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Hard convex body fluids in random porous media: Scaled particle theory

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ABSTRACT

The scaled particle theory (SPT) is applied to describe thermodynamic properties of hard convex body (HCB) fluid in random porous media. To this purpose we extended the SPT2 approach, which has been developed previously for a hard sphere fluid in random porous matrices. The analytical expressions for the chemical potential and the pressure of an HCB fluid in an HCB or an overlapping hard convex body (OHCB) matrix are obtained and analyzed. Within the SPT2 approach a series of new approximations are proposed. The grand canonical Monte Carlo (GCMC) simulations are performed to verify an accuracy of the SPT2 and the developed approaches. The obtained analytical expressions include three types of porosity: the geometrical porosity ϕ_0, the probe particle porosity ϕ and the porosity ϕ^* defined by the maximum packing fraction of a fluid in a given matrix. The effect of nonsphericity parameters of matrix and fluid particles on the thermodynamic properties of a fluid is discussed.

1. Introduction

The thermodynamic properties of a fluid adsorbed in porous materials differ to that in a bulk. Mainly it is caused by the excluded volume effect and by a pore wall presence. The pore walls affect a fluid not only by an attractive interaction with fluid molecules, but also by their geometry. Even without any interaction of a fluid with a porous material (i.e. hard-core interaction), the pore walls change thermodynamics of a fluid essentially, since a pore wall surface area, pore curvatures, and distances between pore walls play an important role. Therefore, a geometrical aspect of porous medium confining a fluid is to be studied. And it is useful not only from a practical point of view, but it is also valuable as a fundamental study. During the years numerous investigations have been done in this area, including a number of theoretical approaches which have been proposed for a model of a fluid in pores [1,2]. One of the most popular models is a fluid in random porous media [3,4]. Within this model a system is presented as a set of spherical particles, a part of them can move and it relates to a fluid, but another part is frozen and depicts solid material, i.e. a matrix. Therefore, a void between matrix particles forms porous medium, in which fluid particles are confined. A main interest to this kind of system is provoked by a large class of inorganic and inorganic/organic hybrid materials forming a random network of mesopores, which are widely used in industry. However, only few of the developed theories are able to describe efficiently the thermodynamic properties of fluids confined in a whole variety of such materials, and practically none of them can give accurate pure analytical expressions even for the simplest model, such as an HS fluid in an HS matrix.

Recently, we proposed an extension of the scaled particle theory (SPT) [8–10], which enabled us to derive the analytical expressions of equation of state for a hard sphere fluid (HS fluid) confined in a hard sphere matrix (HS matrix) or in an overlapping hard sphere matrix (OHS matrix) [5,6]. This approach is based on a combination of the exact treatment of a point scaled particle in an HS fluid with the thermodynamic consideration of a finite size scaled particle. The exact result for a point scaled particle in an HS fluid in a random porous medium was obtained in [5]. A further improvement of the SPT has led us to the SPT2 approach [7]. The expressions obtained in the SPT2 include two types of porosities. One of them is defined by a pure geometry of porous medium (geometrical porosity ϕ_0), and the second one is defined by the chemical potential of a fluid in the limit of infinite dilution (probe particle porosity ϕ). On the basis of the SPT2 approach, the SPT2b approximation was proposed, which reproduced the computer simulation data with a high accuracy at small and intermediate fluid densities [7]. However, the expressions obtained in the SPT2 and in the SPT2b approximations have a divergence at densities corresponding to a fluid packing fraction equal to the probe particle porosity. Consequently, the prediction of thermodynamic quantities at high densities of a fluid becomes incorrect. An accuracy of the SPT2 and the SPT2b also can get worse if fluid and matrix particles are of comparable sizes [7]. In a study of a one-dimensional hard rod fluid in random porous media [11,12] the new approximations SPT2b1, SPT2b2 and SPT2b3 were proposed, and they are free of the mentioned defect. In the SPT2b2 and SPT2b3 approximations a third type of porosity ϕ^* is introduced, and it is defined by the maximum value of packing fraction of a fluid in a porous medium. It was shown that these new approximations essentially

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improve an accuracy of the SPT2 approach. The application of the SPT2 approach for a description of thermodynamic properties of an HS fluid confined in random porous media was reviewed recently in [13].

A remarkable feature of the SPT theory is a possibility to describe systems of hard convex body particles [14,15]. Therefore, in principle an application of the SPT2 approach is not restricted only to a fluid of spherical particles. Matrix particles can be also of nonspherical shape, thereby a wider range of random medium morphologies can be involved in a description. A purpose of the present study is to extend the SPT2 approach to the case of a hard convex-body fluid confined in a hard convex-body matrix. Similarly to our previous studies [5–7,13], we consider two models depicting a porous medium structure. The first model is a hard convex body fluid (HCB fluid) confined in a hard convex body matrix (HCB matrix). The second one is an HCB fluid in an overlapping hard convex body matrix (OHCB matrix). The obtained analytical expressions for these models allow us to calculate the chemical potential and the pressure of a confined fluid within these models. An effect of nonsphericity of fluid and matrix particles on thermodynamic properties of a fluid is studied. The new approximations SPT2b1, SPT2b2 and SPT2b3 are applied and analyzed. To test the developed theory the computer simulations are performed for the case of an HCB fluid in an OHCB matrix using the method of grand-canonical ensemble Monte Carlo (GCMC). Therefore, the corresponding comparison of the SPT results with the GCMC data is made in our study.

The paper is organized as follows. A brief review of a non-standard formulation of the SPT for an HCB fluid is presented in Section 2. In Section 3 this formulation is generalized on the case of an HCB fluid in a random porous medium. In Section 4 the SPT will be applied to describe an HCB fluid in an HCB or an OHCB matrix. Some computer simulation details will be presented in Section 5. In Section 6 we present numerical results obtained from the proposed theory using the different approximations and make a comparison of the different approximations with the simulation data. Also we discuss an effect of the nonsphericity parameters of fluid and matrix particles on thermodynamical properties of a fluid in a porous medium. In the last section some conclusions are drawn.

2. SPT theory for HCB fluid

HCB particles are characterized by three functionals—a volume V, a surface area S and the mean curvature R with a factor $(1\,/\,4\pi)$. For example, for a frequently considered case of a system of spherocylindrical rods with a length l and a radius r, these functionals are

$$V=\pi r^2 l+\frac{4}{3}\pi r^3,\quad S=2\pi rl+4\pi r^2,\quad R=\frac{1}{4}l+r. \tag{1}$$

The basic idea of the SPT approach is an insertion of an additional scaled particle of a variable size into a fluid. With this aim we use the scaling parameter λ_s in such a way that the volume V_s, the surface area S_s and the curvature R_s of a scaled particle are modified as

$$V_s=\lambda_s^3 V_1,\quad S_s=\lambda_s^2 S_1,\quad R_s=R_1\lambda_s, \tag{2}$$

where V_1, S_1 and R_1 are the volume, the surface area and the mean curvature of fluid particle, respectively.

In the original formulation of the SPT theory for HCB fluids [14–18] the contact value of the pair distribution function of fluid particles around a scaled particle is a key function of the theory. However, as it was indicated in [5] for an HS fluid such a formulation cannot be applied directly to fluids in random porous media, because there is no direct relation between the pressure and the contact distribution function which has been found for a fluid in a porous medium. Due to this in [5] a reformulation of the SPT theory was presented, which is slightly different from the original one. In this paper we consider a generalization of this approach for an HCB fluid.

The procedure of insertion of the scaled particle into a fluid is equivalent to a creation of cavity, which is free of any other fluid particles. The key point of considered reformulation of the SPT theory consists in a derivation of the excess chemical potential of a scaled particle μ_s^{ex}, which is equal to a work needed to create a corresponding cavity. The expression of excess chemical potential for a small scaled particle in an HCB fluid is as follows

$$\begin{aligned}\beta\mu_s^{ex}&=\beta\mu_s-\ln\left(\rho_1\Lambda_1^3\right)=-\ln\left(1-\eta_1\left(1+\frac{R_sS_1}{V_1}+\frac{S_sR_1}{V_1}+\frac{V_s}{V_1}\right)\right)\\&=1-\ln\left[1-\eta_1\left(1+3\lambda_s\alpha_1+3\lambda_s^2\alpha_1+\lambda_s^3\right)\right],\end{aligned} \tag{3}$$

where $\beta=1/kT$, k is the Boltzmann constant, T is the temperature, $\eta_1=\rho_1V_1$ is the fluid packing fraction, ρ_1 is the fluid density, Λ_1 is the fluid thermal wave length, $\alpha_1=\frac{R_1S_1}{3V_1}$ is the parameter of nonsphericity of fluid particles.

For a large scaled particle the excess chemical potential μ_s^{ex} is given by a thermodynamical expression for the work needed to create a macroscopic cavity inside a fluid and it can be presented as

$$\beta\mu_s^{ex}=w(\lambda_s)+\beta PV_s, \tag{4}$$

where P is the pressure of fluid and V_s is the volume of scaled particle.

According to the ansatz of SPT theory [5–14], $w(\lambda_s)$ can be presented in the form of expansion

$$w(\lambda_s)=w_0+w_1\lambda_s+\frac{1}{2}w_2\lambda_s^2. \tag{5}$$

The coefficients of this expansion can be found from the continuity of μ_s^{ex} and the corresponding derivatives $\partial\,\mu_s^{ex}/\partial\,\lambda_s$ and $\partial\,^2\mu_s^{ex}/\partial\,\lambda_s^2$ at $\lambda_s=0$. As a result one derives the following expressions

$$\beta w_0=-\ln(1-\eta_1), \tag{6}$$

$$\beta w_1=\frac{3\alpha_1\eta_1}{1-\eta_1}, \tag{7}$$

$$\beta w_2=\frac{6\alpha_1\eta_1}{1-\eta_1}-\frac{9\alpha_1^2\eta_1^2}{(1-\eta_1)^2}. \tag{8}$$

If one sets $\lambda_s=1$ Eq. (4) should give the relation between the pressure and the chemical potential of an HCB fluid. Using the Gibbs–Duhem equation

$$\left(\frac{\partial P}{\partial\rho_1}\right)_T=\rho_1\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_T, \tag{9}$$

we obtain the final expressions for the chemical potential and the pressure of a bulk fluid:

$$\beta\mu_1^{ex}=-\ln(1-\eta_1)+\frac{(1+6\alpha_1)\eta_1}{1-\eta_1}+\frac{\left(\frac{9}{2}\alpha_1+3\right)\alpha_1\eta_1^2}{(1-\eta_1)^2}+\frac{3\alpha_1^2\eta_1^3}{(1-\eta_1)^3}, \tag{10}$$

$$\frac{\beta P}{\rho_1}=\frac{1}{1-\eta_1}+\frac{3\alpha_1\eta_1}{(1-\eta_1)^2}+\frac{3\alpha_1^2\eta_1^2}{(1-\eta_1^3)}, \tag{11}$$

which coincide with the corresponding results obtained in the common SPT theory [15].