MOLECULAR DYNAMICS SIMULATIONS OF INTERACTION OF VOLATILE ORGANIC COMPOUNDS WITH GRAPHENE SURFACE

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Abstract

Graphene is unarguably very promising material for countless applications including also gas sensing. For this particular application, it is very beneficial to understand the nature and strength of interaction of graphene with the adsorbed molecules. Molecular dynamics (MD) simulations matured to a very useful technique providing insights into complex molecular systems on the atomistic scale. However, the prediction potential of classical MD is given by quality of used parameters, including parameters for Lennard-Jones (LJ) term describing dispersion and repulsion part of intermolecular interaction potential. So far, LJ parameters used for graphene have not been thoroughly tested. Using MD we quantified the adsorption enthalpies of several organic volatile molecules (dichloromethane, nitromethane, ethanol, acetone, acetonitrile, ethyl acetate, hexane, cyclohexane, dioxane, benzene, and toluene) to a few layered graphene surface. The calculated adsorption enthalpies were compared with those acquired experimentally using an inverse gas chromatography technique. For each molecule, seven set of simulations were performed with altered LJ parameters and the accuracy of derived adsorption enthalpies was assessed. The average error of $\Delta\langle H^{FF}\rangle$ in respect to ΔH^{exp} suggests that OPLS-AA parameters delivered the best agreement with experiments. Needless to say that all tested LJ parameters were suitable for semi-quantitative estimates of the interaction energies of the molecules with the graphene. This implies that MD simulation can provide correct order of adsorption enthalpies of adsorbates and OPLS-AA in addition provides reliable quantitative estimates.

Keywords: Graphene, nanomaterials, molecular dynamics, force field, adsorption enthalpies

1.   INTRODUCTION

Graphene is a two-dimensional material having many extraordinary properties like enormous surface area, high mechanical strength, high transmittance of light, great thermal conductivity and especially outstanding electronics properties [1-5]. These properties predestine graphene for many promising applications in very diverse areas. Graphene is an exceptionally low-noise material electronically, which makes it a potentially very promising candidate for chemical sensing [6]. There are many molecular dynamics (MD) simulations in the field of graphene, other carbon nanoallotropes and their derivatives [7-9]. Although reliability of classical MD simulations is conditioned by quality of used force field, including Lennard-Jones parameters, these LJ parameters used for graphene have not been thoroughly tested, yet. So far, authors either adopted Lennard-Jones parameters from biomolecular force fields considering validity of a transferability principle [8] or they parameterized their own LJ parameters for their specific case [10]. Because the graphene is predominantly formed by carbon atoms, the majority of interaction with approaching molecules is mediated by them. Therefore, proper Lennard-Jones parameters of carbon atoms are needed for getting reliable results. Here, we tried to compare different LJ parameters, which were either specifically developed for the carbon nano-allotropes or adopted from common force fields. In order to conclude which Lennard-Jones parameters are better for utilizing in the MD simulations of the graphene, adsorption enthalpies of small organic volatile molecules on the graphene surface were calculated via MD simulations $\Delta\langle H^{FF}\rangle$ and the results were compared with experimentally determined adsorption enthalpies ΔH^{exp} from inverse gas chromatography measurements [11,12]. Our critical assessment of Lennard-Jones parameters against experimental data can provide useful information for future MD studies of adsorption properties of graphene and its derivatives.

2. MAIN TEXT

2.1. Methods

The adsorption enthalpies were calculated using MD simulations as follows (equation (1):

$$\Delta\langle H^{FF}\rangle = \Delta\langle E^{FF}\rangle - RT \tag{1}$$

where $\Delta\langle H^{FF}\rangle$, $\Delta\langle E^{FF}\rangle$, $-RT$ correspond to adsorption enthalpy from MD, average interaction energy and enthalpy correction, respectively.

A value of $\Delta\langle H^{FF}\rangle$ was calculated for the adsorption of single molecule from a representative set of small organic molecules on a few-layered graphene surface, while varying the non-bonded LJ parameters σ and ε of the aromatic carbons of the graphene. The molecules were chosen in order to cover diverse set, ranging from nonpolar to polar, from aliphatic across cyclic to aromatic, containing different heteroatoms, namely dichloromethane, nitromethane, ethanol, acetone, acetonitrile, ethyl acetate, hexane, cyclohexane, dioxane, benzene, and toluene.

Table 1 LJ parameters of graphene carbons for different force fields, which are commonly used in the field of MD simulations of graphene

Force field	σ (Å)	ε (kcal·mol^{-1})
Girifalco (gra-gra) [10]	3.41214	0.0551
Cheng&Steele [13]	3.39967	0.0557
Girifalco C$_{60}$-C$_{60}$ [14-16]	3.46900	0.0661
OPLS-AA [17]	3.55000	0.0700
Parm99 [18]	3.39967	0.0860

Periodic model of graphene was used in all MD simulations. As the experiments were carried out using a few-layered graphene, the graphene surface was modeled as six-layered; each layer consisted of 3936 atoms, which were kept rigid on a planar hexagonal lattice with a bond distance set to 0.14 nm. Periodic boundary conditions were applied in all three dimensions of the simulation box with the size of approximately 10 nm × 10 nm × 13 nm. The Newtonian equations of motion were integrated using leap-frog algorithm using 2 fs time step, hydrogen atoms were constrained with LINCS algorithm [19]. All simulations were carried out using GROMACS simulation package [20] in vacuum in NVT ensemble with a temperature of 323 K held with Berendsen thermostat [21]. The electrostatic interaction was treated with cut-off method with a radius of 1.0 nm. Intermolecular vdW interactions were calculated with a cut-off radius of 1.5 nm. Bonded and non-bonded parameters of the organic molecules were described using OPLS-AA force field [22]. The graphene was also described using OPLS-AA force field, but the Lennard-Jones parameters σ, ε of the graphene carbons were varied (see **Table 1**). As the graphene was modelled being periodic, each carbon atom was approximated as an uncharged LJ sphere. At first, each molecular dynamics simulation was equilibrated for 0.2 ns and then a productive 1 ns long simulation was performed. The interaction energy $\Delta\langle E^{FF}\rangle$ of a graphene-molecule system was calculated as an average over 5000 values. Some simulations were extended to 30 ns with the purpose of checking and ensuring that all the simulations successfully converged. In each simulation one molecule was placed in the center of the few-layered graphene surface approximately ~0.35 nm above its surface. For each particular graphene-molecule system of particular LJ parameters 5 independent simulations were performed, which differed in random generations of starting velocities.

2.2. Results and Discussion

The adsorption enthalpies $\Delta\langle H^{FF}\rangle$, as described by equation (1), of the interaction of the graphene-one molecule systems for all studied LJ parameters, together with experimentally determined ΔH^{exp}, are displayed

in **Table 2**. Confidence intervals were obtained based on the statistical analysis equations for small samples containing 5 values (see equation (2)).

$$L = \bar{X} \mp K_n R \qquad\qquad (2)$$

where L, $\bar{X}$, R and K_n correspond to confidence interval, arithmetic mean, a tabulated value and statistics range, respectively.
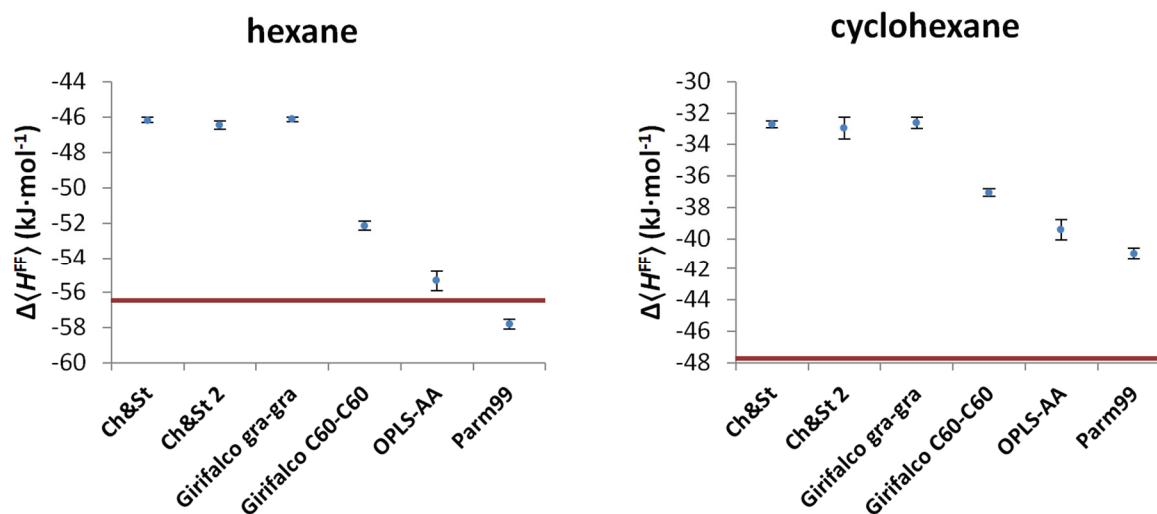
Table 2 Adsorption enthalpies $\Delta\langle H^{FF}\rangle$ calculated with different LJ parameters for graphene carbons and also ΔH^{exp}, both with their confidence intervals (at α = 0.05) for the adsorption of one molecule on the few-layered graphene surface. All values are in kJ·mol^{-1}.

	Ch&St	Ch&St 2	Girifalco gra-gra	Girifalco C$_{60}$-C$_{60}$	OPLS-AA	Parm99	Exp
Dich	-29.5±0.1	-29.6±0.2	-29.5±0.1	-32.8±0.1	-34.8±0.0	-36.6±0.2	-24.7±2.1
Nitr	-28.2±0.2	-28.7±0.6	-28.1±0.2	-31.5±0.2	-33.3±0.1	-35.1±0.0	-26.4±0.4
Etha	-23.0±0.2	-23.2±0.2	-22.9±0.4	-25.5±0.2	-27.5±0.1	-28.5±0.2	-30.5±2.9
Acet	-30.5±0.1	-30.9±0.2	-30.6±0.1	-34.0±0.1	-36.0±0.1	-38.0±0.1	-34.3±1.3
Acni	-22.2±0.5	-22.3±0.6	-21.8±0.6	-24.3±0.5	-25.3±0.1	-27.1±0.7	-31.8±1.3
Etat	-44.5±0.1	-44.8±0.3	-44.5±0.2	-49.8±0.1	-52.9±0.2	-55.7±0.2	-48.1±0.8
Hexa	-46.2±0.2	-46.5±0.3	-46.1±0.1	-52.1±0.3	-55.4±0.7	-57.8±0.3	-56.5±0.8
Cyc	-32.7±0.3	-33.0±0.8	-32.6±0.4	-37.1±0.3	-39.4±0.8	-40.9±0.4	-47.7±1.3
Diox	-35.6±0.4	-35.8±0.5	-35.5±0.3	-40.2±0.4	-43.2±0.3	-45.5±0.5	-45.2±0.4
Benz	-47.1±0.3	-47.6±0.2	-46.9±0.4	-52.0±0.3	-54.6±0.2	-58.8±0.1	-49.8±1.3
Tolu	-49.0±0.5	-49.8±0.3	-49.0±0.2	-54.6±0.4	-57.8±0.3	-61.7±0.3	-57.7±1.7
AE	7.0	6.8	7.1	4.8	4.5	5.5	
SDE	709.9	671.7	723.7	348.5	323.9	459.6	

Ch&St … Cheng&Steele parameters; Ch&St 2 … Cheng&Steele parameters where combining rules were changed (arithmetic mean for σ_{ij}); Girifalco gra-gra … parameters suggested by Girifalco for interaction between two graphene sheets; Girifalco C$_{60}$-C$_{60}$ … parameters suggested by Girifalco for interaction between two fullerene molecules; Parm99 … arithmetic mean for σ_{ij}; AE … Average error; SDE … Squared difference from experiment

The results from **Table 2** demonstrate that comparing to experiments $\Delta\langle H^{FF}\rangle$ for all studied LJ parameters were underestimated in case of some molecules, e.g. for ethanol, acetonitrile, cyclohexane. On the other hand, $\Delta\langle H^{FF}\rangle$ for all studied LJ parameters were overestimated, e.g. for dichloromethane, nitromethane. For the rest of the molecules, there was a particular LJ parameter which gave $\Delta\langle H^{FF}\rangle$ very close to the experimental value. In general, the difference between the calculated and experimental values may be partly explained by the neglect of an electrostatic interaction between an uncharged graphene surface and an approaching molecule or by the absence of a polarization in a pair additive force field. So, the absolute differences of $\Delta\langle H^{FF}\rangle$ and ΔH^{exp} can be accounted to the fact that in reality, there might be other contributions to the total interaction energy of the graphene-molecule interface [11]. The average error (AE) of $\Delta\langle H^{FF}\rangle$ in respect to ΔH^{exp}, averaged through all molecules, suggests that the OPLS-AA parameters, followed by Girifalco C$_{60}$-C$_{60}$, provided the best agreement with experiments. The values of squared difference from experiments (SDE) also confirmed the best agreement of $\Delta\langle H^{FF}\rangle$ with ΔH^{exp} when calculated using OPLS-AA parameters for graphene carbons, followed by Girifalco C$_{60}$-C$_{60}$.

The adsorption enthalpies calculated using molecular dynamics simulations are also graphically displayed in **Figure 1** for acetonitrile and ethyl acetate. For all molecules the same trend of $\Delta\langle H^{FF}\rangle$ was observed and these values correlated with epsilon LJ parameter.

Figure 1 Adsorption enthalpies $\Delta\langle H^{FF}\rangle$ from MD simulations of adsorption of single molecule on the few-layered graphene surface calculated utilizing different studied LJ parameters of graphene carbons. Red line represents experimental value, error bars represent standard deviation determined by five independent simulations.

Many approximations were introduced in our MD simulations; therefore the absolution differences of calculated and experimental enthalpies might not be the most important observable quantity. More important is that if particular LJ parameter is able to differentiate on strongly and weakly bound molecules to the graphene surface, if it is able to order the molecules according to their affinity to the graphene surface. The data showed that all LJ parameters ordered the molecules in a same manner, more importantly with a good agreement with the experimental data. This observance was also statistically tested with Spearman's rank correlation coefficient [23]. On our chosen significance level α = 0.01 the calculated correlation coefficient was higher than a critical value (0.709) for all studied LJ parameters, which means that a strong correlation between the order of ΔH^{exp} and $\Delta\langle H^{FF}\rangle$ was noticed. Therefore, it could be concluded that regardless of used LJ parameters of graphene carbons, MD simulations in our developed protocol may be suitable for semi-quantitative estimates of the interaction energies of the organic volatile molecules with graphene.

Systematically, a biggest deviation of our results from experiments can be seen especially for dichloromethane and acetonitrile. This could be possibly explained such that electronic effects or a cluster formation may contribute to the total interaction energy, which was already published in literature [11,24]. SAPT analysis [11] proposes that that polarization and electrostatics contribute to the total interaction energy more in case of acetone, acetonitrile and dichloromethane than in case of other molecules form our set. This SAPT analysis also completes underestimation of our calculated adsorption enthalpies in comparison with the experiments and advises that if polarization and electrostatic contributions were considered in our MD simulations, other studied LJ parameters would very likely give better agreement with experiments than OPLS-AA parameters.

In the last place, our results were discussed regarding Hansen solubility parameters [25], which are based on mutual miscibility/affinity. Three Hansen solubility parameters δ_d, δ_p, δ_h, relative polarity, calculated and experimental adsorption enthalpies, distance in Hansen space R_a, and molar volume V_m are listed in **Table 3**. Although a correlation of $\Delta\langle H^{FF}\rangle$ with Hansen dispersive solubility parameters was anticipated, unfortunately, the collected data demonstrated no such correlation. Also the rule "like dissolves like" was not confirmed because the distance in Hansen space did not correlate with our calculated enthalpies. On the other hand, some connection between calculated enthalpies and molar volume of the molecules could be observed, where bigger molecules adsorbed on the few-layered graphene surface more.

Table 3 Hansen solubility parameters of the molecules [25] and graphene [26] and other observable quantities

Molecule	rel. polar.	ΔH^{exp} (kJ·mol^{-1})	$\Delta\langle H^{FF}\rangle$ (kJ·mol^{-1})	δ_d (Mpa$^{0.5}$)	δ_p (Mpa$^{0.5}$)	δ_h (Mpa$^{0.5}$)	R_a	V_m (cm^3·mol^{-1})
Dich	0.309	-24.7	-34.8	18.2	6.3	6.1	6.8	63.9
Nitr	0.481	-26.4	-33.3	15.8	18.8	5.1	20.2	54.3
Etha	0.654	-30.5	-27.5	15.8	8.8	19.4	23.8	58.5
Acet	0.355	-34.3	-36.0	15.5	10.4	7.0	5.6	74.0
Acni	0.460	-31.8	-25.3	15.3	18.0	6.1	18.5	52.6
Etat	0.228	-48.1	-52.9	15.8	5.3	7.2	9.2	98.5
Hexa	0.009	-56.5	-55.4	14.9	0.0	0.0	24.9	131.6
Cyc	0.006	-47.7	-39.4	16.8	0.0	0.2	24.0	108.7
Diox	0.164	-45.2	-43.2	19.0	1.8	7.4	15.1	85.7
Benz	0.111	-49.8	-54.6	18.4	0.0	2.0	21.8	89.4
Tolu	0.099	-57.7	-57.8	18.0	1.4	2.0	19.5	106.8
Graphene [26]				18.0	9.3	7.7		

3. CONCLUSION

The prediction potential of classical MD on the graphene and the suitability of tested LJ parameters for the simulations of the graphene were verified. The adsorption enthalpies for eleven organic molecules calculated with different LJ parameters using MD simulations were assessed and all considered LJ parameters provided adsorption enthalpies in a qualitatively good agreement with experimental data. OPLS-AA parameters provided the adsorption enthalpies in the best agreement with experimental data with an average error less than 4.5 kJ·mol^{-1}, which is close to an experimental error of inverse gas chromatography. Needless to say that all tested LJ parameters were suitable for semi-quantitative estimates of the interaction energies of the molecules with the graphene. This implies that MD simulation is able to correctly order the adsorbates in respect to their adsorption enthalpies and to differentiate on strongly and weakly bound molecules. Therefore, our protocol is robust enough with respect to the level of approximation we introduced and may serve to other studies of sensing capacity of the graphene. In conclusion, both LJ parameters adopted from biomolecular force field and LJ parameters derived for their specific issue served well for the purpose of studying the adsorption of molecules on the graphene surface.

4. ACKNOWLEDGEMENTS

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