Adsorption of Mixtures of Yukawa Fluids on Solid Surfaces

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As precursors to the electric double layers, we examine the adsorption of Yukawa fluids on two types of planar walls: (a) hard walls and (b) Yukawa walls. The first type (hard walls) is for the purpose of establishing the baseline; the second type is to mimic the "electric double layers" of an "electrode/electrolyte" interface, since the Yukawa potential tends to the Coulomb interaction when the decay parameter approaches zero.

Type (I) System:

- •Bulk Fluid: (attractive Yukawa interaction)
- •Wall: Hard wall.

Type (II) System:

- •Bulk Fluid: equal molar mixtures of species A and B molecules. A-A and B-B pairs interact via the repulsive Yukawa potential; while the A-B pairs via the attractive Yukawa potential.
- •Wall: interacting with the "ions" via: $w_{j,ext}(x)/kT = w_{HW} - 2\pi M Z_j x$.
- . w_{HW} is the external hard-wall potential. The wall strength parameter (M) will be varied to simulate different degrees of charging via the surface charge density.

Monte Carlo simulations are carried out at temperatures from $T^* = kT/\varepsilon = 0.76$ to 1.25,and densities $\rho^* = \rho\sigma_3 = 0.4$, 0.7, and 0.8. Type I wall exhibits "depletion" at the two low densities, and "enhancement" at the highest density. Type II walls show more complicated behavior. The quantitative relation is modeled by a newly developed closure-based density functional theory with an OZ3-type bridge function.* We delineate the behavior by exhibiting the underlying singlet density, the cavity distribution function, and the chemical potential behavior that give rise to the observed phenomena. Implications on the electric double layers as found on the electrodes in the electrochemistry are explored.

References

[1] L. L. Lee, "*Constructing a new closure theory based on the third-order Ornstein-Zernike equation and a study of the adsorption of simple fluids"*, J. Chem. Phys. **135**, 204706 (2011).