

The Oscillation of Solvation Forces in a Spherical Hard-Wall Pore

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The equilibrium and structural properties of confined fluids within microporous media are of great interest to scientists and engineers seeking to understand the fundamental mechanisms involved in colloid and surface chemistry. Other applications in this area include wetting and spreading, sol-gel fabrication, lubrication, and membrane separations. One of the important experimental advances is the development of the surface force apparatus by Tabor and Winterton.¹ This apparatus, refined into its current form by Israelachvili and his coworkers,² has enabled the direct measurement of the disjoining pressure or the solvation force, which is defined as the normal component of the acting force per unit area exerted by interacting molecules on the surrounding pore wall.

Experimental evidences obtained from these experimental studies² have shown that the strength and range of solvation forces were influenced by the size, shape, and flexibility of the molecules comprising the immersed liquids. Also observed in various kinds of liquids between smooth mica surfaces were the oscillatory solvation forces with decreasing surface separations to a few Angstroms. For quasi-spherical liquids, however, the period of such oscillations at a close distance in a molecular level was found to be approximately equal to the diameter of trapped molecular fluids. Mechanical instabilities occurred when a separation distance was slightly smaller than each force maximum or slightly larger than each force minimum.³

In the present work, we investigated the characteristic behavior of the solvation force for the system of hard-sphere fluids confined inside a spherical hard-wall pore. To this end, grand canonical ensemble Monte Carlo (GCEMC) simulations have been carried out over a wide range of bulk concentrations and pore-size ratios. The GCEMC calculation is known to be the most appropriate method for determining the equilibrium and structural properties of inhomogeneous fluid systems since the chemical potential, the total volume, and the temperature are fixed in the grand canonical ensemble.⁴ As an intermediate between theory and experiment, computer simulations can yield essentially 'exact' experimental data for precisely defined systems. A simple pore model employed here can be used as a convenient reference for more sophisticated real systems. Our simulation results will also provide a basis to discuss whether or to what extent

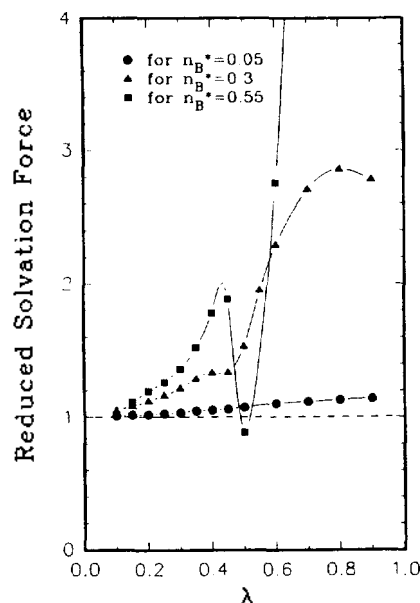


Figure 1. GCEMC results for the reduced solvation force f_s/P_B (f_s =solvation force and P_B =bulk fluid pressure) as a function of $\lambda=d/D$. The dashed line represents the limiting case of $n_B^*=0$.

theoretical approximations appearing in the literature can be applied to predict the thermodynamic properties of such systems.

The only input information required in performing molecular-based simulations, apart from some fixed initial parameters, is the description of interacting potentials. The initialization procedure was first to construct a model pore, devoid of pore fluid particles, and then proceeded directly to the asymmetric GCEMC algorithm proposed by Adams.⁵ The equilibrium condition was maintained by requiring that the chemical potential in the pore phase should be the same as that in the bulk phase. The bulk pressure at a given bulk concentration was calculated with sufficient accuracy using the Carnahan-Starling equation of state.⁶ The configurations were aged, or equilibrated, during the initial 2 million steps before accumulating the equilibrium data, and the GCEMC results reported here were obtained from the final 20-80 million configurations.

Figure 1 illustrates the GCEMC results for the solvation force scaled to the corresponding bulk pressure as a function of particle-to-pore size ratio λ , in which $\lambda=d/D$ and d and D are a molecular diameter of hard-sphere fluids and the spherical pore diameter, respectively. The three sets of GCEMC runs were performed for $n_B^*=0.05$, $n_B^*=0.3$, and $n_B^*=0.55$ ($n_B^*=n_B d^3$ and n_B is the hard-sphere bulk concentration). Although the fundamental mechanics governing the steric effect are basically the same for all systems, the magnitude of solvation forces is seen to be significantly different one system to another. For the sufficiently dilute system of $n_B^*=0.05$, particle-particle interactions in the pore phase become small for any given value of λ and the solvation forces are approximately equal to those in an external bulk phase. In the ideal gas limit of $n_B^*\rightarrow 0$, the solvation force is simply reduced to the bulk pressure as represented by the dashed line in this figure.

The marginal upward trend of solvation forces in the relatively larger pore systems of $\lambda < 0.4$ is primarily due to the increasing influence of particle-particle interactions. The amount of reversible cavity work required to accommodate a particle of size λ in the pore fluid increases with increasing λ . Under these conditions the size-exclusion structural effect leads to the enhancement of solvation forces. One of the most striking features exhibited in this figure is the oscillatory behavior of solvation forces for higher concentrations. The apparent local peaks are clearly displayed in the case of $n_b^* = 0.55$ and the GCEMC curve for the resulting solvation force passes through the maximum peak near $\lambda = 0.4$ and the minimum peak near $\lambda = 0.5$.

For the systems of hard-sphere fluids restricted in the hard-wall pore, the degree of solvation forces corresponds to the local pore density in the vicinity of the acting pore wall. In the range $0.4 < \lambda < 0.5$, where the particle diameter is approximately half the size of the pore, the solvation force decreases dramatically due to density inhomogeneities in the pore fluid. In this transition regime between $\lambda = 0.4$ and $\lambda = 0.5$, the pore density profiles calculated during GCEMC runs indicate that the pore fluid particles formed a predominantly monolayer structure extending two particle diameters across a spherical pore. This suggests that the actual configurations in the pore phase are rapidly changed from three-dimensional to pseudo two-dimensional behavior. In the range $0.5 < \lambda < 1.0$ the accessible pore region can be occupied only by zero or one particle and there is a uniform probability of finding the center of one particle in the pore volume. Beyond $\lambda = 0.5$ concentration effects are obviously more profound since configurations occupied by one particle become more probable state in the grand canonical ensemble. For higher concentration systems the oscillation of the solvation force is directly related to such local pore density variations, namely, the structural reordering in the pore phase.

The above observations are not restricted to a spherical pore system. Similar results obtained in this work have been shown to exist in slit-shape pores⁷ and further simulation studies in cylindrical pores⁸ have also confirmed the existence of oscillatory solvation forces. It is noted that the magnitude of solvation forces for non-interacting hard-sphere fluids^{8a} is qualitatively close to those for adsorbing Lennard-Jones systems.^{8b,8d} In fact, the hard-sphere fluid model combined with sterically exclusive hard-wall potentials is a reasonable approximation to describe spherical molecules trapped in geometrically well-defined pores, for example, compact rigid proteins or enzymes inside cylindrical pores employed in track-etched membranes.⁹ It would be of interest to investigate more realistic spherical models such as zeolite pore systems in order to verify a number of the conclusions observed in our GCEMC simulations. Confirmation of this possibility will be reported in the near future.

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A Simple and Convenient Synthetic Route to the Bis-Indolinospirobenzopyrans

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During the last decade, a large number of works¹⁻⁴ have been published on the behavior of thermo- and photochromic indolinospirobenzopyran dyes. Interest in these compounds is connected with their reversibility between the colorless spiro forms and the merocyanine colored forms. Structural modification of these dyes has been an active area research since the compounds were found to be useful for practical applications³⁻⁷ that these dyes possess, including their use in recording, copying and preparation of display materials. It has been reported⁵⁻⁶ as well that the merocyanine dyes are capable of giving "giant" molecular aggregates, including spiropyran-merocyanine complexes. In order to control the aggregate growth and hence to prepare a novel dimer, we thus undertook synthetic work on bis analogues of indolinosp-