

Nanomechanics of exclusion-zone water

Zsolt Mártonfalvi and Miklós S.Z. Kellermayer*

Department of Biophysics, University of Pécs, Faculty of Medicine, Szigeti út 12., Pécs, H7624 Hungary

*Present address: Department of Biophysics and Radiation Biology, Semmelweis University, Tűzoltó u. 37-47, Budapest, H1094 Hungary

e-mail: miklos.kellermayer.jr@aok.pte.hu, miklos.kellermayer@eok.sote.hu

Intra- and extracellular space is rich in charged biopolymeric surfaces. A vast array of previous studies suggest that the properties of water at and near these surfaces are quite different from that of ordinary bulk water: the ordering of water molecules in co-ordinated multiple layers results in the exclusion of solutes, and thereby leads to the formation of an exclusion zone near the surface. Recent experiments revealed that even large, micron-sized charged particles can be excluded from the vicinity of charged polymeric surfaces to distances reaching hundreds of microns. The exclusion is probably driven by long-range forces, the nature and origin of which remain to be understood.

To investigate the mechanisms of solute exclusion, we combined microfluidics with optical trapping nanomechanics. We followed the collective motion of latex beads (0.5 - 2.0 μm diameter) suspended in aqueous solutions and introduced near the surface of Nafion (synthetic, perfluorinated teflon) in a vertically-mounted sample chamber. Following the entry of the suspension in the chamber, the beads began to rise and move collectively away from the Nafion surface, driven by the vectorial sum of gravitational, buoyancy, frictional and exclusion forces. The velocity of the bead phase boundary decayed exponentially as a function of time. In pure water the time constant of velocity decay was ~ 100 s, and the exclusion zone grew to a width of ~ 200 μm . From the initial velocity of ~ 2.3 $\mu\text{m/s}$ we calculated an exclusion force of ~ 35 fN acting on a single, 1 μm bead. Replacing Nafion with Parafilm completely abolished bead exclusion. Replacing pure water with ethanol solution reduced the width of the exclusion zone. We tested four possible mechanisms that may lead to the generation of the exclusion force: 1) direct pressure by polymer strands dissociating via reptation, 2) direct pressure by entropic polymer brush, 3) direct force applied by moving phase boundary, and 4) physical-chemical gradient that manifests in force. We excluded the reptation and entropic brush mechanisms by imaging and mechanically tapping the Nafion surface with atomic force microscopy. To distinguish between the moving phase boundary versus gradient mechanisms, we trapped beads with optical tweezers in order to relocate them between phases. When beads held, with optical tweezers, in the exclusion zone were released by turning the laser off, they started moving away from Nafion and soon caught up with the bulk of the beads. Thus, it is not a translocating phase boundary that pushes the beads away from the polymer surface. Rather, a physical-chemical gradient is present within the exclusion zone that sustains a distance-dependent force. In sum, the properties and dynamics of water in the vicinity of biolymer surfaces may have direct mechanical consequences. How they might influence biologically important processes such as molecular recognition, enzymatic activity and motor protein function, remain to be resolved.