA monolayer might well have been simulated first in 2005 by Lee et al (ref. 23), as stated at the top of page 25, a number of similar surfactant monolayers have been simulated starting from the early nineties (see the works of, e.g., Pastor, Berkowitz, Klein, Brickmann and others). Also, interfacial dynamics of water at the water/surfactant interface (referred to at the end of the chapter, in the very brief subchapter 3.3) was first analyzed in detail by Westlund et al (Biophys. J. 84, 102, 2003).

- **Why the Candidate used the SPC/E water model, if the PA models considered were all OPLS-based? In general, OPLS force field is compatible with the TIP3P or TIP4P water models, whilst SPC/E (and SPC) models are compatible with the GROMOS and GROMACS force fields.**

- **The Candidate states (pages 26-27) that the increasing area per PA (decreasing surface pressure) leads to a flattening of the water surface. How could it be characterized/quantified?**

- At the bottom of page 28 it is written that the thickness of the PA film was taken as the FWHM of “both C1 atom and tail groups” density profiles. The FWHM of the C1 atoms and of the tail groups density profiles are two different values. Which one of them were regarded as the PA film thickness?

- In chapter 4.2 results of a reference run with (unchlorinated) hexadecane are mentioned. However, this control run is not mentioned in the description of the systems simulated.

Budapest, 28 August 2015



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