Research Report
Proton Transport in Water-filled Nanotubes
NIH, Maryland, USA
April 22 - May 12 2007

Jürgen Köfinger

The purpose of my visit to the group of Gerhard Hummer at the NIH was to parameterise, verify, and extend a simple model for a water-filled carbon nanotubes. This model consists of electric dipoles located on the sites of a one-dimensional lattice [1, 2].

For rapid proton transport through a water-filled nanotube the chain of hydrogen bonded water molecules has to be ordered, i.e. the dipoles have to be oriented in the same direction. Also, if the chain breaks into fragments separated by large gaps, fast proton transport will be prevented. We decided to simulate the fragmentation of a chain with the Monte Carlo method in the grand canonical ensemble. To do so we needed the fugacity for the dipole model that corresponds to the fugacity of a water-filled nanotube that is in contact with a particle and energy reservoir of bulk water at normal conditions. Thus, we compared the transfer free energies of the dipole model to the transfer free energies of the molecular system [3] and modified the fugacity for the dipole model to get agreement between the two curves.

To verify the simulation we compared the relative variance of the particle number of the molecular system and of the lattice system. The relative variance is connected to the isothermal compressibility κ_T via

$$\frac{\mathrm{var}(N)}{\bar{N}} = \rho k_\mathrm{B} T \kappa_\mathrm{T} \tag{1}$$

with ρ being the particle density, k_B Boltzmann's constant, and T the temperature.

In Fig. 1 you can see results for the molecular system and the dipole model for a system with 30 sites, which are in good agreement. Further simulations of the dipole model showed that for increasing system size the growth rate of the peak height of the relative variance gets smaller with increasing fragmentation of the chain. The relative variance of the particle number of the dipole model for different system sizes is shown in Fig. 2.

We were able to show that up to macroscopic length scales, the tube is practically fully occupied at normal conditions. Although the chain of water molecules is fragmented, the number of fragments is low and the gaps are very short (mostly just a single site long). The system prefers to be fully oriented and therefore has a macroscopic dipole moment. This means that carbon nanotubes allow fast long-range proton transfer for macroscopic tube lengths.
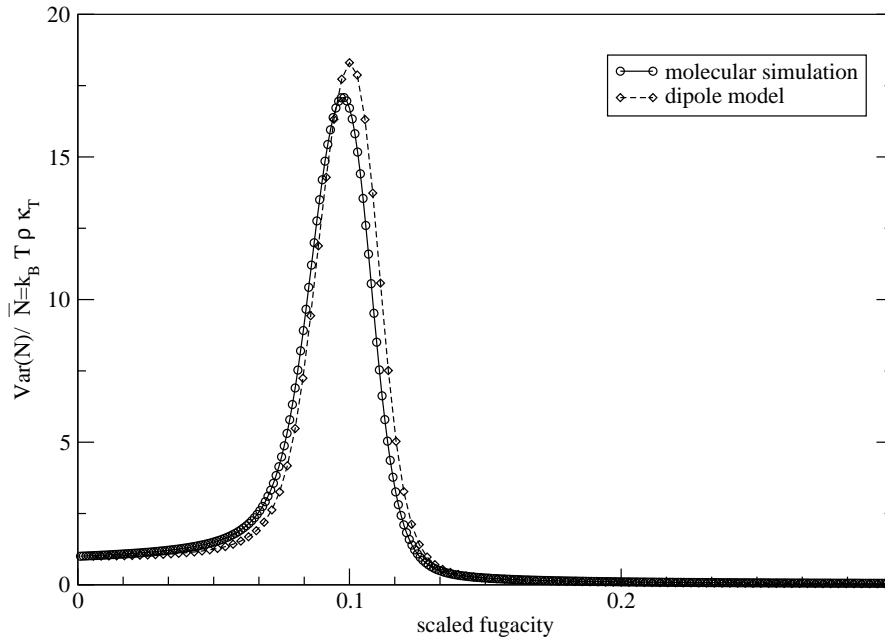
Figure 1: Comparison of the relative variance of the particle (dipole) number of the TIP3P water model with the dipole model for a system size of 30 sites. The scaled fugacity is the fugacity divided by the fugacity at normal conditions.
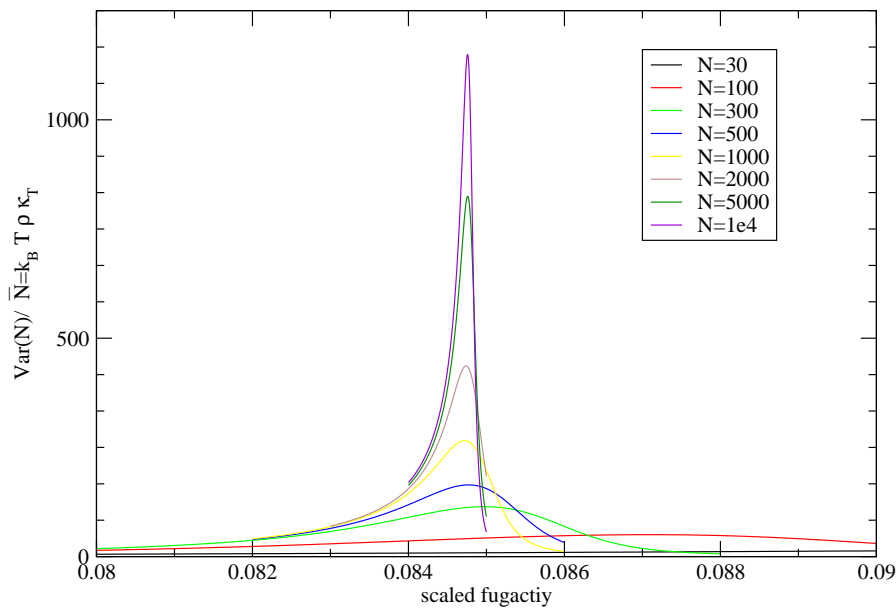

Figure 2: The peak of the relative variance of the particle (dipole) number of the dipole model for different system sizes N (the number of sites). The scaled fugacity is the fugacity divided by the fugacity at normal conditions.

The dipole model does not include the excitation of phonons, the diffusion of protons from the bulk into the tube, and the dissociation of water molecules into hydronium and hydroxide ions within the tube. These effects should not alter our main results. We are also confident that this model can be extended to bundles of nanotubes (i.e. membranes) which might show interesting new phase behaviour.

The next step is to compare the fragment and gap length distributions of the molecular and the lattice system. To do so we use predictions of the dipole model to determine a suitable set of parameters for the molecular simulations, which will be performed by Gerhard Hummer. Meanwhile, we are preparing our results for publication. The interesting phase behaviour of this system will be further examined in an ongoing cooperation with Gerhard Hummer.

References

[1] C. Dellago, M. M. Naor, and G. Hummer, Phys. Rev. Lett. **90**, 10 (2003).

[2] C. Dellago and G. Hummer, Phys. Rev. Lett. **97**, 245901 (2006).

[3] S. Vaitheeswaran, J. C. Rasaiah, and G. Hummer, J. Chem. Phys **121**, 7955 (2004).