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Structure and phase behaviors of confined two penetrable soft spheres

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HIGHLIGHTS

- Study the phase behaviors of two penetrable soft spheres in a hard spherical pore.
- Calculate the exact partition function, one-body density, and equation of state.
- Soft attraction beyond the soft-core potential enhances the van der Waals instability
- Van der Waals for two hard spheres is not observed.

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ABSTRACT

We study the phase behaviors of two penetrable soft spheres, whose interactions include the soft repulsion and attraction, in a hard spherical pore. The exact partition function, one-body density, and equation of state for the confined two penetrable soft spheres have been calculated using the Fourier transform method. The phase diagrams have been determined from the negative compressibility of the van der Waals type, which imitates the phase transition of many particle system. The addition of the soft repulsion and attraction beyond the soft-core potential gives rise to the van der Waals instability. The soft attraction beyond the soft-core potential significantly enhances the van der Waals instability, whereas the soft repulsion reduces the van der Waals instability. For two hard spheres and hard square-well spheres, the van der Waals instability is not observed. However, the addition of a short-range soft repulsion beyond the hard-core gives rise to the van der Waals instability.

1. Introduction

The study of structural and thermodynamic properties of confined fluids has become a field of growing interest [1–5]. The interesting question is whether and how the bulk-phase behavior manifests itself in a finite system. Much work related to the structure and thermodynamics in the pores are limited to systems containing many particles, but not on a few particle system. A few studies have recently been done on the phase behaviors of two particle system in two- and three-dimensional boxes [6–9]. They had demonstrated the liquid–solid like transition, which imitates the phase transition of many particle system.

For a hard spherical pore, Németh and Löwen [10] had studied the freezing problem of N hard disks and hard spheres using molecular dynamics simulations. They showed that for few-particle systems confined in a hard spherical pore, the solid–liquid transition, which is related to the transition from an ergodic to a non-ergodic behavior, does not occur.

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However, their studies have been restricted to the phase behaviors of the hard disks and hard spheres, but not the penetrable soft sphere with the additional repulsive and attractive interactions. More recently, one of authors has calculated the exact one-body density and equation of state for two penetrable soft spheres using the Fourier transform technique [11]. Through this calculation, he has shown that the liquid–solid like transition of two penetrable soft spheres, which is related to the negative compressibility of the van der Waals type, does occur [11,12]. We here extend the Fourier transform technique for studying the structure and thermodynamics of two penetrable soft spheres with two piece-wise constant potentials, which incorporate both the repulsive and attractive potentials. Additions of the repulsive and the attractive interactions beyond the penetrable sphere model are known to profoundly influence the structure and thermodynamics. We have obtained the exact one-body density, partition function, and equation of state for two penetrable soft spheres confined in a hard spherical pore. We have investigated the structure and phase behaviors of two penetrable soft spheres confined in a hard spherical pore. This work is to advance in the understanding of the statistical mechanics of fluid-like small inhomogeneous systems of confined particles.

This paper is organized as follows. In Section 2, we will evaluate the exact partition function and distribution function of two penetrable soft spheres confined in a hard spherical pore using the Fourier transform technique. The wall pressure (or the equation of state) at the spherical pore wall was obtained from the one-body density and partition function in a canonical ensemble. In Section 3, we calculate the structure and phase diagram of two penetrable soft spheres from the negative compressibility of the van der Waals type using the Maxwell construction. Finally, the pore-size and potential dependence of the structure and phase behaviors of two penetrable soft spheres in a hard spherical pore are discussed in details.

2. Model and theory

2.1. Model

We consider the pair potential $\phi(r)$ for two penetrable soft spheres interacting via two piece-wise constant potentials described by

$$\begin{aligned} \phi(r) &= \epsilon_1, && 0 < r < \sigma \\ &= \epsilon_2, && \sigma < r < \delta \\ &= \epsilon_3, && \delta < r < \gamma \\ &= 0, && r > \gamma \end{aligned} \tag{1}$$

where ϵ_1, ϵ_2, and ϵ_3 represent an attractive strength or a repulsive strength. The penetrable model becomes $0 < \epsilon_1 < \infty$ [13,14]. For $\epsilon_1 > 0$, $\epsilon_2 < 0$ and $\epsilon_3 = 0$, the model potential, Eq. (1), becomes a penetrable soft-sphere model with an attraction potential. This model has recently been employed to investigate the liquid–liquid and liquid–solid transition in the bulk phase [15–17]. The pair potential can actually be obtained as effective potentials for instance in polymer mixture [18,19]. For $\epsilon_1 = \infty$, $\epsilon_2 > 0$ and $\epsilon_3 = 0$, the model potential becomes a hard-sphere system with soft repulsion, which was employed to investigate the isostructural solid–solid transition [20,21], the stripe phases [22], and the link between particles interacting through such a potential and quasicrystalline order [23]. For $\epsilon_1 = \infty$, $\epsilon_2 > 0$ and $\epsilon_3 < 0$, it becomes the hard-sphere system with both soft repulsion and soft attraction [24–26]. This model system has been shown to be quite relevant to the phase behaviors such as the liquid–liquid phase transition. For $\epsilon_1 = \infty$, $\epsilon_2 < 0$ and $\epsilon_3 > 0$, it becomes the hard square-well system with a soft repulsion, which was used to study the influence of short-range attractive and repulsive interactions on the phase behavior of colloidal suspensions [27–30].

2.2. Two penetrable soft spheres in a pore

In a system composed of two identical particles in a pore, the one-body density $\rho(\vec{r}_1)$ is given as

$$\rho(\vec{r}_1) = \frac{2}{Z_2(V,T)} \int d\vec{r}_2 \exp[-\beta u(\vec{r}_1, \vec{r}_2)] \tag{2}$$

where $\beta = 1/k_B T$ is the inverse temperature and V the volume of the system. The configuration partition function $Z_2(V,T)$ is defined such as

$$Z_2(V,T) = \int d\vec{r}_1 \int d\vec{r}_2 \exp[-\beta u(\vec{r}_1, \vec{r}_2)]. \tag{3}$$

The total potential energy of the system, $u(\vec{r}_1, \vec{r}_2)$, is given by

$$u(\vec{r}_1, \vec{r}_2) = \phi(|\vec{r}_1 - \vec{r}_2|) + \sum_{i=1}^{2} \phi_{ext}(\vec{r}_i) \tag{4}$$