

NON-EQUILIBRIUM MOLECULAR DYNAMICS SIMULATION OF ELECTROSMOTIC FLOW IN A NANOPORE

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Electroosmotic flow refers to motion of an electrolyte solution along a charged surface in response to an electric field. This phenomenon has been known since the early days of surface science. However, it has only recently become of practical interest, due to its usefulness as a method of transporting and also separating ionic solutions in microporous materials and microfluidic devices. The basic theory of electroosmotic flow was developed a century ago by Smoluchowski and Helmholtz. Electroosmotic flow occurs because the introduction of a solid surface into a liquid generally causes charge separation, with a surface charge bound to the surface and an equal and opposite mobile charge residing in a layer of fluid adjacent to the surface characterized by the Debye thickness. It is the response of the diffuse charge to the electric field which causes electroosmotic flow. The fluid velocity at the wall is assumed to be zero, and rises monotonically to a maximum value at about the Debye thickness, beyond which the velocity profile is uniform.

I have tested this idealized view by directly calculating both Poiseuille (pressure-driven) and electroosmotic flow using nonequilibrium molecular dynamics simulations. I used a primitive fluid model consisting of ions and non-polar solvent molecules confined within a smooth cylindrical pore. Using a detailed analysis of average density and axial velocity profiles, I calculated the local shear viscosity of the fluid as a function of distance from the pore wall. The viscosity profiles from both Poiseuille and electroosmotic flow were in good agreement. The viscosity was uniform everywhere except the first layer of solvent at the wall, where the fluid flow exhibited pronounced non-continuum behavior. Substantial slip occurred at the wall and the velocity rose sharply to a local maximum in the outer part of the first solvent layer, followed by a local minimum in the depletion region between the first and second solvent layers. In the second monolayer and beyond, the response of the fluid was consistent with continuum fluid mechanics predictions. The enhanced transport in the outer part of the first solvent layer is likely due to the strong two-dimensional ordering of the fluid in this region.