The physical properties of small systems are fundamental importance in many industrial fields, such as membrane separation, oil recovery and colloidal stability. Engineering such processes requires molecular understanding of interfacial or confined systems. The study of surface phenomena is far less well developed compared to a vast knowledge of the phase behavior of infinitely large systems. When a system volume is reduced to micro/nano-size level, the physical properties are no longer size independent. Experiments and molecular simulations show that a confined fluid behaves differently from the corresponding bulk fluid. A finite system of interacting molecules itself makes the interaction on a given molecule different.

This work centers on the classical statistical derivation of thermodynamic properties of inhomogeneous fluids from its pair potential through the calculation of cluster integrals and also develops a useful method for modeling systems. In the present work, we study the effect of substrates on the thermodynamic properties of simple fluids using cluster expansion methods. The relevant surface variables for inhomogeneous fluids are directly expressed in terms of molecular interactions. The Mayer-sampling Monte Carlo (MSMC) method is applied to calculate the necessary cluster integrals which contain surface contributions. MSMC is a general technique for evaluation of the integrals appearing in the expression for the virial coefficients, using ideas from free-energy calculations. We report the results of calculation of surface cluster integrals evaluated by using MSMC. These results are then used to calculate the relevant surface properties of inhomogeneous fluids, such as surface tension, specific adsorption isotherm and density distribution in terms of cluster expansion in powers of the density. We also present the effects of slit width and surface attraction on the virial coefficients and thorough them, the thermodynamics of inhomogeneous fluids.