

Thermodynamic characterization of the adsorption of amino acids onto pristine graphene and graphene oxide

Mateo Barria-Urenda, José Antonio Gárate

Abstract

1 Introduction

First synthesized in 2004¹¹, graphene has since experienced an explosive growth in interest¹⁴. For pristine graphene, it's interactions with other particles are mainly due to Van der Waals forces and $\pi - \pi$ stacking.²² As pristine graphene is chemically inert⁶ a classical description of it is expected to suffice in simulations. Multiple molecular dynamics studies on the interactions between proteins and carbon based nanoparticles (CBNs) –such as graphene– have been published^{1,4,5,7,8,10,13,19,21,22}

2 Methods

2.1 Umbrella Sampling

2.2 Well Tempered Multiple Walk Metadynamics

2.3 Molecular Dynamics Simulation

2.4 Quantum Mechanics / Molecular Mechanics

3 Results

3.1 Adsorption Free Energy

3.2 Adsorption Entropy

3.3 Adsorption Energy

3.4 Diffusion

4 Conclusions

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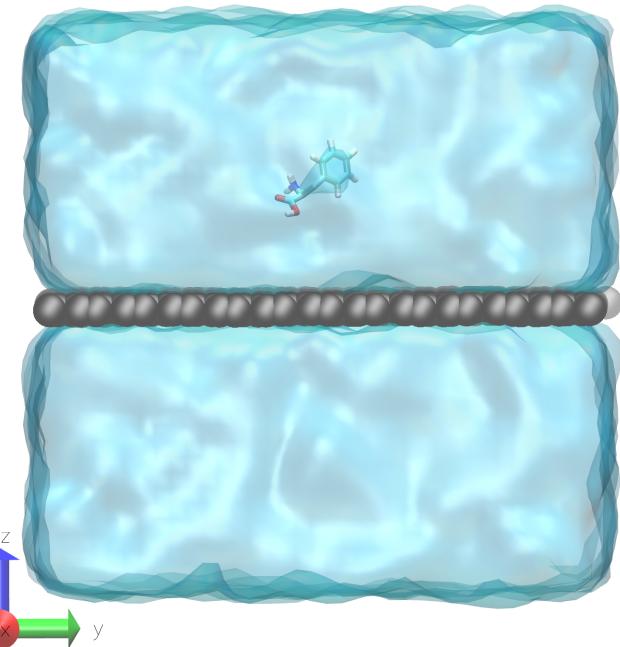


Figure 1: Example of simulated pristine graphene systems. An amino acid (in this case Phenylalanine) above a graphene layer (in gray) inside a periodic water box.

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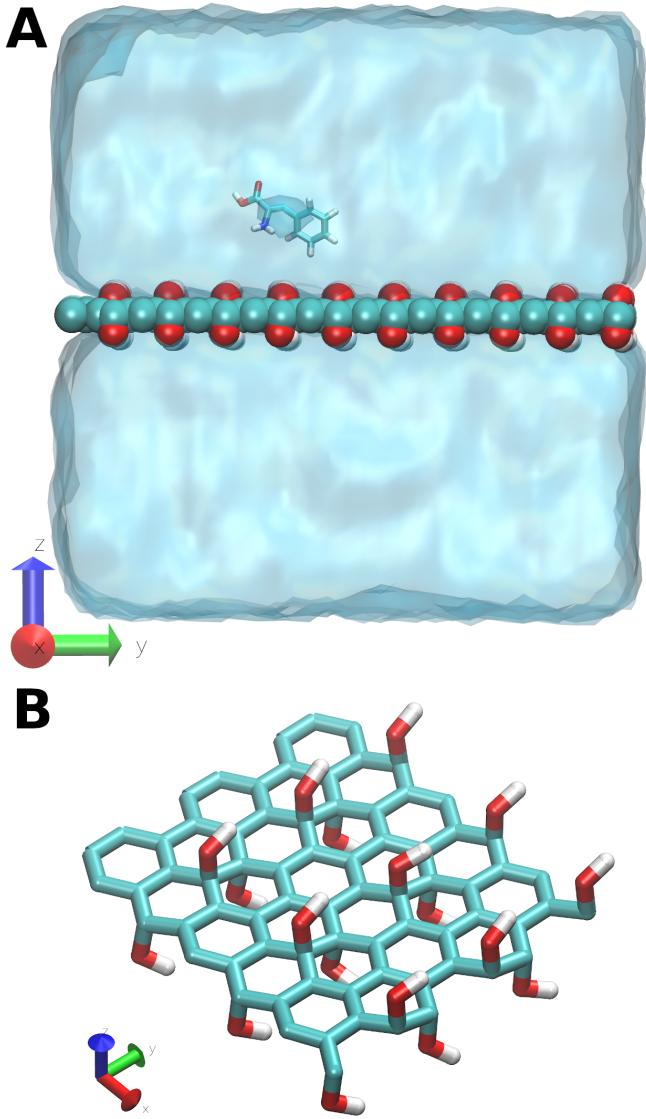


Figure 2: a) Example of simulated oxidized graphene systems. An amino acid (in this case Phenylalanine) above a graphene layer (C in gray, O in red, H in white) inside a periodic water box. b) Segment of the oxidized graphene layer depicting the oxidation pattern. (C in gray, O in red, H in white)

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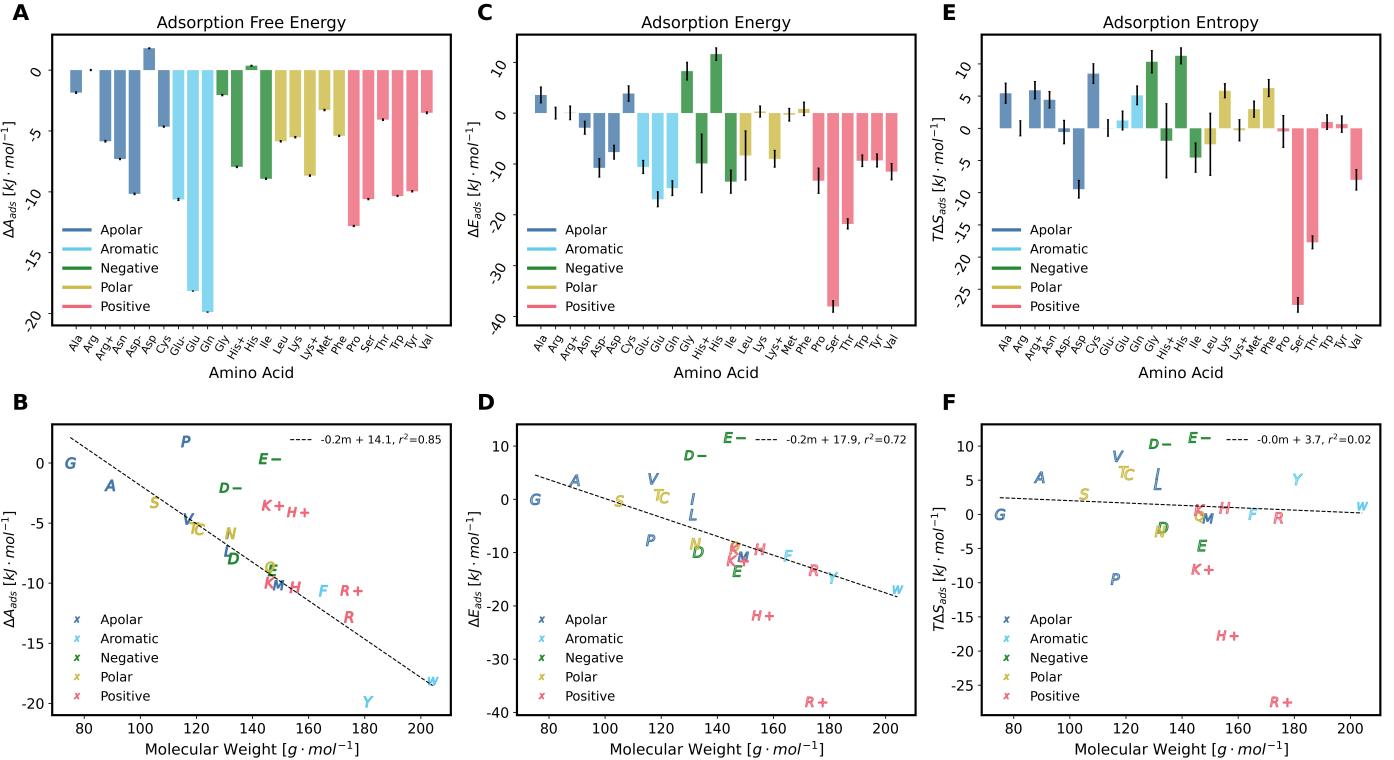


Figure 3: Differences of adsorption over a pristine graphene layer for free energies (ΔA_{ads}), energies (ΔE_{ads}) and entropies ($T\Delta S_{ads}$) for all proteinogenic amino acids. Top row (a, c, and e): ΔA_{ads} , ΔE_{ads} , and $T\Delta S_{ads}$, arranged by amino acid classification on the basis of side-chain interactions. Amino acids are labeled on the x-axis by their three letter code. Bottom row (b, d, and f): ΔA_{ads} , ΔE_{ads} , and $T\Delta S_{ads}$, as a function of molecular weight of the amino acid. Amino acids are labeled by their markers with their one letter code. In all cases amino acids are in a neutral state unless marked with a positive (+) or negative (-) sign.

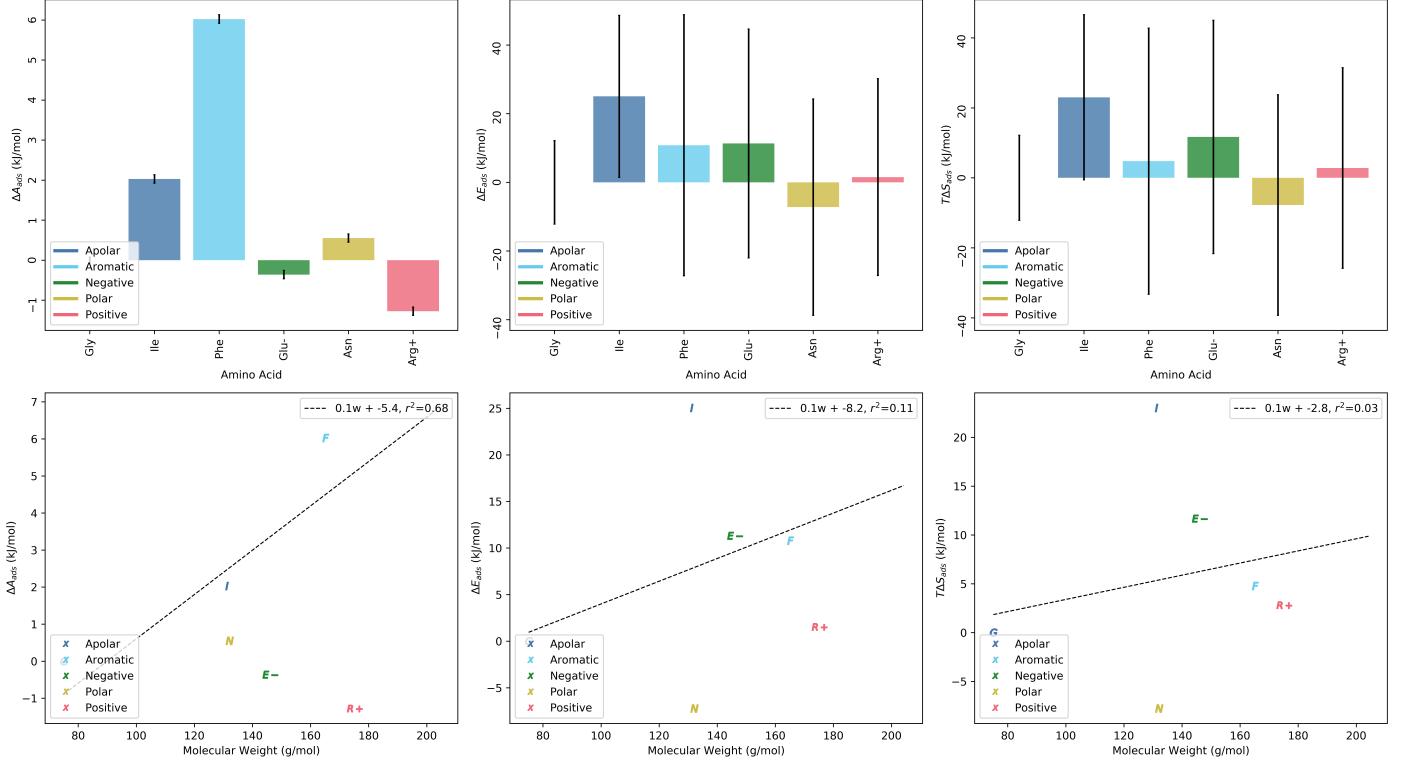


Figure 4: Differences of adsorption over an oxidized graphene layer for free energies (ΔA_{ads}), energies (ΔE_{ads}) and entropies ($T\Delta S_{ads}$) for select amino acids. All values are relative to Glycine's, which is set to 0. Top row (a, c, and e): ΔA_{ads} , ΔE_{ads} , and $T\Delta S_{ads}$, arranged by amino acid classification on the basis of side-chain interactions. Amino acids are labeled on the x-axis by their three letter code. Bottom row (b, d, and f): ΔA_{ads} , ΔE_{ads} , and $T\Delta S_{ads}$, as a function of molecular weight of the amino acid. Amino acids are labeled by their markers with their one letter code. In all cases amino acids are in a neutral state unless marked with a positive (+) or negative (-) sign.

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