

SOLVATION PRESSURE OF SIMPLE FLUIDS IN SPHERICAL PORES

Soong-Hyuck Suh

Department of Chemical Engineering, Keimyung University, Taegu 704-701, Korea

(Received 13 February 1995 • accepted 28 April 1995)

Abstract—Computer simulations via the grand canonical ensemble Monte Carlo method have been carried out to investigate the equilibrium properties of simple fluids distributed between the external bulk phase and the pore phase. Solvation pressures and pore density profiles are computed for the system of hard-sphere fluids inside a spherical hard-wall model pore. For dilute concentrations, the resulting solvation pressures are approximately equal to those in the bulk phase. However, at a moderately dense concentration of $n_B^*=0.4$, a weakly oscillatory behavior of the solvation pressure starts to emerge. The apparent maximum and minimum peaks are exhibited in the case of $n_B^*=0.6$ due to the local density inhomogeneities in the pore phase.

Key words: Solvation Pressure, Pore Density Profile, Spherical Pore, Hard-Sphere Fluid, GCEMC Simulation

INTRODUCTION

The thermodynamic and structural properties of confined fluids in porous media are of great interest to scientists and engineers seeking to understand the fundamental mechanisms involved in the surface and colloid chemistry. One of the most important experimental advances in this area is the development of the surface force apparatus by Tabor and Winterton [1969]. This apparatus, refined into its current form by Israelachvili and his coworkers [Israelachvili and Adams, 1978; Israelachvili, 1982], has enabled the direct measurement of the solvation pressure, 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 from those studies have shown that the strength and range of solvation pressure were influenced by the size, shape and flexibility of the molecules comprising the immersed liquid. For most quasi-spherical liquids, the solvation pressure was oscillated with decreasing surface separations in a molecular dimension. The period of such oscillations at a close distance was found to be approximately equal to the diameter of trapped molecular fluids and mechanical instabilities occurred when a separation distance was slightly smaller than each maximum or slightly larger than each minimum [Marcelja, 1990].

In our earlier papers of Monte Carlo and molecular dynamics studies, we have reported simulation results for the confined hard-sphere [Suh and MacElroy, 1986; MacElroy and Suh, 1986, 1987] and Lennard-Jones fluids [MacElroy and Suh, 1989; Suh et al., 1991] inside the structureless and structured cylindrical micropores. More recently, the system of a spherical model pore [Kim et al., 1993; Suh and Park, 1994] has also been investigated in order to verify whether or to what extent theoretical predictions available in the literature can be applied. The results to be presented here is intended to compliment the previous work [Suh and Park, 1994] with particular emphasis on the characteristic behavior of the solvation pressure due to the inhomogeneous layering effects. In principle those simulation results represent machine experimental data, which are essentially exact for such precisely defined systems. A simple pore model of hard-sphere

fluids in spherical pores will be used as a convenient reference for more sophisticated systems.

COMPUTATIONAL METHOD

The only input information required in performing the molecular-based computer simulations, apart from initial parameters, is the description of interacting potentials. The model potential functions considered here are hard-sphere interactions among pore particles and their hard-wall interactions with a structureless spherical pore. In the grand canonical ensemble the chemical potential, the total volume, and the temperature are fixed. In pore phase simulations the equilibrium condition is maintained by requiring that the chemical potential in the pore fluids should be the same as that in the bulk fluids. Under these conditions the grand canonical ensemble Monte Carlo (GCEMC) calculation is known to be the most appropriate method to investigate the equilibrium properties of inhomogeneous fluid systems [Nicholson and Parsonage, 1982].

The GCEMC method consists of two independent steps. In the first step a randomly chosen particle is moved according to the conventional canonical ensemble Monte Carlo method. The next step proceeds to attempt an addition or a removal of a particle based on the related frequency probabilities. A detailed computational algorithm is described in our previous work [MacElroy and Suh, 1986, 1989; Suh et al., 1991; Suh and Park, 1994] using the asymmetric GCEMC sampling method proposed by Adams [1974, 1975]. The initialization procedure was first to construct the model pore, devoid of pore fluid particles, and then proceeded directly to the GCEMC calculation at a fixed chemical potential. The compound events are repeated as many times as is desired and the approach to equilibrium is followed by monitoring the concentration fluctuations in the pore phase. Since the initial stages generated were not representative of the equilibrium ensemble, the configurations were equilibrated during the 2-4 million steps before accumulating ensemble data. The final results were obtained from the 40-80 million configurations.

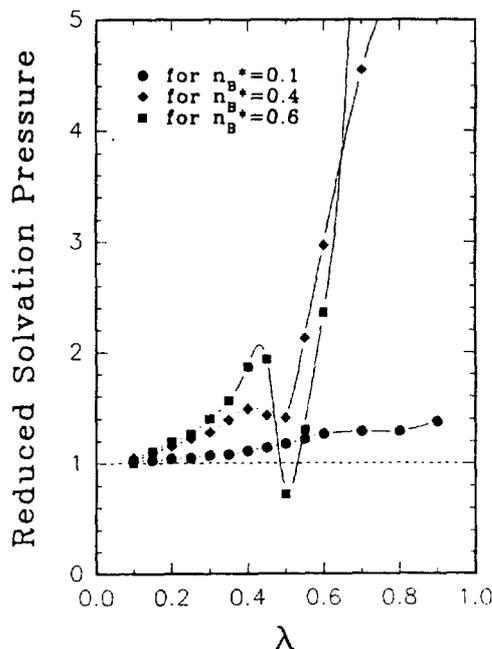


Fig. 1. The reduced solvation pressure as a function of λ . The dashed line represents the limiting case of $n_B^*=0$.

RESULTS AND DISCUSSION

In Fig. 1 we illustrate the simulation results for the solvation pressure as a function of particle-to-pore size ratio λ , in which $\lambda = d/D_p$ and d and D_p are a molecular diameter of hard-sphere fluids and a spherical pore diameter, respectively. The three sets of GCEMC computations in the pore phase were performed at the fixed bulk concentrations of $n_B^* = 0.1, 0.4$ and 0.6 ($n_B^* = n_B d^3$ where n_B is the hard-sphere bulk concentration). Bulk phase simulations were not performed since the chemical potential of bulk hard-sphere fluids for any given concentrations adopted in this work can be calculated with sufficient accuracy using the Carnahan-Starling equation of state [Reed and Gubbins, 1973]. For comparison with an external bulk phase, simulation results are presented in the reduced form scaled to the corresponding bulk fluid pressure.

The characteristic behavior of the solvation pressure obtained from GCEMC calculations is shown to be significantly different from one system to another. At sufficiently low concentrations, both particle-particle and particle-wall interactions in the pore phase become negligible for any given values of λ . In the case of the ideal gas limit $n_B^* \rightarrow 0$, the solvation pressure is simply reduced to the corresponding bulk pressure represented as the dashed line in this figure. For the dilute system of $n_B^* = 0.1$, the resulting solvation pressures are approximately equal to those in the bulk phase. The marginal upward trend in the range $\lambda < 0.4$ is primarily due to the increasing influence of particle-particle interactions. In this case the amount of reversible cavity work required to accommodate a particle into the pore fluid increases with the increment of λ -values.

One of the most interesting features shown in Fig. 1 is the oscillatory behavior of solvation pressures for higher concentrations as observed in the experimental studies of quasi-spherical liquids trapped between two mica surfaces [Israelachvili, 1982; Marcelja, 1990]. As we increase concentrations, a weakly oscillatory

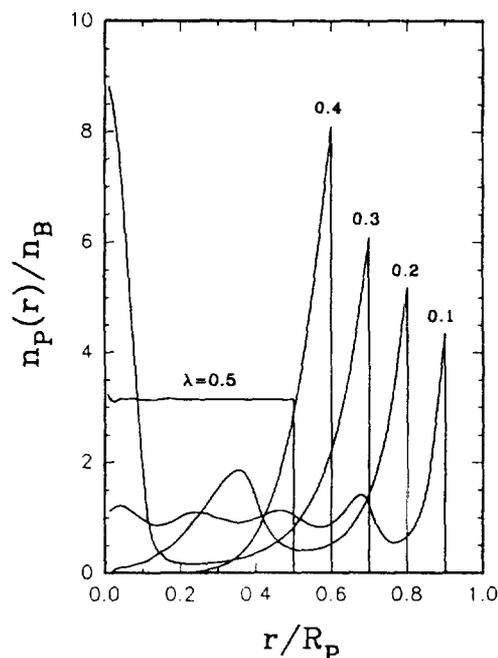


Fig. 2. The normalized pore density profiles for λ in the range 0.1 to 0.5 at a fixed bulk concentration, $n_B^* = 0.6$.

behavior starts to emerge at the moderately dense concentration of $n_B^* = 0.4$ and the concentration dependencies are more profound at $n_B^* = 0.6$. The apparent local peaks are displayed in this case and the GCEMC pressure curve passes through the maximum peak near $\lambda = 0.4$ and the minimum peak near $\lambda = 0.5$. In the transition regime between $\lambda = 0.4$ and $\lambda = 0.5$ the solvation pressure decreases dramatically. The concentration and pore-size dependencies on the solvation pressure result mainly from the local density inhomogeneities in the confined pore fluids. Under these conditions one may expect configurational phenomena of this nature to play an important role in determining the degree of solvation pressures.

In Fig. 2 the normalized pore density profiles, $n_p(r)/n_B$, were plotted for a few selected λ -values at a fixed bulk concentration of $n_B^* = 0.6$ to illustrate the manner in which the local pore densities change with decreasing pore sizes. Pore density profiles were calculated during GCEMC simulations by dividing the pore radius R_p into equal increments. It is observed from GCEMC pore profiles in this figure that the pore fluid even in larger pore systems ($\lambda = 0.1$) experiences the non-continuum structural layering. Local density oscillations arise with a wavelength of the order of the particle size. In the case of $\lambda = 0.2$ the double-layered structure is formed inside the pore with the higher peak near the pore wall. This trend is also shown for $\lambda = 0.3$ but the main peak moves to the pore center. For the system of $\lambda = 0.4$, where the particle diameter is approximately half the size of the pore, the pore fluid particles construct a predominantly monolayer structure extending two particle diameters across a spherical pore. Beyond $\lambda = 0.5$ the accessible pore region can be occupied at most one particle only. The resulting density profiles for $\lambda \geq 0.5$ are constant over the pore volume since there is a uniform probability of finding the center of one particle in the pore volume. This indicates that the actual pore configurations for dense systems change rapidly, namely, the structural reordering in the pore phase.

The above observations are not restricted to the spherical pore

system. Similar results have been shown to exist in slit-shape pores [Snook and van Megen, 1980; Magda et al., 1985; Balbuena et al., 1993] and further simulation studies have confirmed the existence of oscillatory solvation pressures in cylindrical pores [MacElroy and Suh, 1987, 1989; Suh et al., 1991]. For such systems the solvation pressure is directly related to the local pore density close to the pore wall. It is also noted in these simulation studies that the magnitude of solvation pressures for non-interacting hard-sphere fluids is qualitatively close to those for adsorbing Lennard-Jones systems. In many situations, the hard-sphere fluid model combined with sterically exclusive hard-wall potentials is a reasonable approximation to describe spherical molecules confined inside geometrically well-defined pores, for example, compact rigid proteins or enzymes inside cylindrical pores employed in track-etched membranes [Deen, 1987]. In this sense the GCEMC results obtained in this work can provide the basis for a discussion on the steric size-exclusion effects of such pore systems at a molecular level.

ACKNOWLEDGEMENT

This research was supported in part by the Bisa Research Grant of Keimyung University. The author also wishes to thank Mr. Yoon-Tae Lee in implementing simulation data during this work.

REFERENCES

- Adams, D. J., "Chemical Potential of Hard-Sphere Fluids by Monte Carlo Method", *Mol. Phys.*, **28**, 1241 (1974).
- Adams, D. J., "Grand Canonical Ensemble Monte Carlo for a Lennard-Jones Fluid", *Mol. Phys.*, **29**, 307 (1975).
- Balbuena, P. B., Berry, D. and Gubbins, K. E., "Solvation Pressures for Simple Fluids in Micropores", *J. Phys. Chem.*, **97**, 937 (1993).
- Deen, W. M., "Hindered Transport of Large Molecules in Liquid-Filled Pores", *AIChE J.*, **33**, 1409 (1987).
- Israelachvili, J. N., "Forces between Surfaces in Liquids", *Adv. Coll. and Interface Sci.*, **16**, 31 (1982).
- Israelachvili, J. N. and Adams, G. E., "Measurement of Forces between Two Mica Surfaces in Aqueous Electrolyte Solutions in the Range 0-100 nm", *J. Chem. Soc. Faraday Trans. I*, **74**, 975 (1978).
- Kim, S.-C., Suh, J.-K. and Suh, S.-H., "Density Profiles of Fluids Confined in a Spherical Cavity", *Mol. Phys.*, **79**, 1369 (1993).
- Marcelja, S., p. 99-151 in "Liquids at Interfaces", Charvolin, J., Joanny, J. F. and Zinn-Justin, J. eds., North-Holland, Amsterdam (1990).
- MacElroy, J. M. D. and Suh, S.-H., "Concentration and Non-Continuum Effects in Size-Exclusion Partitioning", *AIChE Symp. Ser.*, **82**, 133 (1986).
- MacElroy, J. M. D. and Suh, S.-H., "Computer Simulation of Moderately Dense Hard-Sphere Fluids and Mixtures in Microcapillaries", *Mol. Phys.*, **60**, 475 (1987).
- MacElroy, J. M. D. and Suh, S.-H., "Simulation Studies of a Lennard-Jones Liquid in Micropores", *Mol. Simul.*, **2**, 313 (1989).
- Magda, J., Tirrell, J. M., Davis, H. T., "Molecular Dynamics of Narrow, Liquid-Filled Pores", *J. Chem. Phys.*, **83**, 1888 (1985).
- Nicholson, D. and Parsonage, N. G., Chap. 4 in "Computer Simulation and the Statistical Mechanics of Adsorption", Academic Press, New York (1982).
- Reed, T. M. and Gubbins, K. E., Chap. 9 in "Applied Statistical Mechanics", McGraw-Hill, New York (1973).
- Snook, I. K. and van Megen, W., "Solvation Forces in Simple Dense Fluids I", *J. Chem. Phys.*, **72**, 2907 (1980).
- Suh, S.-H. and MacElroy, J. M. D., "Molecular Dynamics Simulation of Hindered Diffusion in Microcapillaries", *Mol. Phys.*, **58**, 445 (1986).
- Suh, S.-H., Kim, J.-S. and Park, C.-Y., "Equilibrium Partitioning for Hard-Sphere and Lennard-Jones Fluids inside Cylindrical Micropores", *HWAHAK KONGHAK*, **29**, 742 (1991).
- Suh, S.-H. and Park, H.-K., "Thermodynamic and Structural Properties of Hard-Sphere Fluids Confined within a Spherical Hard-Wall Pore", *KJChE*, **11**, 198 (1994).
- Tabor, D. and Winterton, R. H. S., "The Direct Measurement of Normal and Retarded van der Waals Forces", *Proc. Roy. Soc. A*, **312**, 435 (1969).