

Adsorption of Associating Fluids at Active Surfaces: A Density Functional Theory

S. Tripathi S and W.G. Chapman C

Department of Chemical Engineering, Rice University, Houston, TX, U.S.A.

Systems of complex fluids (e.g. hydrogen bonding fluids, hydrocarbons, proteins, polymers) interacting with active solid surfaces (surfaces with heterogeneity in solid fluid interaction across the surface) have caught significant interest because of their wide range of potential applications such as, but not limited to, environmental remediation, biochemical separations, design of biosensors and molecular computing. Most of the work toward understanding such systems has primarily been through molecular simulations. Some of the theories that have attempted to account for surface heterogeneity employ a continuous, smeared wall-fluid interaction potential. This, however, is not a realistic characterization of systems where fluid molecules bond or associate with functional groups on the surfaces, such as water adsorbing on activated carbon. We present a novel density functional theory (DFT) to account for surface heterogeneity in the form of discrete, directional association sites distributed over the surface. We study and present the fluid structure and adsorption behavior of several model fluids and demonstrate that the extent, and even the nature of adsorption (Langmuir etc.), vary with the number of association sites on the individual fluid molecules. The effects of surface-groups density, the bulk fluid chemical potential and the fluid-fluid and wall-fluid association parameters are also discussed. Competition between the fluid-fluid and solid-fluid association is analyzed to determine the conditions under which steric hindrance and cooperative bonding effects become significant. All the theoretical findings are compared with Monte Carlo simulations.