



Nano-confined ionic liquid [emim][PF₆] between graphite sheets: A molecular dynamics study



Sirous Salemi, Hamed Akbarzadeh ^{*}, Somayeh Abdollahzadeh

Department of Chemistry, Hakim Sabzevari University, Sabzevar, Iran

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ABSTRACT

We have presented molecular dynamics (MD) simulations on the IL [emim][PF₆] confined between the graphite sheets with the different distances of 1, 2, 3, 4, and 5 nm. The vertical and longitudinal pressures and compressibility factors have been calculated and two separate equations of state for the vertical and longitudinal directions for the confined system have been derived by considering the anisotropic pressure tensor.

We have also investigated the effects of pore size and pore loading on the structural and dynamical properties of the confined ions. Our structural results showed a significant layering at the IL-graphite interface which indicates strong interaction between the IL and the graphite sheets. Our radial distribution function (RDF) results showed that the cation–anion RDF is greater than the other RDFs, indicating a strong interaction between cations and anions which is responsible for the H-bond formation. The average number of the hydrogen bonds also increased as the pore size decreased. The average number of the H-bonds also increases as the pore loading increases. Our dynamical results showed that the self diffusion coefficient of both cations and anions increases with increase in pore size. Also, the self diffusion of the confined ions decreases with increasing the pore loading.

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1. Introduction

The study of ionic liquids (ILs) in a confined state presents an exciting challenge and is of importance in practical applications [1]. Such a hybrid material (an inorganic porous material filled with a IL) represents a novel class of materials with promising applications [2]. Owing to the high specific surface area of the porous material and the peculiar properties of IL (such as low volatility, low flammability, high ionic conductivity, and high thermal stability) [3–8] these materials have important applications such as energy-storage devices (electrochemical batteries, supercapacitors) [9–11], lubricants [12], and drug delivery systems [2,4,13,14]. The understanding of the phase behavior of confined ILs has also attracted great attention due to their relevance in catalytic processes, lubricants, nanocomposites, fuels, and solar cells [15–22]. Many interesting phenomena have been also reported regarding the effects of nanoconfinement on changes in the melting point, crystal structure, and chemical reactivity of confined species [1,2,16,18,21,23–28]. For example, Kanakubo et al. [16] reported an intriguing melting-point-depression of 1,3-dialkylimidazolium-based ionic liquids confined in controlled pore glasses. Chen et al. [18] also found a transition of [bmim][PF₆] from liquid to a high melting-point crystal when it was confined in multiwalled CNTs. Sha et al. [21] reported a drastic phase transition in [dmim][Cl] ionic liquid confined between two graphene walls. Singh et al. [27] simulated the structural and

dynamical properties of the ionic liquid (IL) [bmim][PF₆] confined inside multiwalled carbon nanotubes (MWCNTs). They found that the diameter of the MWCNT and the pore loading have a profound influence on the structural and dynamical properties of the confined IL. Feng et al. [28] carried out molecular dynamics (MD) simulations to investigate the solid–liquid transition of ionic liquid 1-ethyl-3-methyl imidazolium bromide ([emim][Br]) by different approaches. They achieved a coexisting solid–liquid system in the microcanonical ensemble method. Recently, Li et al. [26] confined [emim][Br] ionic liquid in porous SiO₂ nanoparticles. They showed that the confinement in the nanopores leads to a compression of molecular size and an increase in the melting point. Also, Ori et al. [2] performed MD simulations in the isobaric–isothermal ensemble to investigate the structure and dynamics of an ionic liquid confined at ambient temperature and pressure in hydroxylated amorphous silica nanopores. They found that the local structure of the confined ionic liquid is mostly driven by electrostatic interactions. More recently, Akbarzadeh et al. [1] performed MD simulations to study the thermodynamics, structure, and dynamical behavior of 1-ethyl-3-methylimidazolium hexafluorophosphate [emim][PF₆] during the melting process inside carbon nanotubes (CNTs) with different radii.

However, little is understood about the morphology and phase behavior of the ILs in nanometer-scale confinement [22]. The actual structure of confined ILs is rarely understood at the atomic level and further experimental and theoretical investigations are expected to provide deep insight into the factors dominating the phase behavior of confined liquids [26].

^{*} Corresponding author.

E-mail address: akbarzadehhamed@yahoo.com (H. Akbarzadeh).

Table 1

The parameters of the fit to the extended EoS (Eqs. 5–7).

I	Y	Y_1	Y_2	Y_3
L	f	1.2434	0.2604	0.7703
	g	-3.9123	-0.4439	0.7568
	h	-0.0217	-0.0059	0.8047
H	f	0.8341	0.2939	0.5208
	g	-2.3755	-0.8759	0.3862
	h	0.0689	-0.0749	0.1889

The first goal of this paper is to determine two separate equations of state for the vertical and longitudinal directions for the IL confined between the graphite walls by considering the anisotropic pressure tensor. Such a fundamental investigation has not been performed before.

The second goal of this research is to understand how structural and dynamical properties of an IL [emim][PF₆] confined between the graphite walls are affected by the distance between the walls (the pore size effect). Such fundamental understanding is crucial to optimize the performance of several alternative energy devices, such as electrochemical double layer capacitors (EDLCs) and

dye-sensitized solar cells (DSSCs), as the molecular-level properties of confined ILs, affect the macroscopic performance of these devices [27].

2. Simulation details

The MD simulations have been performed on the IL [emim][PF₆] confined between the two graphite sheets with the different distances of 1, 2, 3, 4, and 5 nm. For each distance, several simulations with a different number of the IL molecules have been performed. All simulations have been carried out in the NVT ensemble with the Nosé–Hoover algorithm with the DL_POLY program version 4.03 [29] at 300 K. The equations of motion were integrated using the Verlet leapfrog algorithm and a time step of 1 fs. The relaxation time used for thermostat is 0.1 ps. Electrostatic interactions are calculated with the Ewald summation technique. The cutoff for long-range potentials is chosen as 15 Å. Periodic boundary conditions were applied in all three directions. To avoid artificial influence from periodic images, IL-graphite sheets were kept in the center of a simple orthorhombic box with vacuum on both sides separating it from the next periodic image in Z direction. Simulations have been run long enough to overcome the initial configurations. The simulations were carried out for 5 ns of equilibration

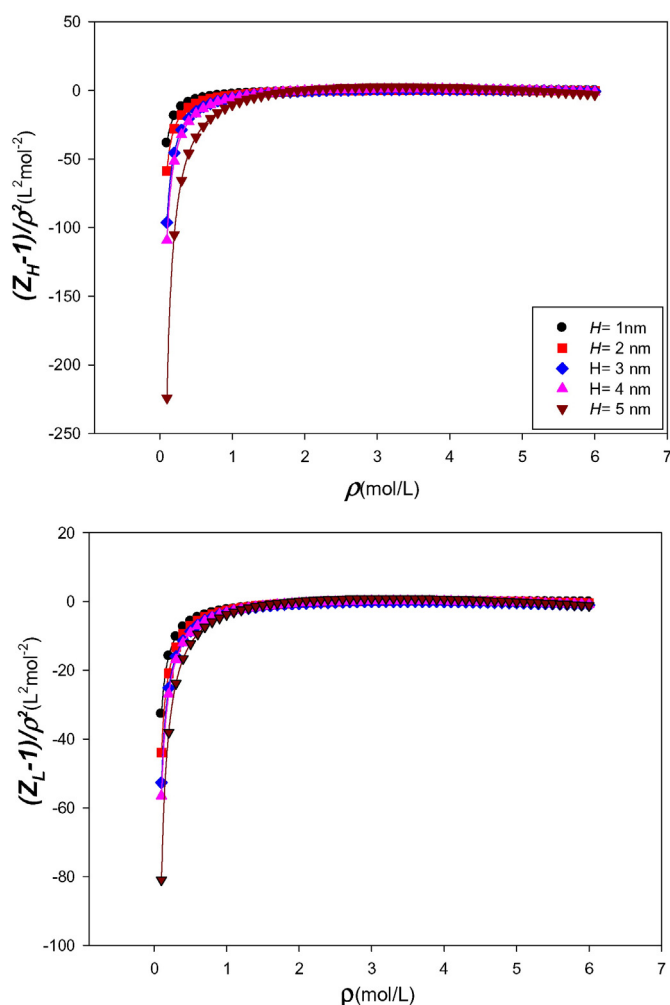


Fig. 1. The graphs of $(Z_H - 1) / \rho^2$ and $(Z_L - 1) / \rho^2$ versus density for the confined IL at different pore sizes which have been obtained from fitting to the simulation results.

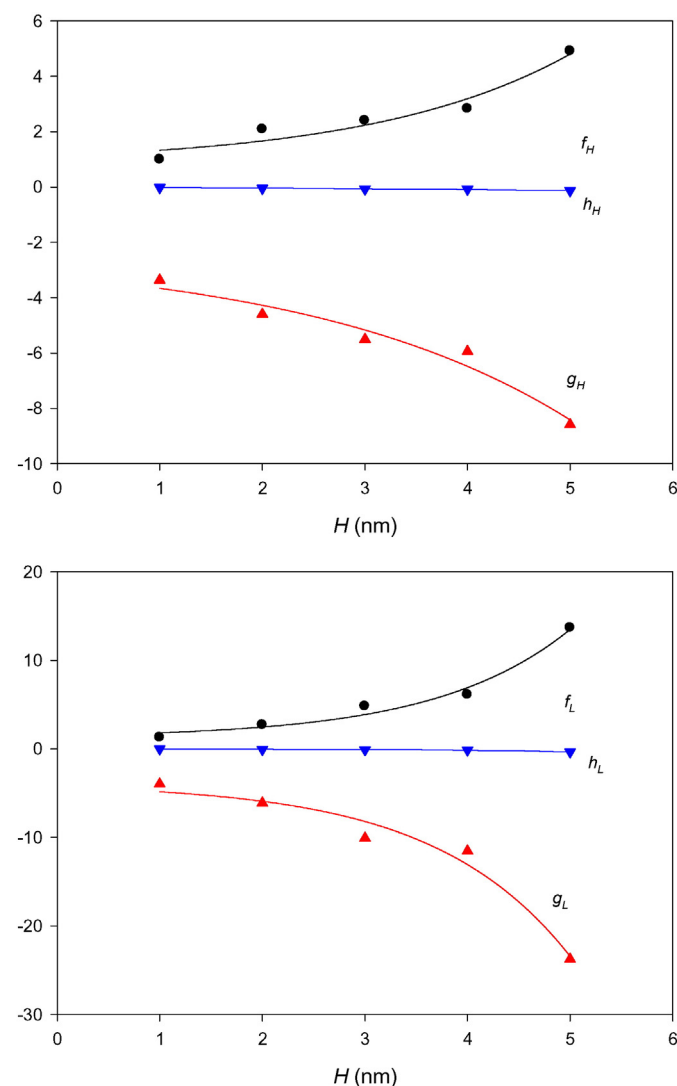


Fig. 2. The pore size dependence of the EoS parameters.

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