Molecular theory of hydrodynamic boundary conditions in nanofluidics

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We propose the first-ever statistical-mechanical derivation and calculation of the hydrodynamic slip length. Our approach is based on combination of linear response theory and equilibrium molecular theory of solvation. The slip length derived is related to the fluid organization near the solid surface, as governed by the solid-liquid and liquid-liquid interaction. In the wide range of shear rates and surface-liquid interactions, the slip length is expressed in terms of the Green-Kubo-Nakano relations as a function of the anisotropic inhomogeneous time correlation function of density fluctuations of the liquid in contact with the surface. The time dependence of the correlation function is factored out by treating it in the hydrodynamic limit. The spatially inhomogeneous two-body correlation function is represented in the Kirkwood-like approximation as a product of the three-dimensional density distributions of interaction sites of the liquid near the surface and the site-site pair correlations of the bulk liquid. The presented treatment generalizes the phenomenological definition of the friction coefficient (as well as the slip length) to a tensor quantity, which reflects an anisotropic nature of an ordered crystalline or nanopatterned surface. This enables theoretical prediction of friction forces acting aslant to the liquid flow direction for such surfaces. We derive generic analytical expressions for the liquid-surface friction coefficient (and slip length) for an arbitrary surface-liquid interaction potential. We further illustrate it by numerical calculations for a laminar flow of nine different molecular liquids at ambient conditions in contact with the (100) FCC surface of gold, copper and nickel modeled by using OPLS models for liquids and the Steele potential for crystalline surfaces. The obtained values for slip length range from few to hundreds of nanometers and microns, and are consistent with experimental measurements.