Monte Carlo simulations of *n*-butane and *n*-octane adsorbed onto graphite and a molecular model of activated carbon

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Abstract

In this work we report results of Monte Carlo simulations of *n*-butane and *n*-octane adsorbed onto graphite and a molecular model of activated carbon, with the aim to provide simplified models that will allow the study of these kind of systems with lower computational and time costs. A combination of Coarse Grain models (CG) and Monte Carlo simulations (MC) were used. Adsorbates were reduced from four atoms to one pseudoatom and the adsorbent carbons from two atoms to one pseudoatom. We compare the results between atomistic models results and CG models for *n*-alkanes (single and mixture) adsorption on carbon surfaces, and we took into account the isosteric heat too. The simulation results showed an excellent agreement with the atomistic model for *n*-alkanes adsorption on graphite, using the CG model. However, for the activated carbons studied there is no longer such a good agreement between atomistic models and coarse-grained models.

Keywords Coarse grain models · Graphite · Activated carbon · Alkanes

1 Introduction

Adsorption phenomena were widely studied for their potential impact on environmental remediation and separation of compounds. Alkane adsorption is particularly important to storage gases. In the last years there had been a great interest in the study of alkane adsorption on carbonaceous materials, mainly in activated carbons (Fletcher and Thomas 1999; Foley et al. 2001; Fletcher et al. 2006; Severson and Snurr 2007; Liu et al. 2017).

Activated carbons are disordered materials and cannot be characterized completely from experiments, therefore realistic models of activated carbons are necessary to predict the properties of adsorbed phases (Albesa et al. 2012a).

It is important to take into account that, to study the adsorption of any substance on carbonaceous materials, studying the adsorption of these substances on graphite

should be the first step since it is a surface that can be characterized and serves as a zero-order approximation to study adsorption on more complex materials (Albesa et al. 2008).

In recent decades, computer simulations have become an indispensable tool for studying molecules in confined spaces. The increase in computational speed and better molecular modeling algorithms allow simulations of larger systems with greater precision. The need to achieve larger simulated time scales and system sizes requires further simplification of atomistic models, even those based on empirical potentials. Recently several approaches called “coarse grain” (CG) have been developed with that goal in mind. The philosophy of these CG approaches is generally the same: to achieve a simpler description of the effective interactions in a given system without losing the ability of the resulting models to predict the properties of interest (Chiu et al. 2010; Shelley et al. 2001; Maerzke and Siepmann 2001; Moggetti et al. 2009; Gobbo et al. 2013; Shang et al. 2017; Jiang et al. 2017).

In the present work we will study the adsorption of *n*-butane and *n*-octane on graphite and activated carbons using two models for the alkane molecules and two models for the carbon atoms of the adsorbents.

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2 Methodology

In the present work, aggregates of polyaromatic molecules containing 24, 54, 96 and 150 carbon atoms are used to simulate the surface (Albesa 2010).

Monte Carlo simulations were performed using the grand canonical ensemble (μ , V , T), since the number of molecules is not a fixed variable, information can be obtained about the average number of particles in the system as a function of external conditions. In this ensemble, in addition to the fact that the particles present in the system can be moved and evaluated, according to the acceptance rule of Eq. (1), particles are also created and destroyed in the system with acceptance probabilities are given by Eqs. (2) and (3) respectively;

$$P_{mov} = \min \left\{ 1, \exp \left(-\frac{\Delta E}{kT} \right) \right\} \quad (1)$$

$$P_{cre} = \min \left\{ 1, \frac{1}{(N+1)} \exp \left(B - \frac{\Delta E}{kT} \right) \right\} \quad (2)$$

$$P_{des} = \min \left\{ 1, N \exp \left(\frac{\Delta E}{kT} - B \right) \right\} \quad (3)$$

$$B = \ln \left(\frac{fV}{k_B T} \right) \quad (4)$$

where P_{cre} is the probability of accepting the creation step, P_{des} is the probability of accepting the destruction of a particle, and V is the volume of the system, N the number of particles. The considerations and parameters taken into account in the simulations were:

- (i) 10σ cubic simulation box
- (ii) Cut-off radius of 4σ ;
- (iii) Number of thermalization steps creation/destruction/displacement 2.5×10^7 , number of steps for the statistical average 5.0×10^4 ;
- (iv) No long-range corrections were made due to the cut-off radio

Another advantage of the GCMC method is that information about isosteric heat can also be obtained. (Albesa et al. 2012b).

The potential energy of interaction between two particles is calculated using the well known 12-6 Lennard-Jones potential (Eq 5).

$$U_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (5)$$

where r is the separation distance between the two particles.

Table 1 - Lennard-Jones parameters

	ϵ/kT	$\sigma(A)$
C4H10 M8	350	5.2
C4H10 M1	421	4.3
CH2	46	3.95
CH3	98	3.75
C (graphite)	28	3.4
C (CG)	56	4.3

Fig. 1 Butane adsorption isotherms with the different models. AAg all atom graphite, CGg coarse grained graphite

The LJ parameters are listed in Table 1.

Martin and Siepmann parameters were used to simulate *n*-butane and *n*-octane with the atomistic model (Martin and Siepmann 1998).

For coarse-grain models, a 4-to-1 reduction was made for butane and octane, that is, four C atoms are represented by a single interaction site. For the coarse grain modeling of the graphite, the 2-to-1 reduction was used (Gobbo et al. 2013).

The interaction energy between a fluid particle and a carbon atom is also calculated by the LJ potential. The total energy is calculated by adding all the interactions of pairs between the particles of the fluid, and between the individual carbon atoms and the particles of the fluid.

3 Results

3.1 Adsorption on graphite

Figure 1 shows the adsorption isotherms for butane with the different models considered in the present work. There is an excellent agreement among all of them, showing that the new parametrization of CG-butane is good and that it not only agrees with the CG graphite model but can also be used in the completely atomistic graphite model. Likewise,

Fig. 2 Snapshots of **a** adsorption of 4SLJ-butane, **b** adsorption of CG-butane

Fig. 3 Isosteric heat of adsorption of butane onto graphite

the C bead used in the coarse grain model also shows good agreement with the experimental results (Ross and Good 1956) when used in the 4-site butane model.

The difference observed is mainly due to the shape of the adsorbed molecules, the CG model, being completely spherical allows a more compact packing, which results in a better accommodation of the particles on the surface of graphite. As seen in Fig. 2, most of *n*-butane molecules adopt the configuration parallel to the surface and have the flat zig-zag arrangement. We see from the adsorption isotherms at 303 K that there are no 2D transitions in the formation of the first layer.

Figure 3 shows the results of the isosteric heats of adsorption obtained in the simulations, these results show a good agreement with those obtained in the literature (Chirnside and Pope 1964).

The isotherms of Fig. 4 correspond to the adsorption of *n*-octane on graphite at 400 K, and in Fig. 5 the values obtained for the isosteric heats are shown. The agreement between the 8-site model and the coarse grain model of two sites is better

Fig. 4 Octane adsorption isotherms with the different models. AAg all atom graphite, CGg coarse grained graphite

Fig. 5 Isosteric heat of adsorption of octane onto graphite

Fig. 6 Snapshots of **a** adsorption of 4SLJ-octane, **b** adsorption of CG-octane

Fig. 7 Mixture adsorption isotherms with the different models. *AAg* all atom graphite, *CGg* coarse grained graphite

even than in the case of *n*-butane. This is explained by the fact that, in this case, the coarse-grained model of two sites already has a form factor incorporated, since by having two interaction sites separated from one another, the orientation of the molecules begins to play an important role. In Fig. 6 it is observed that the preferred orientation is parallel to the surface. The isosteric heats agree with those obtained experimentally (Eisen et al. 1971; Elkington and Curthoys 1969).

3.2 Mixture gas adsorption

Adsorption simulations of equimolar mixtures of *n*-octane and *n*-butane at 400 K were performed on graphite. In Fig. 7 the results of the isotherm are shown.

The selectivity of the species is written as

$$S_{ij} = \frac{\left(\frac{n_i}{n_j}\right)}{\left(\frac{x_i}{x_j}\right)} \quad (6)$$

Fig. 8 Selectivity octane-butane

S_{ij} is the selectivity, n_i/n_j is the number of adsorbed molecules and x_i/x_j is the gas phase composition.

The selectivity is shown in Fig. 8 and the coincidence is observed throughout the pressure range, which shows that both models work very well to study the adsorption of mixtures on graphite.

For both models, the degree of separation is greater at low pressures. This is because at these pressures the *n*-butane practically does not adsorb on the surface of the graphite.

3.3 Adsorption on molecular models of activated carbon

When studying the adsorption of *n*-butane on models of carbonaceous substrates more complicated as activated carbons, it is found that there is no longer such a good agreement between atomistic models and coarse-grain models (Fig. 9).

This is due to two factors that can be analyzed separately. First, the morphology of the activated carbons causes a distribution of pore sizes, from micropores to macropores, to occur. The pseudo-atoms of C of the coarse-grain model are

Fig. 9 Adsorption isotherms for activated carbons

30% larger than the atoms of C of the atomistic model, this generates that, by overlapping, the available volume of the micropores of the coarse-grain model is smaller than in the

atomistic model. Consequently, the available place for the adsorption of the molecules is smaller, and the adsorption is lower in the coarse grain model for the C-graphitic.

Fig. 10 Snapshots of **a** adsorption of 4SLJ-butane on C24 AA, **b** adsorption of CG-Butane on C24 CG, **c** Adsorption of 4SLJ-butane on C150 AA, **d** adsorption of CG-butane on C150 CG

The inverse effect is observed when considering the two models for the molecules that are adsorbed: the coarse grain model, as mentioned before, has a spherical symmetry, which implies that the molecules can be adsorbed in smaller interstices with greater ease than molecules of the atomistic model (Fig. 10).

Being inverse effects, the coarse-grain model for butane molecules, along with the coarse grain model for graphite, works better than when the models are considered separately.

4 Conclusions

Our Monte Carlo computer simulations, conducted using a new set of Lennard-Jones parameters, which we termed “mixed” parameters, are able to reproduce both the features of the isotherms (before and after gate-opening) as well as the values of the isosteric heat better than other sets of parameters that had been used in previous simulation studies of sorption in coarse grain simulations. We verified the transferability of this potential by performing calculations for butane and octane with excellent results.

The simulation results for the *n*-alkanes adsorption on graphite, using the CG model, showed an excellent agreement with the atomistic model. However, for the activated carbons studied there is no longer such a good agreement between atomistic models and coarse-grain models, probably due to the porous structure of materials and their smaller porous size.

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