

Molecular simulation of fluid dynamics on the nanoscale

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Abstract: Molecular dynamics simulation is applied to Poiseuille flow of liquid methane in planar graphite channels, covering channel diameters between 3 and 135 nm. On this length scale, a transition is found between the regime where local ordering induced by the wall dominates the entire system and larger channel diameters where the influence of boundary slip is still present, but of a more limited extent. The validity of Darcy's law for pressure-driven flow through porous media is not affected by the transition between these regimes.

On the nanometer length scale, continuum approaches like the Navier-Stokes equation break down, cf. Karniadakis et al. (2005). Therefore, the study of nanoscopic transport processes requires a molecular point of view and preferably the application of molecular dynamics (MD) simulation.

In the past, MD could be applied to small systems with a few thousand particles only, due to the low capacity of computing equipment. Consequently, a large gap between MD simulation results on the one hand and experimental results as well as calculations based on continuum methods was present. The constant increase in available computational power is eliminating this barrier, and the characteristic length of the systems accessible to MD simulation approaches micrometers, see also Bernreuther and Vrabec (2005) for a discussion of efficient massively parallel simulation algorithms and their implementation.

The present work deals with the flow behavior of liquid methane, modeled by the truncated and shifted Lennard-Jones (LJTS) potential, cf. Allen and Tildesley (1987), confined between graphite walls. While the LJTS potential can also be applied to the interaction between the solid wall and the fluid, the carbon structure itself is modeled using a rescaled variant of the Tersoff (1988) multi-body potential. The unlike interaction parameters of the LJTS potential acting between methane and carbon were determined according to the Lorentz-Berthelot combination rule with the Lennard-Jones parameters of Wang et al. (2000) for 'pure' sp² configured carbon.

MD simulations of methane confined between

graphite walls with up to 4,800,000 interaction sites, i.e. carbon atoms and methane molecules, were conducted while the channel diameter was varied to include both the boundary-dominated regime and the transition to the continuum regime. A pressure gradient was induced by an external gravitation-like acceleration acting on all methane molecules and a force in the opposite direction acting on the carbon atoms of the graphite wall. The flow was regulated using a proportional-integral controller such that the wall velocity was zero while the fluid reached a specified average velocity.

The fluid-solid interaction induces a local ordering in the vicinity of the wall. For channel diameters below 5 nm, cf. Fig. 1, this effect determines the structure of the entire system. The resulting velocity profile is affected by the local structure and therefore does not exhibit an exactly parabolic shape. However, aggregated quantities such as the slip velocity and the slip length, serving as boundary conditions for higher-order CFD methods and in particular for Navier-Stokes solvers, can be determined by extrapolating a parabolic fit as shown in Fig. 2.

For channel diameters between 20 and 50 nm, the boundary slip undergoes a qualitative transition, cf. Fig. 3. In an extremely narrow channel the regular ordering of the fluid molecules due to the vicinity of the wall entirely dominates not only the static structure, but also the fluid dynamics. With respect to the characteristic direction of the system, this highly ordered structure does not support the extreme velocity gradient that would be implied by the no-slip condition.

However, down to molecular length scales, the pressure drop $-\Delta p/\Delta z$ is approximately propor-

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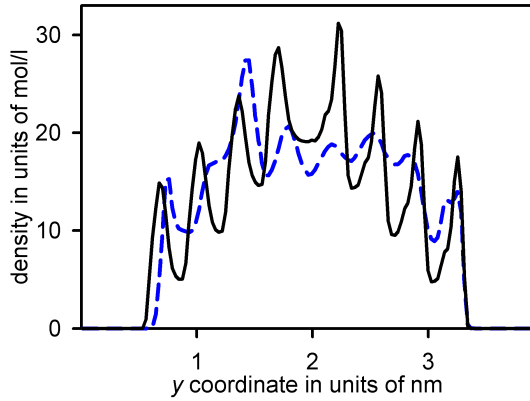


Figure 1: Density profile for liquid methane at a temperature of 175 K in confined within a planar graphite channel with a diameter of 3 nm from MD simulation, averaged over the time intervals from 60 to 120 ps (—) and from 420 to 480 ps (---) after simulation onset.

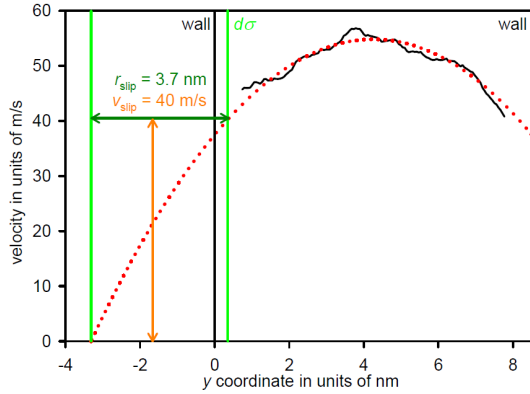


Figure 2: MD simulation results (—) with a parabolic fit ($\cdot\cdot\cdot$) for the velocity profile during Poiseuille flow of liquid methane through a planar graphite channel with a diameter of 8.5 nm for an average flow velocity of 50 m/s at a density of 19 ± 1 mol/l in the central region of the channel and a temperature of 166.3 K.

tional to the average velocity \bar{v}_z and inversely proportional to the cross-sectionional area of the channel, cf. Fig. 3, in agreement with Darcy's law. Therefore, it can be concluded that the qualitative transition between boundary-dominated laminar flow and laminar flow which is only influenced by boundary slip to a certain extent is not reflected by a corresponding change for the effective adhesive forces acting between the fluid and the solid.

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Allen, M. P. & Tildesley, D. J. 1987 *Computer Simulation of Liquids*, Clarendon, Oxford.

Bernreuther, M. & Vrabeč, J. 2005 Molecular simulation of fluids with short range potentials. *High Performance Computing on Vector Systems*, Springer, Heidelberg, pp. 187-195.

Giovambattista, N., Debenedetti, P. G. & Rossky, P. J. 2007 Effect of surface polarity on water contact angle and interfacial hydration structure. *J. Phys. Chem. B*, Vol. 111, pp. 9581-9587.

Karniadakis, G., Beskok, A. & Aluru, N. 2005 *Microflows and Nanoflows: Fundamentals and Simulation*, Springer, New York.

Tersoff, J. 1988 Empiric interatomic potential for carbon, with applications to amorphous carbon. *Phys. Rev. Lett.*, Vol. 61, pp. 2879-2882.

Wang, Y., Scheers Schmidt, K. & Gösele, U. 2000 Theoretical investigations of bond properties in graphite and graphitic silicon. *Phys. Rev. B*, Vol. 61, pp. 12864-12869.

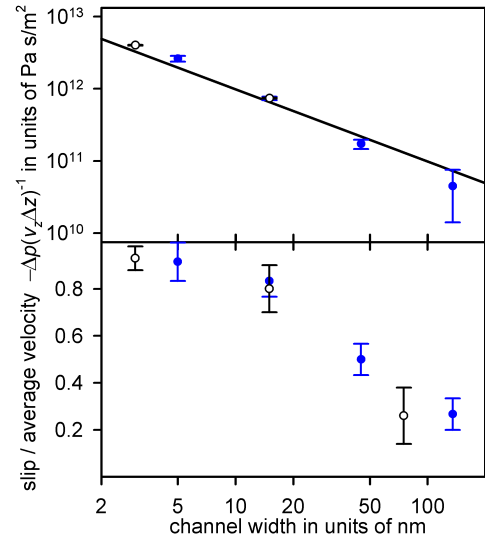


Figure 3: Pressure drop $-\Delta p$ in terms of \bar{v}_z and the channel length Δz (top) as well as slip velocity in terms of \bar{v}_z (bottom), for Poiseuille flow of saturated liquid methane at a temperature of $T = 166.3$ K and average velocities \bar{v}_z of 10 m/s (circles) and 30 m/s (bullets), in dependence of the channel width; solid line: Darcy's law.