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Q1 Flow and structure of fluids in functionalized nanopores

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HIGHLIGHTS

- Enhanced flow has been observed in gases and water inside nanotubes.
- We use molecular dynamics simulations to study the flow of fluids inside solvophilic and solvophobic nanopores.
- Two fluids are modeled: a standard Lennard Jones fluid and a two length scale fluid.
- Distinct flow and structural properties were observed for each fluid.
- Nanopore–fluid and fluid–fluid interaction play a significant roll in the fluid structure and flow.

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ABSTRACT

We investigate through non-equilibrium molecular dynamics simulations the structure and flow of fluids in functionalized nanopores. The nanopores are modeled as cylindrical structures with solvophilic and solvophobic sites. Two fluids are modeled. The first is a standard Lennard Jones fluid. The second one is modeled with an isotropic two-length scale potential, which exhibits in bulk water-like anomalies. Our results indicate distinct dependence of the overall mass flux for each species of fluid with the number of solvophilic sites for different nanotubes' radii. Also, the density and fluid structure are dependent on the nanotube radius and the solvophilic properties of the nanotube. This indicates that the presence of a second length scale in the fluid–fluid interaction will lead to distinct behavior. Also, our results show that chemically functionalized nanotubes with different radii will have distinct nanofluidic features. Our results are explained on the basis of the characteristic scale fluid properties and the effects of nanoconfinement.

1. Introduction

Most liquids contract upon cooling at constant pressure and diffuse slower upon compression. This is not the case of a wide range of materials that expand as the temperature is decreased and move faster as the pressure grows. Liquid water is the most known of this anomalous materials [1] but it is not the only one. The maximum diffusion coefficient at constant temperature was observed not only in water [2] but also in silicon [3] and silica [4]. The maximum density is present not only in water [5] but also in silicon [4], silica [6], Te [7], Bi [8], Si [9], $Ge_{15}Te_{85}$ [10], liquid metals [11], graphite [12] and BeF_2 [13]. The origin of the unusual behavior observed in anomalous materials is the presence of two characteristics length Q3 scale. While non anomalous liquids can be described on the framework of the van der Waals one length scale potential, anomalous materials exhibit two characteristic scales. Then it became natural to associate the thermodynamic and dynamic

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anomalous behavior of these materials with a core-softened (CS) potentials with two length scale (TLS) in the bulk since the seminal works by Jagla [14–16]. Since then, several TLS potential able to reproduce the anomalous behavior of water in bulk [17,14,18–24] or under confinement [25–34] were proposed.

Recently a new puzzle was added to the list of anomalous behavior of water. Experiments and simulations show that the mobility of water through nanotubes' membranes exceeds the values calculated from continuum hydrodynamics models by more than three orders of magnitude [35–41]. This behavior is also observed in non anomalous materials such as ionic liquids [42], hydrogen, methane, nitrogen, air, of oxygen, of argon [43,44]. In this case, however, the fast flow exceeds predictions by only one order of magnitude [35,36]. Naturally, two questions arise: what is the mechanism behind the fast flow in nanoconfinement and why in the case of water it is much faster.

In the particular case of water, the hydrophobicity adds up to this already complex problem [45,46]. While for the hydrophobic wall–water interaction in a homogeneous tube the flow is faster than in the pure hydrophilic wall–water interaction [47,48], for an heterogeneous wall–water system the flow is faster as the system becomes fully hydrophilic [45,49].

The existence of confining structures in which hydrophobic and hydrophilic sites are present is not just a theoretical assumption. Recent methods allowed the synthesis of nanotubes similar to CNTs, boron-nitride nanotubes (BNNTs) [50] and carbon doped BNNTs [51]. Chemically functionalized nanotubes can have hydrophobic and hydrophilic sites, similar to biological channels, which have distinct solvophobic properties depending on the amino acids formed. Also, gas adsorption and storage in doped and chemically treated nanotubes have been recently investigated [52,53]. Therefore studying these systems is not only a theoretical challenge but it has realistic applications.

In this paper we explore the differences and similarities between the anomalous and non anomalous fluids flow by computer simulations. We compute the mobility of a water-like system under solvophilic, solvophobic and mixed confinement. This behavior is then compared with the flow of a non anomalous, standard LJ fluid also confined within an attractive, a repulsive and a mixed walls. Our results aim to shed some light in the controversial results both in the water-like and non anomalous confinement in the different types of wall–fluid interactions.

The paper is organized as follows: in Section 2 we introduce the model and describe the methods and simulation details; the results are given and discussed in Section 3; and in Section 4 we present our conclusions.

2. The model and the simulation details

In this paper all physical quantities are computed in the standard Lennard-Jones (LJ) units [54], for instance

$$r^* \equiv \frac{r}{\sigma}, \qquad \rho^* \equiv \rho\sigma^3, \quad \text{and} \quad t^* \equiv t\left(\frac{\epsilon}{m\sigma^2}\right)^{1/2}, \tag{1}$$

for distance, density of particles and time, respectively, where σ is the distance parameter, ϵ the energy parameter and m the mass parameter. Since all physical quantities are defined in reduced LJ units, the * is omitted, in order to simplify the discussion.

Two types of fluids are analyzed: a water-like fluid and a non anomalous fluid. Both are modeled by coarse-graining potentials. The water-like system is represented by a two length scales interaction potential and the non anomalous fluid is depicted by a one length scale interaction potential. In both cases the system is modeled by spherical particles with effective diameter σ and mass m. The water-like particles interact through the three dimensional TLS core-softened potential

$$U_{ij}^{\mathrm{TLS}}(r_{ij}) = \epsilon'\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \sum_{i=1}^{3}\frac{B_i}{B_i^2 + (r_{ij} - C_i)^2}, \tag{2}$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between fluid particles i and j. The first term on the right is the standard 12-6 LJ potential [54], while the second term corresponds to Lorentzian distributions centered at C_i with amplitude $1/B_i$. In this paper, the potential parameters are: $k = 3$, $\epsilon' = 0.6$, $B_1 = 0.3$, $B_2 = -1.5$, $B_3 = 2.0$, $C_1 = 1.0$, $C_2 = 1.8$ and $C_3 = 3.0$, resulting in the TLS potential showed in the Fig. 1. The first length scale is at $\approx$ 1.0, the particle diameter. The second length scale is located at $\approx$ 1.5. This type of effective potential exhibits the density, diffusion and structural anomalous behavior present in water and it has been used as a coarse-graining model for system with thermodynamic, dynamic and structural anomalous behavior. In fact, Pinheiro and co-authors have shown that this potential have water like anomalies in bulk [56]. The majority of the molecular water models are conceived focusing on accurately described hydrogen bonds and charge distributions since many of the water uncommon properties are believed to come from its highly directional interactions. Examples are solvation and properties, which depend on polarization. On the other hand, the literature have many examples [17,14,18–21] in which systems with the absence of anisotropic interactions may still present in some of the water features. Some of its anomalous behavior may come from purely volumetric effects, which particularly is our focus in this work. Particularly, enhanced flow has been observed for TLS fluid confined inside nanotubes [39–41].

The non anomalous particles interact through the standard Lennard-Jones potential also shown in Fig. 1 and given by,

$$U_{\mathrm{LJ}}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right], \tag{3}$$

where ϵ is the depth of the attractive well. The LJ potential is shown as the green dotted line in Fig. 1. This potential has been used to model simple one length scale system in which the density, diffusion and structural anomalous behavior observed in

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