Equation of state of hard-sphere fluid in nanoporous media

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Abstract. The present work is devoted to the study of fluid equations of state in nanoporous media. The modeling is carried out in the framework of the molecular dynamics method using the potential of hard spheres. The dependences of the compressibility factor on packing fraction are studied for various characteristic pore sizes, porosities, and types of grains packing of a porous medium. It is shown that for all cases considered, deviations of the obtained equations of state from the Carnahan-Starling equation of state are insignificant. These deviations may be due to the presence of restricted zones in a porous medium inaccessible to fluid molecules that is also discussed in the work.

1. Introduction

In connection with the active development of micro- and nanoscale devices [1-2], processes occurring at the nanoscale attract increasing attention from the scientific community. One of the important directions is the study of the thermodynamics of liquids and gases located in micro- and nanoporous media [3-4]. A consistent investigatin of thermodynamic processes occurring in fluids located in porous media is impossible without finding the corresponding equations of state. This paper studies the dependence of the equation of state on the properties of a nanoporous medium. To find the equation of state, two algorithms are used: an algorithm based on the use of virial, and an algorithm based on the calculation of the momentum transmitted to the solid surfaces of the system. For simulations, the authors apply the method of molecular dynamics modeling, which is one of the powerful tools for studying various phenomena and processes in systems at nano- and micro-scales. The potential of solid spheres is used as the interaction potential. The choice of this potential is due to the transparent introduction of definitions of porosity, mean free path, etc. During the study, the porosity, the characteristic pore size, and the type of packing of the granules of the porous medium are changed.

2. System and methods

To simulate the dynamics of fluid molecules, a standard molecular dynamics algorithm was used in the approximation of the potential of hard spheres [5]. A consistent study of the processes occurring in a fluid in a porous medium is impossible without finding the corresponding equation of state. For this, first of all, it is necessary to determine the fluid pressure. In turn, two algorithms can be used to find it: an algorithm based on the finding of the virial, and that based on the calculation of the momentum transmitted to the solid surfaces of the system. In the first case, the pressure $p$ in the system can be calculated according to [6]:

$$p = \frac{1}{V} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{F_{ij}}{r_{ij}}$$
\[ p = \frac{N}{3V} \sum_{i=1}^{\infty} m_i v_i^2 + \frac{1}{3V} \sum_{i \neq j} r_{ij} \cdot F_{ij}(r_{ij}). \]

Here \( N \) is the number of particles, \( m \) is the particle mass, \( v \) is the particle velocity, \( V \) is the volume of the system in question, \( r_{ij} \) is the distance between the centers of particles \( i \) and \( j \) and \( F_{ij} \) is the interaction force of particles \( i \) and \( j \). In the model of hard spheres, the interaction potential is discontinuous, and, therefore, the interaction force has the form of \( \delta \)-function. However, for a medium in equilibrium, ensemble-average values can be replaced by time averages and the force virial \( r_{ij} \cdot F_{ij}(r_{ij}) \) can be calculated through momentum transfer in collisions, then

\[ p = \frac{N}{3V} \sum_{i=1}^{\infty} m_i v_i^2 + \frac{1}{3V} \sum_{i \neq j} r_{ij} \frac{\Delta p_{ij}}{\Delta t}, \]

here \( \Delta p_{ij} \) is the sum of changes in the momentum modulus of the \( i \)-th molecule over time \( \Delta t \) due to a collision with the \( j \)-th molecule.

An alternative approach to calculating pressure is to find the total momentum transferred by the molecules to the particles of the porous medium. This method of finding the pressure is less difficult; however, it allows determining the pressure distribution only along the impermeable boundaries of the calculation domain, but not in the whole volume, in contrast to the method based on finding the virial.

Both algorithms have a certain area of applicability. An algorithm based on the use of virial is obtained under the assumption of a uniform distribution of density and pressure in the system under study. In the presence of significant density inhomogeneities, questions about the introduction of thermodynamic quantities, the applicability of space averaging, and the adequacy of this algorithm become especially relevant. The algorithm based on the calculation of the momentum transmitted to the solid surfaces of the system does not require averaging over space and, therefore, is devoid of this drawback. However, a structured layer of molecules \([4]\) may form near the solid surfaces. The density of the layer of molecules adjacent to the surface is higher than the system average, and, consequently, the pressure at the surface will be higher. Thus, both described algorithms have certain disadvantages. Significant differences in the predictions of the algorithms are observed in systems where the surface layer is comparable with the size of the system, i.e. in very narrow pores. Most likely, in such cases, both algorithms are not applicable and need to be corrected. In connection with the indicated limitations of the algorithms, only those systems are considered in which the volume of the surface layer is several times smaller than the volume of the pores themselves. In these cases, the discrepancy between the predictions of the algorithms does not exceed several percent.

Numerical modeling of any physical system should be preceded by verification of the modeling algorithm used. When testing the implemented algorithm, the correspondence of the simulation data to the equation of state of the hard-sphere fluid in the free volume is verified. The equation of state of a hard-sphere fluid in a free volume is well described by the Carnahan-Starling model \([5]\):

\[ Z = \frac{pV}{Nk_B T} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \]

Here \( Z \) is the compressibility factor, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( \eta \) is the packing fraction. Packing fraction in turn:

\[ \eta = \frac{\pi}{6} \frac{N \sigma^3}{V}, \]

here \( \sigma \) is the diameter of the solid sphere. Further in the work, the studied equation of state will be presented in this form. Figure 1 presents a comparison of the dependence of the compressibility factor on the packing fraction calculated according to the Carnahan-Starling model with molecular dynamics calculations made by created program.
Figure 1. Compressibility factor versus packing fraction. The solid line corresponds to the Carnahan-Starling equation of state; the hollow markers are MD modeling data.

The simulation data is consistent with the Carnahan-Starling curve, which indicates good accuracy of the implemented algorithm.

Particles of a porous medium are also determined by the potential of solid spheres, but, unlike fluid molecules, remain motionless during the entire calculation. In total, three types of packing of particles of a porous medium are considered: cubic volume-centered packing, simple cubic packing and cubic face-centered packing, see Figure 2.

Figure 2. Illustration of the types of considered particle packings of a porous medium: (a) cubic body-centered packaging, (b) simple cubic packaging and (c) cubic face-centered packaging.

Further, the following notation will be used for the system under study. Porosity is denoted by $\phi = V_F / V_S$, where $V_F$ is the pore volume and $V_S$ is the total volume of the porous sample. The ratio of the particle diameters of the porous medium to the diameters of the fluid molecules is denoted as $\lambda$. In the present work, this ratio will be equal to several tens, therefore, assuming the size of the molecules of the model fluid to be comparable with the size of real molecules, nanoporous media are considered in the work.

3. Results and discussion

When modeling the equation of state in a porous medium, the dependence of the compressibility factor on the packing fraction for different types of packing of granules of the porous medium was established, see Figure 3.
Figure 3. Compressibility factor versus packing fraction in porous media. The solid line corresponds to the Carnahan-Starling equation, the triangles correspond to cubic body-centered packing, the circles correspond to simple cubic packing and the crosses correspond to cubic face-centered packaging. \( \lambda = 20 \) and \( \phi = 0.5 \) for all packagings.

The compressibility factors for different packings almost do not differ from each other and turn out to be very close to the curve corresponding to the Carnahan-Starling equation. Thus, the influence of the type of packing on the thermodynamics of the fluid has not been established in any case with pore sizes tens of times larger than the size of the fluid molecules. This begs the natural question: At what pore sizes is it possible to observe a significant deviation of the equation of state in a porous medium from the Carnahan-Starling equation? To answer this question, a study was made of the dependences of the compressibility factor on the packing fraction at various porosities and characteristic pore sizes, see Figure 4 and Figure 5.

Figure 4. Compressibility factor versus packing fraction in porous media. The solid line corresponds to the Carnahan-Starling equation, the circles correspond to \( \lambda = 40 \), the crosses correspond to \( \lambda = 20 \), the triangles correspond to \( \lambda = 15 \) and the squares correspond to \( \lambda = 10 \). Particles of a porous medium are located in nodes of simple cubic packing, \( \phi = 0.5 \).
A decrease in the ratio of the diameters of the granules of the porous medium to the fluid molecules leads to an increase in the compressibility factor compared to the free volume. However, in media with a relatively high porosity, this increase is only a few percent compared to the compressibility factor in free volume, see Figure 4.

![Figure 4. Compressibility factor versus packing fraction in porous media. The solid line corresponds to the Carnahan-Starling equation, the squares correspond to \( \varphi = 0.5 \), the triangles correspond to \( \varphi = 0.25 \) and the crosses correspond to \( \varphi = 0.05 \). Particles of a porous medium are located in nodes of simple cubic packing, \( \lambda = 20 \).](image)

Figure 5. Compressibility factor versus packing fraction in porous media. The solid line corresponds to the Carnahan-Starling equation, the squares correspond to \( \varphi = 0.5 \), the triangles correspond to \( \varphi = 0.25 \) and the crosses correspond to \( \varphi = 0.05 \). Particles of a porous medium are located in nodes of simple cubic packing, \( \lambda = 20 \).

A decrease in porosity also leads to an additional increase in the compressibility factor in a porous medium, see Figure 5. This increase may be due to the presence of restricted zones in a porous medium. Restricted zones are understood as zones into which fluid molecules cannot enter, for example, the center of a fluid molecule cannot approach the surface at a distance less than its radius. Additional restricted zones also arise in the contact areas of the granules of the porous medium and, therefore, their size depends on the geometry, porosity and characteristic pore sizes. When calculating the pressure and density, the presence of such zones must be taken into account, since the effective pore volume becomes smaller than the real one due to restricted zones. A direct estimate of the volume of the restricted zones is challenging, especially for disordered porous systems. At the same time, it is possible to estimate the volume of restricted zones by calculating the corrected compressibility factor and the corrected packing fraction. When calculating them, normalization will be performed not on the real pore size, but on the effective size. An estimate of the effective pore size can be obtained by assuming that the equation of state in a porous medium corresponds to the volume equation of state, see Figure 6.
Figure 6. Corrected compressibility factor versus corrected packing fraction in porous media. The solid line corresponds to the Carnahan-Starling equation, the squares correspond to \( \phi = 0.5 \), the triangles correspond to \( \phi = 0.25 \) and the crosses correspond to \( \phi = 0.05 \). Particles of a porous medium are located in nodes of simple cubic packing, \( \lambda = 20 \).

The exact correspondence of the equations of state in a porous medium to the equation of state in volume was obtained when restricting zones were estimated at 11.5\%, 8\%, and 6\% of the pore volume, for \( \phi = 0.05 \), \( \phi = 0.25 \), and \( \phi = 0.5 \), respectively.

Conclusions
Summarizing the results, we can draw a definite conclusion: the difference between the equations of state in porous media and in free volume is due to the presence of restricted zones in the near-surface zone. The volume of the restricted zones increases with decreasing porosity, as well as a decrease in the ratio of the particle diameter of the porous medium to the diameter of the fluid molecules. The larger the volume these zones occupy, the more the compressibility factor increases in comparison with the corresponding value in the free volume. However, significant differences in the equations of state of fluid in a porous medium from the Carnahan-Starling equation of state will be observed only when the volumes of restricted zones are commensurate with the pore volume, i.e. with characteristic pore sizes of several tens of molecules.

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