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Nanotube diameter dependency of anisotropic pressure of an ionic liquid confined in a carbon nanotube: A molecular dynamics study for [emim][PF_6] case

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ABSTRACT

We have presented molecular dynamics (MD) simulations of 1-ethyl-3-methylimidazolium hexafluorophosphate [emim][PF_6] inside carbon nanotubes (CNTs) with different diameters. By considering the anisotropic pressure tensor for the ionic liquid inside the CNTs, the parameters of an equation of state (EoS) for the radial and axial directions have been derived. The nanotube diameter dependency of the EoS parameters has been also investigated.

1. Introduction

Room-temperature ionic liquids (RTILs) have attracted extensive attention in recent years for several applications such as green solvents for chemical synthesis, catalysis, separations, electrolytes for electrochemistry, and photovoltaic [1–5]. Ionic liquids (ILs) have generated tremendous excitement as a new class of solvent systems having the potential to serve as an environmentally friendly alternative to the traditionally used volatile organic compounds [6]. Understanding of the dynamics of ionic liquids is also critical for smarter use in industry as reaction media [6–10]. Recently, Daschakraborty and Biswas [8] predicted the Stokes shift dynamics of a dipolar solute in binary mixtures of an ionic liquid (IL) with water and acetonitrile using a semi-molecular theory in good agreement with experimental results. They also developed studying the dielectric relaxation (DR) dynamics in ionic liquids (ILs) [10]. Pal and Biswas [9] also explored an interconnection between timescales of dynamic heterogeneity (DH) in an IL ([Bmim][PF_6]) and slow solvation of a dipolar solute using molecular dynamics (MD) simulations employing realistic interaction potentials for both the IL and the solute.

The study of ionic liquids in a confined state also presents an exciting challenge and is of importance in practical applications. The understanding of the phase behavior of confined RTILs has attracted great attention due to their relevance in catalytic processes, lubricants, nanocomposites, fuels, and solar cells [11–19]. For example, Kanakubo et al. [12] reported an intriguing melting-point-depression of 1,3-dialkylimidazolium-based ionic liquids confined in controlled pore glasses. Ne'ouze et al. [15] found that when BMINO3 was entrapped by silver nanoparticles, the thermal stability of the ionic liquid in the composite became much higher than that of the neat BMINO3. Also, Sha et al. [17] reported a drastic phase transition in [Dmim][Cl] ionic liquid confined between two graphene walls. Chen et al. [14] also found a transition of [bmim][PF_6] from liquid to a high melting-point crystal when it was confined in multiwalled CNTs. Recently, Singh et al. [5] performed molecular dynamics (MD) simulation to study the structural and dynamical properties of the ionic liquid (IL) [$BMIM^+$][PF_6^-] 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. More recently, Salemi et al. [19] presented MD simulations on the IL [emim][PF_6] confined between the graphite sheets with the different distances of 1, 2, 3, 4, and 5 nm. They calculated the vertical and longitudinal pressures and two separate equations of state for the vertical and longitudinal directions for the confined system have also derived. Their results showed a significant layering at the IL-graphite interface.

Despite of these investigations on ionic liquids, little is understood about the morphology and phase behavior of RTILs in nanometer-scale confinement [18]. Therefore, we have presented MD simulations of 1-ethyl-3-methylimidazolium hexafluorophosphate [emim][PF_6] inside carbon nanotubes (CNT) with different radii. The recently proposed equation of state (EoS) of Sadeghi and Parasafar [20] for water inside CNTs has been investigated and extended in terms of density and nanotubes size for the system inside the CNTs at constant temperature.

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By considering the anisotropic pressure tensor, two separate equations of state for the radial and axial directions for the system inside the CNTs have been derived.

2. Theory

For the IL [emim][PF$_6$] confined inside a nanotube, the radial and axial forces are different. Thus, the IL inside the nanotube is an anisotropic system for which the pressure tensor has to be used instead of a scalar pressure. Parsafar et al. [20,21] also showed that for a wide variety of fluids and solids, the average configurational energy per particle may be given by:

$$\frac{U}{\rho^2} = K_6 + \frac{K_3}{\rho} + K_{12}\rho^2 \tag{1}$$

where $\rho = 1/V$ is the molar density. Following the notation used by Parsafar et al. [20,21], the exact thermodynamic EoS for the radial component of pressure tensor can be written as:

$$\frac{(Z_R - 1)}{\rho^2} = f_R + \frac{g_R}{\rho} + h_R\rho^2 \tag{2}$$

where the parameters f_R, g_R, and h_R are functions of the nanotube radius (R) at constant temperature as:

$$f_R = f_{R1} + f_{R2}\ R \tag{3}$$

$$g_R = g_{R1} + g_{R2}\ R \tag{4}$$

$$h_R = h_{R1} + h_{R2}\ R\ . \tag{5}$$

The EoS for the axial component of pressure tensor can be also written as:

$$\frac{(Z_L - 1)}{\rho^2} = f_L + \frac{g_L}{\rho} + h_L\rho^2 \tag{6}$$

where the parameters f_L, g_L, and h_L are functions of the nanotube radius as:

$$f_L = f_{L1} + \frac{f_{L2}}{R} + \frac{f_{L3}}{R^2} \tag{7}$$

$$g_L = g_{L1} + \frac{g_{L2}}{R} + \frac{g_{L3}}{R^2} \tag{8}$$

$$h_L = h_{L1} + \frac{h_{L2}}{R} + \frac{h_{L3}}{R^2}\ . \tag{9}$$

Therefore, our extended EoS has presented for the IL molecules inside the CNTs by Eqs. (3) and (7) and the nanotube size dependent parameters presented by Eqs. (3)–(5) and (7)–(9). Each parameter of the EoS has two contributions: one is related to the thermal pressure and other to the internal pressure, and they have opposite signs [21]. Therefore, it is generally impossible to predict their signs. However, g and f are related to the attraction and repulsion interaction of the effective pair potential, respectively. The term $h\rho^2$ is a small repulsion contribution, whose contribution is insignificant, except at extremely high pressures.

3. Simulation details

The force field of [emim][PF$_6$] have used in this work is from the systematic all-atom force filed developed by Lopes et al. [22]. In these simulations, the CNTs have kept in fixed position. For the intermolecular interactions between ionic liquid and CNT, we have used Lennard–Jones potential utilizing the geometric mean for ε and the arithmetic mean for σ. The MD simulations have performed on the [emim][PF$_6$] inside five different CNTs with radii of 0.75, 1, 1.25, 1.5, and 1.75 nm, respectively. For each CNT, several simulations with a different number of the ionic liquid molecules have performed. All simulations have carried out in the *NVT* ensemble with the constant temperature of 300 K. In these simulations, we have used Nose-Hoover thermostat algorithm [23,24] with DLPOLY 4.03 package [25]. The relaxation time for thermostat is 0.1 fs. The periodic boundary conditions are applied only in the axial direction of the CNT. To avoid artificial influence from periodic images, IL-CNTs have kept in the center of a simple orthorhombic box with vacuum on both sides separating it from the next periodic image in Z direction. The Z distance has kept large enough to avoid any interaction between ions and its periodic image. (One side of the box is equal to the length of the nanotube (5 nm)). The equation motions have integrated using the Verlet leapfrog algorithm [26] with the integration time step of 0.5 fs. The columbic long range interactions have calculated using Ewalds' method with a precision of 10^{-6}. All interatomic interactions between the atoms in the simulation box have calculated within the cutoff distance 15 Å. To relax strained contacts in the initial configurations, first the systems have energy-minimized. All the system have then melted to 650 K to improve mobility of molecules and

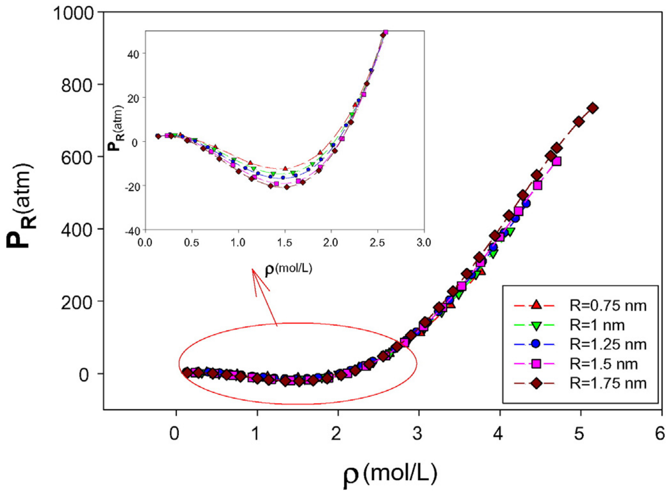

Fig. 1. Radial pressure versus the IL density inside the CNTs with the different radii at T = 300 K (the dash lines are shown to guide the eye).

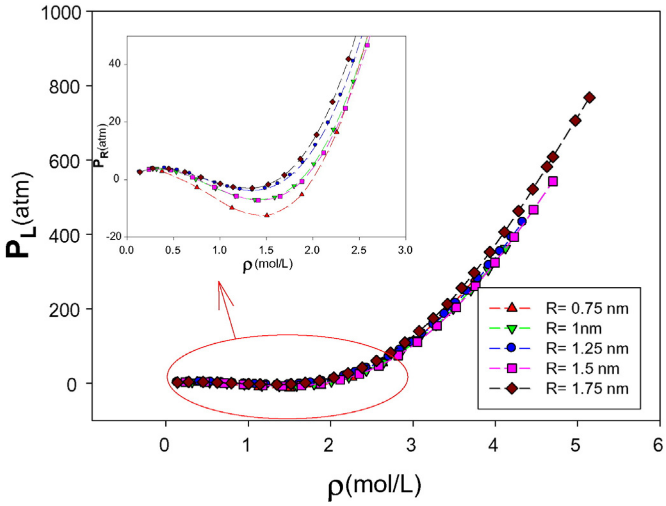

Fig. 2. Axial pressure versus the IL density inside the CNTs with the different radii at T = 300 K (the dash lines are shown to guide the eye).