THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

SIMULATIONS OF WATER CLUSTERING IN VAPOUR, HYDROCARBONS AND POLYMERS

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Cover: Snapshot of water cluster between Na⁺ and Cl⁻ ions in decane at 450 K.

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ABSTRACT

It is commonly known that water plays a crucial role in many natural and industrial processes. One of these processes is the formation of water trees, and the subsequent breakdown of polyethylene used for high voltage cable insulation purposes. It has been shown by others that the mechanism for water molecules diffusing through amorphous polyethylene includes the formation of small water clusters. Gibbs Ensemble Monte Carlo molecular simulations have been performed to study the clustering of vapour phase water under vapour - liquid equilibrium conditions at temperatures ranging from 300 K to 600 K. The increase in vapour density with increasing temperature leads to a radical increase in the fraction of molecules belonging to clusters with two or more water molecules. It is also seen that the size of the clusters increases with temperature. The topologies of the smaller clusters, up to pentamers, have also been studied. A structural transition is observed from a large percentage with cyclic topology, which is the minimum energy configuration, at lower temperatures to predominantly linear clusters, favoured by entropic effects, at higher temperatures. Similar water properties have been observed in simulations where the vapour phase has been replaced with a hydrocarbon rich phase (n-alkanes and polyethylene). Application of an external electric field to the polymer system reduces the water solubility and affects the water structure. A dramatic increase in water solubility in the hydrocarbon phase is observed when two oppositely charged ions are introduced in the hydrocarbon. The structure of the water changes from several small clusters, in the absence of ions, to a single large cluster with a rod-like shape. The cluster is extremely stable during the simulation. Application of an external electric field may enhance or reduce the effect of the ions depending on the direction of the field. Based on these observations is an alternative mechanism for water tree propagation proposed.

Keywords: Cluster, Gibbs Ensemble, Monte Carlo, Water, Polyethylene, External field, Ion.
LIST OF APPENDED PAPERS AND MANUSCRIPTS

This thesis is based on the work contained in the following appended papers and manuscripts:

I.  **Simulation of water vapour clusters in equilibrium with liquid water**  
    Erik Johansson, Kim Bolton and Peter Ahlström  
    Computer Physics Communications, **169**, 1-3 (2005).

II. **Simulation of vapor water clusters at vapor – liquid equilibrium**  
    Erik Johansson, Kim Bolton and Peter Ahlström  

III. **Atomistic simulation studies of polymers and water**  
    Erik Johansson and Peter Ahlström  
    Springer Lecture Notes in Computational Science, in press.

IV. **Monte Carlo simulations of equilibrium solubilities and structure of water in n-alkanes and polyethylene**  
    Erik Johansson, Kim Bolton, Doros Theodorou and Peter Ahlström  

V. **Water absorption in polyethylene under external electric fields**  
    Erik Johansson, Kim Bolton and Peter Ahlström  

VI. **Formation of rod-like structures of water between oppositely charged ions in decane and polyethylene**  
    Erik Johansson, Kim Bolton, Doros Theodorou and Peter Ahlström  
    Manuscript, submitted.

VII. **Molecular simulation of the effect of ionic impurities and external electric fields on rod-like water clusters in polyethylene**  
    Erik Johansson, Kim Bolton and Peter Ahlström  
    Manuscript.
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PREFACE

This thesis for the degree of Doctor of philosophy reports on work carried out at the School of Engineering, University College of Borås and at the School of Chemical Engineering, National Technical University of Athens. The Swedish Graduate School in Materials Science is gratefully acknowledged for the funding of this project. Kungl. och Hvitfeldtska Stiftelsen and SoftComp Network of Excellence are acknowledged for travelling scholarships.

This thesis is mainly intended as an introduction to the methods used in the study and to the field of water clusters under different conditions. The main part of the results of the study are reported in the appended papers.

I would like to thank my supervisors, Peter Ahlström and Kim Bolton, for all the support they have given me during this time. I would like to thank Rodney Rychwalski at Materials and Manufacturing Technology for accepting me as a student. I am also grateful to Prof. Doros Theodorou at National Technical University of Athens, Greece and Dr. Thijs Vlugt at Universiteit Utrecht, the Netherlands, for fruitful discussions and kind help. There are many others to who I am grateful for their help. You are not forgotten. Thank you all!

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Erik Johansson