Atomistic simulation studies of polymers and water

Peter Ahlström, Erik Johansson, Kim Bolton

School of Engineering, University College of Borås, S-501 90 Borås, Sweden
peter.ahlstrom@hb.se

Abstract. A Monte Carlo simulation study of water and hydrocarbons aiming at understanding the degradation of polyethylene cable insulation is presented. Atomistic simulations of water, hydrocarbons and ions are presented. The SPC/E and TraPPE potential functions are used. The equilibrium distributions and clustering of water in vapour and in hydrocarbons was investigated using Gibbs-ensemble Monte-Carlo simulations. Ions have also been added in the hydrocarbon phase where they were found to act as attractors for the formation of water clusters.

1 Introduction

In this work we present atomistic simulation studies of hydrocarbons and water and discuss the application of the methods in order obtain information about the properties of amorphous polymers and water

We will report some preliminary results from a study of the interaction between hydrocarbons and water with special emphasis on mechanisms responsible for the breakdown of polyethylene insulation of high voltage cables. Polyethylene is a semicrystalline polymer but in the present study we will limit ourselves to study hydrocarbons resembling the amorphous regions and water. We are interested in the interaction of the polymer to water and ions since these are thought to play a central role in the breakdown of the polymer.

In order to study the breakdown of polyethylene sheaths in high voltage insulation materials a complex system has to be studied including impurities due to the production of the polymers (ionic catalyst residues etc.).

In order to separate the different possible causes for the degradation of polyethylene in real cables, a series of simulations of increasing complexity is performed. We start with simple systems like water and hydrocarbons, to fine-tune simulation parameters to experimental data before the complexity of long polymers is introduced.

2 Simulation methods

The choice of simulation method depends both on the system (i.e. what methods are possible) and the properties of interest (i.e. what methods are desirable). In this work different Monte Carlo (MC) methods have been used to study the interaction between alkanes (which could be regarded as ethylene oligomers) on one hand and water and ions on the other hand.

The simulations of water and alkanes were performed using MC methods, mainly Gibbs ensemble (GEMC) [2] simulations using configurational bias [3] to enhance the acceptance probability.

For water the well-known SPC/E-model of Berendsen et al. [1] was used. For the alkanes, initially the TraPPE [4] united atom model was used together with the SPC/E-model for water since this combination gave realistic solubilities of water in short-chained alkanes at same time as both models give realistic densities of the pure phases. The Lennard-Jones parameters for the interaction between water and hydrocarbons were slightly adjusted in order to approximately reproduce the experimental mole fraction of water in hydrocarbons.

3 Results

3.1 Water clusters

The study of the interaction of polyethylene with water was commenced by a study [5] on the properties of water in equilibrium with its own vapour since these properties will be of high relevance to the behaviour of water in polyethylene where the water properties will be similar to those of water vapour. This study gave valuable information about the structure of water vapour. Among others we notice an entropy-driven crossover from cyclic to linear clusters with increasing temperature. The crossover temperature was about 400 K both for tetramers and pentamers.

3.2 Water, ions and hydrocarbons

As a first step towards modelling of the full polyethylene system, water and hydrocarbons without and with the presence of ions were

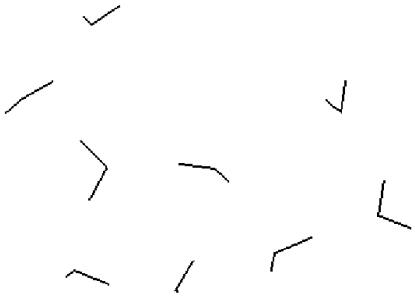

Fig. 1. A pure water cluster with nine water molecules as obtained in the simulations. Figure made by use of gOpenMol [8]

simulated. The first, very preliminary results indicate that the presence of ions in the alkane phase leads to the formation of water clusters that connect the ions. This is similar to results obtained in water vapour phase in the absence of alkanes [6]. This points towards a possible mechanism for the degradation of polyethylene in the presence of catalyst ions left after polymerization in which the ions act as "attractors" for water molecules which then take part in the formation of so-called water trees which are a first step in the degradation of the polyethylene.

4 Outlook

The next step will be to model the interaction between water and amorphous polyethylene. This can be done using an atomistic model as long as the polymer is in an amorphous liquid-like state. To obtain the full picture the semicrystallinity of polyethylene has to be taken into account. This can be done using mesoscopic simulation methods., e.g., [7] and will the subject of further study. We believe, however, that our results regarding the amorphous regions will give highly relevant information that can be used with mesoscale information in order to obtain the full picture.

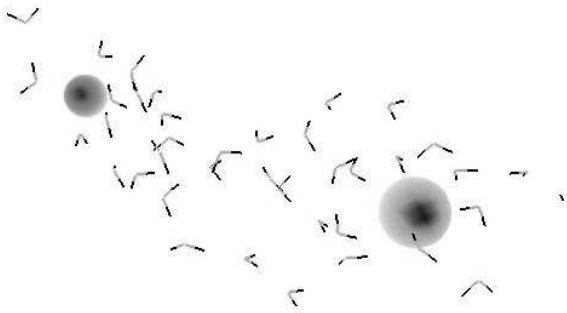

Fig. 2. A water cluster formed between a Na^+-ion (back left) and a Cl^--ion (front right) in decane which is in equilibrium with liquid water. For clarity the decane molecules are omitted. Figure made by use of gOpenMol [8]

References

1. H.J.C. Berendsen, J.R. Grigera and T.P. Straatsma, The Missing Term in Effective Pair Potentials, J.Phys. Chem. 91, 6269–6271 (1987).
2. A,Z, Panagiotopoulos, Direct Determination of Phase Coexistence Properties of Fluids by Monte-Carlo Simulation in a new ensemble, Molec.Phys, **61** (1987) 813–826.
3. J.I. Siepmann, D. Frenkel Configurational Bias Monte-Carlo - A New Sampling Scheme for Flexible Chains, Mol.Phys. **75** (1992) 59–70.
4. M.G. Martin, and J.I. Siepmann, Transferable potentials for phase equilibria. 1. United-atom description of n-alkanes, J.Phys.Chem.B, **102** (1998) 2569–2577.
5. E. Johansson, K. Bolton, P. Ahlström, Simulations of Vapor Water Clusters at vapor-liquid equilibrium Journal of Chemical Physics, 123 (2005), 024504.
6. S.V. Shevkunov, A. Vegiri, Equilbrium structures of the N=64 water cluster in the presence of external electric fields, J.Molec.Struct. (Theochem) **574** (2001) 27-38.
7. F. Müller-Plathe, Coarse-Graining in Polymer Simulation: From the Atomistic to the Mesoscopic Scale and Back, ChemPhysChem, **3** 2002, 754–769.
8. Leif Laaksonen(2001), gOpenMol v.2.0. `http://laaksonen.csc.fi/gopenmol/gopenmol.html`