408b A Novel Algorithm for the Calculation of Diffusivities in Confined Media - Application to Loading Dependence of Self-Diffusion in Cnts

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We have introduced a novel very efficient algorithm [1] which accelerates Molecular Dynamic simulations of diffusivities in confined media by a factor 25 to 5 orders of magnitude and lead to the same self-diffusion coefficients and heat transfer across the rigid interface as across a fully flexible interface. The central idea of the algorithm is that, due to the collision with the wall, some randomness is introduced into the system. At the level of flexible framework simulations, this randomness, related to the thermal fluctuations, is treated exactly, but this effect can also be mimicked stochastically, such that each gas molecule that hits an atom of the wall has a probability of exchanging momentum. This is similar in spirit to the Lowe-Andersen (LA) thermostat [2] for constant temperature (bulk) dissipative particle dynamics simulations. The LA thermostat is modified such that it works on interface fluid collisions. The parameters of this Lowe-Andersen interface-fluid collision (LA-IFC) thermostat can be obtained from simulations of a flexible carbon nanotube (CNT). In this way, the influence of a flexible interface is introduced in a simulation of a rigid CNT, which is considerably faster than simulating a flexible CNT whereby it leads to virtually the same results.

This approach was applied to the investigation of self-diffusivities of CH4, He and SF6 in CNTs. Skoulidas et al. [3] found a rather high self-diffusivity for low loadings, even higher than the corresponding gas value. It will be shown that this is due to the rigid walls assumption. For a flexible nanotube one obtains a diffusion coefficient that is more than one order of magnitude lower than that reported by Skoulidas et al. [3]. The novel algorithm leads to virtually the same diffusion coefficients as obtained for the flexible CNT.

[1] S. Jakobtorweihem, M.G. Verbeek, C.P. Lowe, F.J. Keil, B. Smit, submitted. [2] C. P. Lowe, Europhys. Lett. 47 (1999) 145 [3] A.I. Skoulidas, D.M. Ackerman, J.K. Johnson, D.S. Sholl, Phys. Rev. Lett. 89 (2002) 185901 185901