Computational Materials Science 114 (2016) 160–166

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Molecular simulation of adsorption and separation of pure noble gases and noble gas mixtures on single wall carbon nanotubes

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ARTICLE INFO

Article history:
Received 2 October 2015
Received in revised form 5 December 2015
Accepted 17 December 2015
Available online 4 January 2016

Keywords:
Adsorption
Carbon nanotubes

ABSTRACT

Grand Canonical Monte Carlo simulations were performed to systematically study the adsorption and separation of noble gases on single wall carbon nanotube (SWCNT) bundles. Pure noble gases, as well as binary and ternary mixtures, were simulated in carbon nanotube systems under various conditions. Adsorption data was collected at 100 K and 300 K over a wide range of pressures. Carbon nanotube bundles present distinct adsorption capacities towards different noble gases. In particular, larger and heavier noble gases are easier to be adsorbed at low pressure, while lighter atoms with smaller sizes can be better stored at high pressure. For noble gas mixtures with equal molar loadings, selective adsorption was observed and the selectivity inverted at different pressure ranges according to the choice of mixtures. Furthermore, the influence of loading proportion of the components on the adsorption behavior was investigated by varying the loading partial pressure in binary mixtures from 1% to 99%. The results suggest gas–CNT interactions dominate the adsorption selectivity at low loading conditions, whereas the entropic effect plays a more important role at high loadings.

1. Introduction

Single wall carbon nanotubes (SWCNTs) have attracted intense research interest [1,2]. Excellent mechanical, electrical, thermal and structural properties enabled by their pristine tubular structure have been discovered with these materials [3,4]. Particularly, the large specific surface area and high pore volume of carbon nanotubes qualify them for potential applications as adsorbents in many applications including gas storage [5], environmental contamination removal [6], and separation membranes [7]. Multiwall nanotubes have also been proposed as gas separation tools [8,9].

The application of gas separation and adsorption for mixtures of noble gases is highly important and has been studied to some extent in the literature. However, studies over the complete range of noble gases and large pressure ranges are still missing. The adsorption properties of single wall carbon nanotubes have been widely studied for a variety of adsorbate molecules, such as nitrogen [10], hydrogen [11], carbon dioxide [12] and methane [13]. Noble gases with their monatomic simple spherical structures, fit many adsorption models and have been widely utilized for porous materials characterizations. Experimental adsorption data has been collected for helium [14], argon [15], krypton [13], and xenon [16] in different single wall carbon nanotube systems.

Molecular modelling including molecular dynamics (MD) and Monte Carlo (MC) has also been applied for noble gas adsorption on CNTs. Atomistic simulations can help understand the detailed adsorption process including dynamic and thermal properties. For the study of noble gas adsorption on single wall carbon nanotubes, Simonyan et al. performed grand canonical Monte Carlo (GCMC) simulations of Xenon adsorption on single wall carbon nanotubes at Xe critical temperature [17]. Jalili and Majidi simulated the adsorption processes of Xe and Kr on SWCNTs by MD and found adsorption primarily on the inside surfaces of CNTs [18]. Besides pure noble gas adsorption, Foroutan and Nasrabadi used MD to model binary and ternary noble gas mixtures (Ar–Kr–Xe) for adsorption on SWCNT arrays and found selective adsorption [19,20]. Nojini et al. predicted the adsorption and separation of helium/argon mixtures by single SWCNTs with GCMC [21].

Mixed gas adsorption on SWCNTs has also been simulated for nitrogen/oxygen [22], methane/ethane [23], and carbon dioxide/methane [24] mixtures. Selective adsorption was observed in all cases. Most studies focus on the adsorption of equal molar gas loadings. The influence of component loading proportions on adsorption is still not well understood.

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http://dx.doi.org/10.1016/j.commatsci.2015.12.031
0927-0256/

In addition to the studies on gas adsorption, the influence of SWCNTs packing structures has been investigated. Jiang and Stanley compared nitrogen adsorption on infinite periodic CNT bundles and finite bundles with external surface [25]. The effect of the ends of nanotubes on the bundle was simulated by Calbi and Riccardo [26]. LaBrosse and Johnson compared the adsorption on carbon nanotube bundles with defect and nondefect interstitial channels [27,28].

However, very few experimental or computational studies have focused on the selective adsorption and subsequent potential for separation of noble gas mixtures, which is meaningful for the physical separation and storage of radioactive nuclear reaction waste gases, in which the chemically inert noble gases are major components [29]. Although the previous work has shown much of the basic interaction modes between nanotubes and gases previous work has not yet systematically studied the adsorption and separation of the whole series of noble gases and particularly many-component mixtures in SWCNTs. E.g. in nuclear fuel reprocessing mixtures of the whole range of noble gases are present at the same time and need to be controlled [30]. CNTs have the potential to help manage these gas products but a better understanding of nanotube gas interaction in many-component mixtures is needed to employ CNTs as separation tools in these systems. This will be addressed here.

In the present work, grand canonical Monte Carlo was used to investigate the adsorption of the whole series of noble gases on periodic uniform single-walled carbon nanotube bundles under various circumstances. Adsorption isotherms of pure noble gases, as well as binary and ternary noble gas mixtures, were determined by simulations at both low (100 K) and room temperatures (300 K). In addition, different loading proportions in binary mixtures were simulated to illustrate their influence on the adsorption behavior of the single wall carbon nanotube system.

2. Simulation model and methods

Carbon nanotubes have been observed experimentally to exist in bundles [31]. The simulation model in this study includes 9 hexagonally packed open-end single-walled carbon nanotubes (SWCNTs) corresponding to the van der Waals interactions preferred alignment [25], as shown in Fig. 1. All SWCNTs are of the (10, 10) armchair type with a diameter of 13.56 Å, as these are the experimentally most abundant ones [16,32]. The influence of SWCNT chirality on gas adsorption was not considered here as the influence of SWCNT chirality on hydrogen adsorption and diffusion has been determined earlier by both, ab initio and molecular mechanics simulations [33,34]. These studies showed that the adsorption of hydrogen is not affected by the chirality of the nanotubes. For noble gases, with monatomic spherical shape, we expect the influence of the CNT chirality on the adsorption to be negligible. The length of the nanotubes (and correspondingly the system size in the axial direction as we use infinitely long nanotubes) was 49.2 Å (20 unit cells). Periodic boundary conditions were applied in all three directions to simulate the intrinsic nanotube bundles without considering packing defects and the influence of the ends and external surfaces.

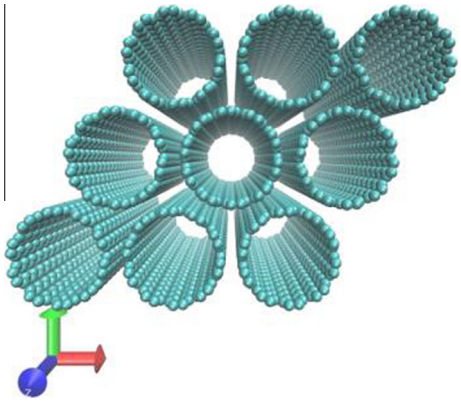

Fig. 1. Carbon nanotube bundle simulation model.

All nanotubes were treated as completely rigid without intramolecular vibrations which is considered to have only slight influence on the adsorption [22]. The C–C bond length was 1.42 Å and the inter-nanotube distance was 3.2 Å, as observed in experiments corresponding to the van der Waals gap between nanotubes [31,35]. Noble gas atoms were treated as spherical monatomic molecules with only van der Waals potentials modeled by a Lennard–Jones 12–6 potential

$$\phi_{ij} = 4\varepsilon_{ij}\left[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6}\right]$$

where r denotes the pair distance between atom i and j; ε_{ij} and σ_{ij} represent the depth of the potential energy well and the intermolecular collision diameter, respectively. Lennard–Jones (L–J) parameters for carbon and gases were taken from literature (cf. Table. 1) [36,37] where k_B is the Boltzmann constant. Lorentz–Berthelot mixing rules were used for unequal atoms:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2.$$

The L–J potential cutoff distance was 20.0 Å.

Potential energy distributions of each noble gas atom across the radial direction of an isolated (10, 10) SWCNT are plotted in Fig. 2. The vertical lines in the figure indicate the CNT walls with $x = 0$ denoting the center of the CNT. For all noble gases, the depths of potential energy wells inside the CNTs are deeper than the ones outside the tubes, which are attributed to confinement effect induced by the carbon nanotube curvature structures. Moreover, the gas atoms in larger sizes with stronger carbon-gas potentials show deeper potential energy wells than the smaller ones both inside and outside the nanotube.

Grand Canonical Monte Carlo (GCMC) [38,39] with fixed chemical potential (μ), volume (V), and temperature (T) was chosen for this study. In GCMC, the SWCNT bundle is considered in contact with an infinite gas reservoir which is not explicitly modeled. Gas particles are exchanged between the reservoir and the nanotube bundle. The pressure is defined through the chemical potential in the reservoir, which is constant and connected to the chemical potential by an equation of state. Equilibration in the system is reached when the chemical potential and the temperature of the gases inside and outside the SWCNTs are equal. Temperature is controlled by the acceptance criterion of GCMC as that ensures the μVT ensemble. All simulations were performed with the open source MCCCS Towhee code [40] to understand the noble gas adsorption behavior in single-walled carbon nanotube bundles. The chemical potential applied for each adsorption simulation represents the μ value of the corresponding bulk gas phase. Separated isothermal–isobaric simulations with only gas molecules were

Table 1
Lennard–Jones parameters of carbon and noble gases.

Element	ε/k_B (K)	σ (Å)
C	28.2	3.4
He	10.2	2.56
Ne	35.6	2.75
Ar	120	3.40
Kr	171	3.60
Xe	221	4.10