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Molecular dynamics study on the interfacial properties of mixtures of monomers of polyvinylpyrrolidone (PVP)-based battery binders on graphene and graphite surfaces

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ABSTRACT

This study investigates the behavior of two different mixtures of monomers of polyvinylpyrrolidone (PVP)-based battery binders, polyvinylpyrrolidone:polyvinylidene difluoride (PVP:PVDF) and polyvinylpyrrolidone:polyacrylic acid (PVP:PAA), at graphene and graphite interfaces using classical molecular dynamics simulations. The aim is to identify the best performing monomer binder blend and carbon-based material for the design of battery-optimized energy devices. The PVP:PAA monomer binder blend and graphite are found to have the best interaction energies, densification upon adsorption, and more ordered structure. The adsorption of both monomer binder blends is strongly guided by the higher affinity of PVP and PAA monomeric molecules for the surfaces compared to PVDF. The structure of adsorbed layers of PVP:PVDF monomer binder blend on graphene and graphite develops more quickly than PVP:PAA, indicating faster kinetics. This study complements a previous density functional theory study recently reported by our group and contributes to a better understanding of the nanoscopic features of relevant interfacial regions involving mixtures of monomers of PVP-based battery binders and different carbon-based materials. The effect of a blend of commonly used monomer binders on carbon-based materials is essential for obtaining tightly bound anode and cathode active materials in lithium-ion batteries, which is crucial for designing battery-optimized energy devices.

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I. INTRODUCTION

Lithium-ion batteries (LIBs) have become one of the most important power sources for portable electronic devices, electric vehicles, and renewable energy storage systems. The performance and safety of LIBs are closely related to the properties of electrode materials, separator, and electrolyte. Among them, the binder is a critical component in maintaining the structural integrity of the electrode, facilitating ion and electron transport, and enhancing the adhesion between the active material and the current collector. Therefore, optimization of binder materials has been a major focus of research in recent years. Polyvinylpyrrolidone (PVP),

polyvinylidene difluoride (PVDF), and polyacrylic acid (PAA) are widely used as binders in LIBs due to their good adhesion, mechanical strength, and electrochemical stability. These binders have shown to provide several chemical and physical advantages for improving the safety and performance of LIBs. Some of the chemical advantages include enhanced adhesion between the active material and the current collector,^{1–3} resulting in better electron transfer and more stable cycling performance of the battery; improved wettability of the electrode by the electrolyte,^{4–6} which improves the battery's rate capability and power density; and improved safety of LIBs by reducing the risk of thermal runaway (the presence of PVP in the binder system has been shown to increase the thermal stability of

the electrode, which reduces the likelihood of thermal runaway during high-temperature operation or overcharging^{7–9}). The physical advantages of these binders include enhanced mechanical strength of the electrode,^{2,10} which can reduce electrode cracking and particle detachment during cycling, and improved electrode porosity,^{11,12} which can enhance ion diffusion and reduce the internal resistance of the battery.

However, the performance of these binders on graphene and graphite surfaces, which are commonly used as electrode materials in LIBs, is not well understood. In addition, the potential benefits of binary blends of these binders have received limited attention. Therefore, this manuscript aims to investigate the performance of mixtures of monomers of PVP-based battery binders (PVP:PVDF and PVP:PAA) on graphene and graphite surfaces and evaluate their potential as binder materials for next-generation LIBs. The properties of binder materials are closely related to the morphology, composition, and surface chemistry of the electrode materials. Graphene and graphite are widely used as anodes in LIBs due to their high specific surface area, excellent electrical conductivity, and low cost. However, the performance of graphene and graphite electrodes can be affected by various factors, such as the aggregation of active materials, the formation of solid–electrolyte interphase (SEI) layers, and adhesion between the active material and the current collector. The binder plays a crucial role in addressing these issues by improving the contact between the active material and the current collector and preventing the detachment and aggregation of the active material during the charge–discharge process.^{13–15} Likewise, it is also very important to ensure that the graphene and graphite surfaces are flat and their stiffness is appropriately managed to ensure effective adhesion of the binder to the electrode material in LIBs. If the graphene and graphite surfaces are not flat, and their stiffness is reduced, adhesion between the binder and the electrode surface may be weakened, leading to decreased stability and performance of the battery.^{16,17} In particular, in the case of a rough surface, the effective surface area of the electrode material may decrease, leading to a decrease in the capacity of the battery. In addition, nonuniform distribution of the binder material on the electrode surface may lead to localized areas with low adhesion, resulting in reduced electron transfer and overall performance of the battery.¹⁸

The use of binary blends of binder materials can provide synergistic effects and improve the performance of LIBs. For example, the authors of the work of Zheng *et al.*¹⁹ reported enhancement of the PVDF binder's performance by mixing it with poly(ethylene-block-poly(ethylene glycol) (PE-PEG), poly(propylene carbonates) (PPC), and ultrahigh molecular weight of poly(ethylene oxide) (PEO) and showed more uniform electrode with better electron conduction network. In addition, the authors of the work of Song *et al.*²⁰ and Huang *et al.*²¹ reported the use of PVP:PAA binary blend as a binder for LIB and found that the blend improved the electronic conductivity and ionic diffusion of the electrodes compared to individual binders. However, there is a lack of research on the use of these binders and their binary blends on graphene and graphite surfaces. Therefore, this manuscript aims to investigate the performance of mixtures of monomers of PVP-based battery binders (PVP:PVDF and PVP:PAA) on graphene and graphite surfaces and evaluate their potential as binder materials for next-generation LIBs.

Molecular dynamics (MD) simulations can provide a molecular-level understanding of the interactions between the monomer binder molecules and the graphene/graphite surfaces. MD simulations have been widely used in battery research to study the behavior of materials at the atomic level and provide insights into the adsorption, conformation, and diffusion of the binder molecules on the electrode surfaces. MD simulations can also provide information that is difficult to obtain experimentally, such as the binding energy and the distribution of binder molecules on the surface. They have been used in several studies to investigate the behavior of binder molecules in LIBs. A MD simulation study of the traction-separation response at the interface between PVDF binder and graphite in the electrode of LIB was studied in the work of Lee *et al.*,²² and more recently another MD study on the binding effectiveness between undoped conjugated polymer binders for batteries was published in the work of Xu *et al.*²³ Furthermore, the authors of the work of Xiong *et al.*²⁴ also studied the influence of PAA binder neutralization degree on the initial electrochemical behavior of a silicon/graphite electrode. However, there is a lack of detailed research on the use of MD simulations to study the behavior of PVP, PVDF, PAA, and their binary blends on graphene and graphite surfaces. This manuscript aims to fill this gap by performing MD simulations to provide a molecular-level understanding of the interactions between the monomer binder molecules and the electrode surfaces. This work aims to provide insights into the role of monomer binders in LIBs and guide the development of improved binder materials for next-generation batteries.

II. METHODS

Classical MD simulations were carried out with the MDynaMix v.5.2²⁵ molecular modeling package. Regarding the length of systems used in this study to mimic real PVP, PVDF, and PAA polymers, it should be noted that monomeric models were used. Monomer MD simulations offer computational efficiency, particularly in large-scale systems involving adsorption on graphene or graphite surfaces, as well as enable systematic analysis of individual components in the mixtures. This approach provides fundamental insights into the interactions and energetics governing the mixtures' behavior on Li-ion battery anode surfaces. Furthermore, the use of monomer mixtures, such as the 50%–50% composition ratio investigated in this study, is relevant to certain experimental conditions and pre-polymer systems where binder components are applied in their monomeric form and subsequently polymerized *in situ*. These MD simulations serve as a foundation for future investigations, including those involving polymers, and contribute to the development of improved binder systems for battery applications. The chemical structures of these repeating units of PVP, PVDF, and PAA monomeric models are defined in the MD simulations using the force field parameters reported in Table I. For PVP, the repeating unit has a five-membered lactam ring and a $-\text{CH}_2-\text{CH}_3$ group. For PVDF, the repeating unit has a carbon–carbon single bond and two fluorine atoms (one for each carbon). For PAA, the repeating unit is acrylic acid, which has a carboxylic acid group and a vinyl group. The specific details of the force field parameters for these monomeric models are shown in Table I and were obtained from SwissParam database (Merck Molecular Force Field²⁶), except atomic charges,

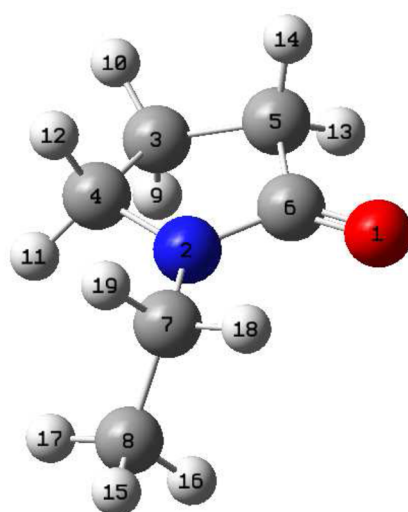
TABLE I. Force field parameterization used for MD simulations.

The general form of the applied force field is

$$E = \sum_{\text{bonds}} k_r (r - r_{eq})^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_{eq})^2 + E_{tor} \\ + \sum_i \sum_j \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}} \right\}$$

Graphene and graphite were maintained as rigid along the simulations, thus dihedrals (E_{tor}) were null for all the molecules. Improper dihedrals were described according to

$$E_{improper} = k_\phi (\phi - \phi_0)^2$$

**PVP**

Label	q	σ_{ii} (Å)	ϵ_{ii} (kJ mol ⁻¹)	No.
O1	-0.597 83	3.029 05	0.502 08	1
N1	-0.156 24	3.296 32	0.836 80	2
C1	-0.121 92	3.875 41	0.230 12	3
C2	-0.041 44	3.875 41	0.230 12	4
C3	-0.185 88	3.875 41	0.230 12	5
C4	0.527 39	3.563 59	0.460 24	6
C5	0.123 57	3.875 41	0.230 12	7
C6	-0.215 77	3.875 41	0.230 12	8
H4	0.061 53	2.351 97	0.092 048	9
H4	0.066 06	2.351 97	0.092 048	10
H3	0.067 86	2.351 97	0.092 048	11
H3	0.055 79	2.351 97	0.092 048	12
H5	0.089 83	2.351 97	0.092 048	13
H5	0.083 12	2.351 97	0.092 048	14
H1	0.060 67	2.351 97	0.092 048	15
H1	0.073 76	2.351 97	0.092 048	16
H1	0.047 96	2.351 97	0.092 048	17
H2	0.054 99	2.351 97	0.092 048	18
H2	0.006 56	2.351 97	0.092 048	19

TABLE I. (Continued.)

Number of Bonds			r_{eq} (Å)	k_r (kJ mol ⁻¹ Å ⁻²)
Atom numbers				
18	7		1.093	1435.0745
1	6		1.222	3899.333
15	8		1.093	1435.0745
7	19		1.093	1435.0745
7	8		1.508	1282.1115
7	2		1.436	1404.364
6	2		1.369	1755.1505
6	5		1.492	1261.639
16	8		1.093	1435.0745
14	5		1.093	1435.0745
8	17		1.093	1435.0745
2	4		1.436	1404.364
5	13		1.093	1435.0745
5	3		1.508	1282.1115
4	12		1.093	1435.0745
4	3		1.508	1282.1115
4	11		1.093	1435.0745
3	10		1.093	1435.0745
3	9		1.093	1435.0745

Number of Angles			θ_{eq} (deg)	k_θ (kJ mol ⁻¹ rad ⁻²)
Atom numbers				
4	2	6	119.6	494.41
4	2	7	117.909	672.67
6	2	7	119.6	494.41
4	3	5	109.608	512.48
4	3	9	110.549	383
4	3	10	110.549	383
5	3	9	110.549	383
5	3	10	110.549	383
9	3	10	108.836	310.74
2	4	3	109.96	632.32
2	4	11	107.646	445.64
2	4	12	107.646	445.64
3	4	11	110.549	383
3	4	12	110.549	383
11	4	12	108.836	310.74
3	5	6	107.517	467.91
3	5	13	110.549	383
3	5	14	110.549	383
6	5	13	108.385	391.44
6	5	14	108.385	391.44
13	5	14	108.836	310.74
1	6	2	127.152	546.2
1	6	5	124.41	564.87
2	6	5	112.735	592.57
2	7	8	109.96	632.32
2	7	18	107.646	445.64
2	7	19	107.646	445.64
8	7	18	110.549	383
8	7	19	110.549	383
18	7	19	108.836	310.74

TABLE I. (Continued.)

Number of Angles					θ_{eq} (deg)	k_{θ} (kJ mol ⁻¹ rad ⁻²)
Atom numbers						
7	8	15			110.549	383
7	8	16			110.549	383
7	8	17			110.549	383
15	8	16			108.836	310.74
15	8	17			108.836	310.74
16	8	17			108.836	310.74

Number of Dihedrals					δ (deg)	k_{ϕ} (kJ mol ⁻¹ m)
Atom numbers						
1	6	2	4	0	-0.6694	1
1	6	2	4	180	13.167	2
1	6	2	4	0	-0.3054	3
1	6	2	7	0	-0.6694	1
1	6	2	7	180	13.167	2
1	6	2	7	0	-0.3054	3
1	6	5	3	0	1.7238	1
1	6	5	3	180	0.2929	2
1	6	5	3	0	0.682	3
1	6	5	13	0	1.3807	1
1	6	5	13	180	-2.9455	2
1	6	5	13	0	0.6443	3
1	6	5	14	0	1.3807	1
1	6	5	14	180	-2.9455	2
1	6	5	14	0	0.6443	3
2	4	3	5	0	0.6276	3
2	4	3	9	0	0.8912	3
2	4	3	10	0	0.8912	3
2	6	5	3	0	-1.9414	1
2	6	5	3	180	2.3263	2
2	6	5	3	0	2.9037	3
2	6	5	13	0	-0.8619	1
2	6	5	13	180	1.4477	2
2	6	5	13	0	0.1799	3
2	6	5	14	0	-0.8619	1
2	6	5	14	180	1.4477	2
2	6	5	14	0	0.1799	3
2	7	8	15	0	0.8912	3
2	7	8	16	0	0.8912	3
2	7	8	17	0	0.8912	3
3	4	2	6	0	-2.1464	1
3	4	2	6	180	1.4518	2
3	4	2	6	0	1.9832	3
3	4	2	7	0	0.6276	3
4	2	6	5	0	1.3556	1
4	2	6	5	180	12.8825	2
4	2	6	5	0	1.0627	3
4	2	7	8	0	0.6276	3
4	2	7	18	0	1.6318	3
4	2	7	19	0	1.6318	3
4	3	5	6	0	0.1381	1
4	3	5	6	180	-0.3264	2

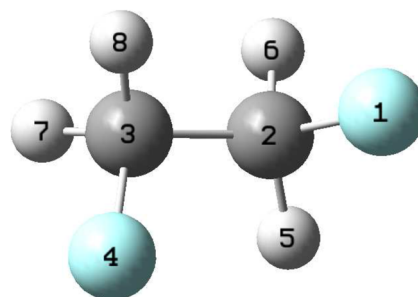
TABLE I. (Continued.)

Number of Dihedrals					δ (deg)	k_{ϕ} (kJ mol ⁻¹ m)
Atom numbers						
4	3	5	6	0	0.2971	3
4	3	5	13	0	1.3389	1
4	3	5	13	180	-1.318	2
4	3	5	13	0	0.5523	3
4	3	5	14	0	1.3389	1
4	3	5	14	180	-1.318	2
4	3	5	14	0	0.5523	3
5	3	4	11	0	1.3389	1
5	3	4	11	180	-1.318	2
5	3	4	11	0	0.5523	3
5	3	4	12	0	1.3389	1
5	3	4	12	180	-1.318	2
5	3	4	12	0	0.5523	3
5	6	2	7	0	1.3556	1
5	6	2	7	180	12.8825	2
5	6	2	7	0	1.0627	3
6	2	4	11	0	-4.3932	1
6	2	4	11	180	2.8493	2
6	2	4	11	0	0.046	3
6	2	4	12	0	-4.3932	1
6	2	4	12	180	2.8493	2
6	2	4	12	0	0.046	3
6	2	7	8	0	-2.1464	1
6	2	7	8	180	1.4518	2
6	2	7	8	0	1.9832	3
6	2	7	18	0	-4.3932	1
6	2	7	18	180	2.8493	2
6	2	7	18	0	0.046	3
6	2	7	19	0	-4.3932	1
6	2	7	19	180	2.8493	2
6	2	7	19	0	0.046	3
6	5	3	9	0	-0.5356	1
6	5	3	9	180	0.1213	2
6	5	3	10	0	-0.5356	1
6	5	3	10	180	0.1213	2
7	2	4	11	0	1.6318	3
7	2	4	12	0	1.6318	3
9	3	4	11	0	0.5941	1
9	3	4	11	180	-2.8995	2
9	3	4	11	0	0.6569	3
9	3	4	12	0	0.5941	1
9	3	4	12	180	-2.8995	2
9	3	4	12	0	0.6569	3
9	3	5	13	0	0.5941	1
9	3	5	13	180	-2.8995	2
9	3	5	13	0	0.6569	3
9	3	5	14	0	0.5941	1
9	3	5	14	180	-2.8995	2
9	3	5	14	0	0.6569	3
10	3	4	11	0	0.5941	1
10	3	4	11	180	-2.8995	2
10	3	4	11	0	0.6569	3

TABLE I. (Continued.)

Number of Dihedrals					δ (deg)	k_{ϕ} (kJ mol ⁻¹ m)
Atom numbers						
10	3	4	12	0	0.5941	1
10	3	4	12	180	-2.8995	2
10	3	4	12	0	0.6569	3
10	3	5	13	0	0.5941	1
10	3	5	13	180	-2.8995	2
10	3	5	13	0	0.6569	3
10	3	5	14	0	0.5941	1
10	3	5	14	180	-2.8995	2
10	3	5	14	0	0.6569	3
15	8	7	18	0	0.5941	1
15	8	7	18	180	-2.8995	2
15	8	7	18	0	0.6569	3
15	8	7	19	0	0.5941	1
15	8	7	19	180	-2.8995	2
15	8	7	19	0	0.6569	3
16	8	7	18	0	0.5941	1
16	8	7	18	180	-2.8995	2
16	8	7	18	0	0.6569	3
16	8	7	19	0	0.5941	1
16	8	7	19	180	-2.8995	2
16	8	7	19	0	0.6569	3
17	8	7	18	0	0.5941	1
17	8	7	18	180	-2.8995	2
17	8	7	18	0	0.6569	3
17	8	7	19	0	0.5941	1
17	8	7	19	180	-2.8995	2
17	8	7	19	0	0.6569	3
Number of Improper					ϕ_0 (deg)	k_{ϕ} (kJ mol ⁻¹)
Atom numbers						
6	2	1	5	0	77.6885	
5	3	6	14	0	0	
5	14	6	13	0	0	
2	7	6	4	0	-12.0416	
7	8	2	18	0	0	
7	18	2	19	0	0	
3	4	5	10	0	0	
3	4	5	9	0	0	
4	3	2	12	0	0	
4	12	2	11	0	0	
8	15	7	16	0	0	
8	15	7	17	0	0	

TABLE I. (Continued.)



PVDF

Label	q	σ_{ii} (Å)	ϵ_{ii} (kJ mol ⁻¹)	#
F1	-0.269 81	2.904 33	0.564 84	1
C7	0.145 76	3.875 41	0.230 12	2
C8	0.139 38	3.875 41	0.230 12	3
F2	-0.268 82	2.904 33	0.564 84	4
H7	0.083 06	2.351 97	0.092 048	5
H7	0.042 33	2.351 97	0.092 048	6
H6	0.043 91	2.351 97	0.092 048	7
H6	0.084 19	2.351 97	0.092 048	8

Number of Bonds Atom numbers			r_{eq} (Å)	k_r (kJ mol ⁻¹ Å ⁻²)
1	2		1.36	1809.9525
2	3		1.508	1282.1115
2	5		1.093	1435.0745
2	6		1.093	1435.0745
3	4		1.36	1809.9525
3	7		1.093	1435.0745
3	8		1.093	1435.0745

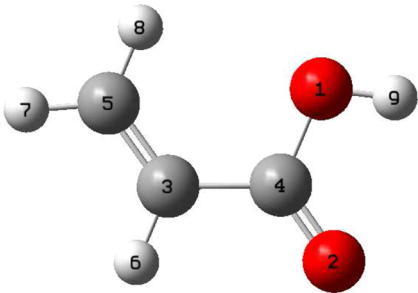
Number of Angles Atom numbers				θ_{eq} (deg)	k_θ (kJ mol ⁻¹ rad ⁻²)
1	2	3		108.313	737.71
1	2	5		107.897	526.93
1	2	6		107.897	526.93
3	2	5		110.549	383
3	2	6		110.549	383
5	2	6		108.836	310.74
2	3	4		108.313	737.71
2	3	7		110.549	383
2	3	8		110.549	383
4	3	7		107.897	526.93
4	3	8		107.897	526.93
7	3	8		108.836	310.74

Number of Dihedrals Atom numbers					δ (deg)	k_ϕ (kJ mol ⁻¹)	m
1	2	3	4		0	-0.8117	1
1	2	3	4		180	-1.138	2

TABLE I. (Continued.)

Number of Dihedrals				δ (deg)	k_ϕ (kJ mol ⁻¹)	m
Atom numbers						
1	2	3	4	0	2.9414	3
1	2	3	7	180	1.0795	2
1	2	3	7	0	0.6067	3
1	2	3	8	180	1.0795	2
1	2	3	8	0	0.6067	3
4	3	2	5	180	1.0795	2
4	3	2	5	0	0.6067	3
4	3	2	6	180	1.0795	2
4	3	2	6	0	0.6067	3
5	2	3	7	0	0.5941	1
5	2	3	7	180	-2.8995	2
5	2	3	7	0	0.6569	3
5	2	3	8	0	0.5941	1
5	2	3	8	180	-2.8995	2
5	2	3	8	0	0.6569	3
6	2	3	7	0	0.5941	1
6	2	3	7	180	-2.8995	2
6	2	3	7	0	0.6569	3
6	2	3	8	0	0.5941	1
6	2	3	8	180	-2.8995	2
6	2	3	8	0	0.6569	3

Number of Improper				ϕ_0 (deg)	k_ϕ (kJ mol ⁻¹)
Atom numbers					
2	3	1	5	0	0
2	3	1	6	0	0
3	4	2	7	0	0
3	4	2	8	0	0



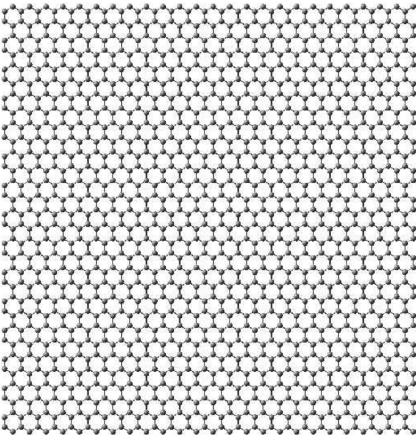
PAA

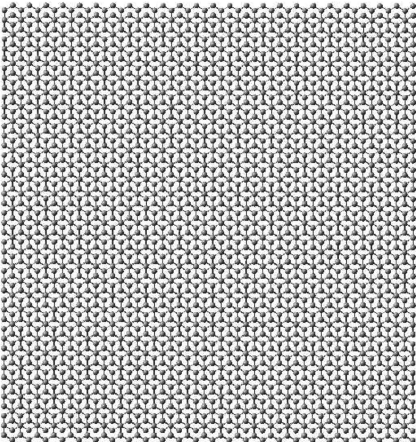
Label	q	σ_{ii} (Å)	ϵ_{ii} (kJ mol ⁻¹)	No.
O2	-0.581 92	3.153 78	0.636 386	1
O3	-0.551 16	3.029 05	0.502 08	2
C7	-0.208 7	3.723 96	0.284 512	3
C8	0.728 67	3.563 59	0.460 24	4
C9	-0.310 52	3.723 96	0.284 512	5
H6	0.151 65	2.351 97	0.092 048	6
H7	0.173 31	2.351 97	0.092 048	7
H8	0.186 06	2.351 97	0.092 048	8
H9	0.412 6	0.400 01	0.192 464	9

TABLE I. (Continued.)

Number of Bonds				r_{eq} (Å)	k_r (kJ mol ⁻¹ Å ⁻²)	
Atom numbers						
1	4			1.355	1746.7195	
1	9			0.981	2229.093	
2	4			1.222	3899.333	
3	5			1.333	2862.019	
3	6			1.083	1556.724	
3	4			1.468	1374.553	
5	7			1.083	1556.724	
5	8			1.083	1556.724	
Number of Angles				θ_{eq} (deg)	k_θ (kJ mol ⁻¹ rad ⁻²)	
Atom numbers						
4	1	9		111.948	351.09	
4	3	5		111.297	328.2	
4	3	6		117.291	293.27	
5	3	6		121.004	322.18	
1	4	2		124.425	695.55	
1	4	3		106.51	561.26	
2	4	3		122.623	563.67	
3	5	7		121.004	322.18	
3	5	8		121.004	322.18	
7	5	8		119.523	219.8	
Number of Dihedrals				δ (deg)	k_ϕ (kJ mol ⁻¹)	m
Atom numbers						
1	4	3	5	180	5.23	2
1	4	3	6	180	5.23	2
2	4	1	9	0	3.4769	1
2	4	1	9	180	12.87	2
2	4	1	9	0	-0.1213	3
2	4	3	5	180	5.23	2
2	4	3	6	180	5.23	2
3	4	1	9	0	0.5356	1
3	4	1	9	180	9.4558	2
3	4	1	9	0	0.5397	3
4	3	5	7	180	3.7656	2
4	3	5	8	180	3.7656	2
6	3	5	7	180	25.104	2
6	3	5	8	180	25.104	2
Number of Improper				ϕ_0 (deg)	k_ϕ (kJ mol ⁻¹)	
Atom numbers						
4	3	1	2	0	76.4835	
3	5	4	6	0	7.23	
5	7	3	8	0	3.615	

TABLE I. (Continued.)

			
GRAPHENE			
Number of Nonbonded Atom	q	σ_{ii} (Å)	ϵ_{ii} (kJ mol ⁻¹)
C	0.0000	3.5500	0.2929

			
GRAPHITE			
Number of Nonbonded Atom	q	σ_{ii} (Å)	ϵ_{ii} (kJ mol ⁻¹)
C	0.0000	3.5500	0.2929

which were inferred from ChelpG charges previously reported in a density functional theory (DFT) simulation study carried out by our group recently.²⁷ Graphene and graphite surfaces (Table I) were modeled as rigid entities composed of noncharged carbon atoms interacting through Lennard-Jones potential with interaction parameters ($\epsilon = 0.2929$ kJ mol⁻¹ and $\sigma = 3.55$ Å) previously reported.^{28,29} Regarding the stiffness of graphene and graphite surfaces, it is important to note that it was managed by adjusting the force field parameters reported in Table I and using a Nose-Hoover thermostat³⁰ for controlling the temperature in MD simulations. The

interfaces of interest (PVP:PVDF-graphene, PVP:PVDF-graphite, PVP:PAA-graphene, and PVP:PAA-graphite) were modeled using the systems reported in the supplementary material (Table S1). Periodic boundary conditions (PBCs) were applied in the three space directions (including z-axis perpendicular to the studied interfaces) for all the considered systems. Regarding simulations involving graphene, a graphene sheet in the armchair configuration, containing 1500 carbon atoms with dimensions of 62×62 Å², was built and placed in the xy plane. Regarding simulations involving graphite, a graphite sheet, made up of three graphene sheets

containing 4500 carbon atoms, with dimensions of $62 \times 62 \times 6 \text{ \AA}^3$, was built and placed in the xyz plane. Monomer binder blends (PVP:PVDF and PVP:PAA) were placed on top of the sheets initially at $3 \text{ \AA}$ (Table S1).

Initial cubic simulation boxes were built with Packmol program.³¹ Simulations were carried out applying a two-step consecutive procedure: (i) 1 ns equilibration in the NVT (isochoric–isothermal) ensemble (assured by the constancy of total potential energy) followed by (ii) 10 ns production, also in the NVT ensemble. Simulations were carried out at 293 K for all systems. The Nose–Hoover method³⁰ was used for temperature control, with 30 ps as the time constant for the thermostat. The Tuckerman–Berne double time step algorithm³² (with long- and short-time steps of 1 and 0.1 fs) was applied for solving the equations of motion. The Ewald method³³ ($15 \text{ \AA}$ for cutoff radius) was applied for handling Coulombic interactions. The excluded volume interactions between particles were defined by a Lennard–Jones potential, which models the attraction and repulsion between particles, using the parameters sigma (σ_{ij}) and epsilon (ϵ_{ij}) specified in the force fields (Table I) for each particle type and a $15 \text{ \AA}$ cutoff distance for the non-bonded interactions. The Lorentz–Berthelot mixing rules were also used for cross terms. The visualization, data analysis, and post-processing of MD trajectories were done with VMD³⁴ software. It should be noted that the simulation time evolution of interacting strength (interaction energy, E_{inter}) between the PVP/PVDF/PAA monomer binder and the 2D surface in the 10 ns production NVT simulations was obtained from the MD simulation output file, by adding the electrostatic and Lennard–Jones intermolecular interaction energy contributions between the corresponding interacting pairs (PVP–2D surface, PVDF–2D surface, and PAA–2D surface) at each simulation time, every 0.03 ns.

III. RESULTS AND DISCUSSION

A. PVP:PVDF monomer binder blend on graphene/graphite interfaces

The first interfaces analyzed in this work are obtained from the adsorption of PVP:PVDF monomer binder blend on graphene and graphite surfaces. Densification and layering of this monomer binder blend on these surfaces have not been previously reported. In a DFT simulation study carried out by our group recently,²⁷ we showed that PVP:PVDF monomer binder blend is physisorbed onto the graphene surface with -19.90 kJ/mol interaction energy showing parallel arrangement and with PVP and PVDF monomer binder molecules placed at $\approx 3 \text{ \AA}$. Therefore, the structure of the adsorbed PVP:PVDF monomer binder blend on graphene (and graphite) was first analyzed through the number density profiles in a perpendicular direction to the 2D surfaces, Fig. 1. Results in Fig. 1(a) show that adsorption of PVP:PVDF monomer binder blend on graphene leads to densification and layering with an oscillatory damped behavior (highly structured region). This region is characterized by four adsorption layers of PVP (peaks [1], [3], [4] and [5], separated by a less-dense layer, peak [2], between [1] and [3]), and four adsorption layers of PVDF molecules (peaks [1], [2], [3] and [4]), with a very intense first adsorption layer. The maxima of peak [1] (with PVP and PVDF monomer binder molecules placed at 2.7 and $2.8 \text{ \AA}$ respectively regarding graphene surface) strongly agrees with DFT results reported by our group recently,²⁷ where monomer binder molecules

were found to be located at $\approx 3 \text{ \AA}$. The concentration of PVP in the first adsorption layer is notably higher than that of PVDF, exhibiting an enrichment ratio of 3. This ratio is obtained by dividing the area under the peak [1] for PVP ($0.0073 \text{ \AA}^{-2}$) by the corresponding area under the peak [1] for PVDF ($0.0024 \text{ \AA}^{-2}$). It is important to highlight that the areas of the peaks were calculated using Origin-Pro 8.5 software³⁵. Furthermore, PVP molecules are placed slightly closer to the graphene surface in comparison with PVDF. PVP tends to concentrate in peak [1], whereas in the rest of the adsorbed layers, there is greater competition between PVP and PVDF, with PVDF roughly closer to the surface than PVP. The planar arrangement of PVP and PVDF molecules in the first adsorbed layer is confirmed in Fig. 2(a), being placed in different regions on top of the graphene surface, with PVP placed slightly closer to the 2D surface in comparison with PVDF (2.5 – $2.6 \text{ \AA}$ for the first maxima in PVP oxygen and carbon atoms vs $2.8 \text{ \AA}$ in PVDF carbon atoms). In the case of graphite [Fig. 1(b)], the reported results also show that adsorption of PVP:PVDF monomer binder blend leads to a highly structured region above the 2D surface, with four adsorbed layers of PVP (peaks [1], [3], [4], and [5], separated by a less-dense layer, peak [2], between [1] and [3]) and PVDF molecules (peaks [1], [2], [3], and [4]), with a very intense first adsorption layer [1]. In [1], there is a larger concentration for PVP than PVDF (number for enrichment is 1.6). The area under the peak [1] for PVP is $0.0102 \text{ \AA}^{-2}$ and for PVDF is $0.0065 \text{ \AA}^{-2}$. Furthermore, PVP molecules are placed slightly closer to the graphite surface in comparison with PVDF. PVP tends to concentrate in [1], whereas in the rest of the adsorbed layers, there is greater competition between PVP and PVDF, with PVDF roughly closer to the surface than PVP. As in the case of graphene, the planar arrangement of PVP and PVDF molecules on graphite in the first adsorbed layer is confirmed in Fig. 2(b), being placed in different regions on top of the graphite surface and with PVP placed slightly closer to the surface in comparison with PVDF ($2.3 \text{ \AA}$ for the first maxima in PVP oxygen and carbon atoms vs $2.4 \text{ \AA}$ in PVDF carbon atoms). However, the reported results on graphite also show some differences in comparison with graphene. A first adsorbed layer is formed by PVP and PVDF molecules, with much larger concentration for PVDF molecules on graphite than on graphene (number for enrichment is 2.7). The area under peak [1] for PVDF on graphite is $0.0065 \text{ \AA}^{-2}$ [Fig. 1(b)] and on graphene is $0.0024 \text{ \AA}^{-2}$ [Fig. 1(a)]. Likewise, there is also a larger concentration for PVP molecules on graphite than on graphene (number for enrichment is 1.4). The area under peak [1] for PVP on graphite is $0.0102 \text{ \AA}^{-2}$ [Fig. 1(b)] and on graphene is $0.0073 \text{ \AA}^{-2}$ [Fig. 1(a)]. In addition, PVP and PVDF molecules are placed slightly closer to the graphite surface in comparison to the graphene surface [2.3 and $2.4 \text{ \AA}$ for the first maxima reported in Fig. 1(b) vs 2.7 and $2.8 \text{ \AA}$ for the first maxima reported in Fig. 1(a)]. For the rest of the adsorbed layers, this behavior is also observed. Therefore, PVP:PVDF monomer binder blend adsorption from a 2D surface like graphite leads to better results in terms of much larger concentration of PVDF in the first layer (and also a larger concentration of PVP) and closer interactions compared to a 2D surface like graphene.

The development of the PVP and PVDF-adsorbed layers on graphene and graphite surfaces is analyzed through the time evolution of PVP and PVDF–graphene/graphite interaction energies reported in Fig. 3. The adsorbed layers are developed in 2 ns (determined through the constancy of interaction energies) for both

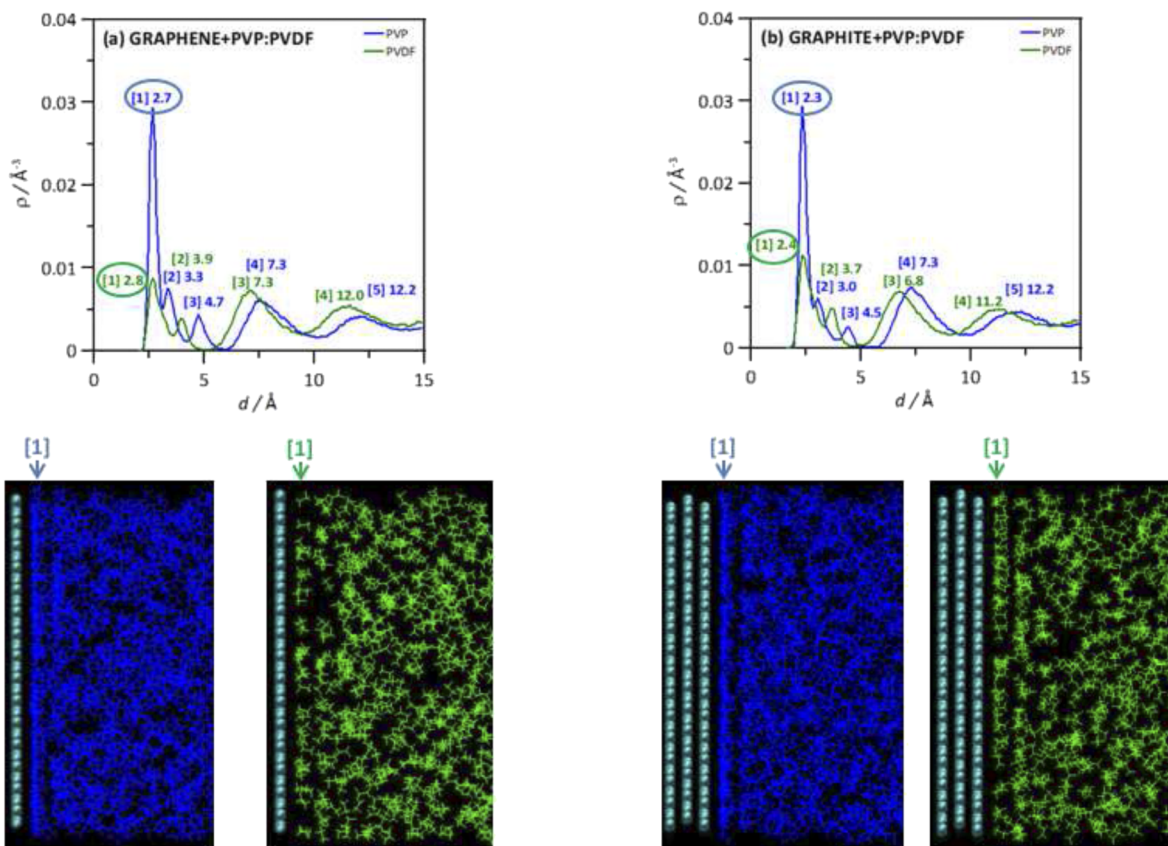


FIG. 1. Number density profiles for the centers of mass of PVP (N1 atom) and PVDF (C7 atom) molecules in a perpendicular direction to graphene/graphite for (a) GRAPHENE+PVP:PVDF and (b) GRAPHITE+PVP:PVDF. Graphene/graphite is placed at $d = 0$. All values are at 293 K. The numbers inside each panel show the d ($\text{\AA}$) corresponding to the maxima. Atom labeling as in Table S1.

graphene and graphite surfaces, which shows that the structure of adsorbed layers is developed very quickly (rapid kinetics). This quick adsorption is guided mainly by the higher affinity of PVP molecules for both surfaces compared with PVDF; this effect is quantified by the PVP/PVDF-graphene/graphite interaction energies reported in Fig. 3, which have a less positive sign for PVP than for PVDF in both surfaces (interaction energy value with a more negative sign indicates more favorable interactions and thus higher surface affinity). Comparing graphite with graphene, the sign of the PVDF-graphite interaction energy is twice as less positive [~ 8500 kJ/mol for graphite, Fig. 3(b), and ~ 18000 kJ/mol for graphene, Fig. 3(a)], and the sign of the PVP-graphite interaction energy is four times as less positive [~ 3500 kJ/mol for graphite, Fig. 3(b), and ~ 14000 kJ/mol for graphene, Fig. 3(a)], so PVP/PVDF-graphite interactions are more favorable when compared with graphene; it should be remarked that density profiles reported in Fig. 1 showed that PVP and PVDF molecules are placed at shorter distances of graphite than graphene (2.3 and 2.4 $\text{\AA}$ for graphite vs 2.7 and 2.8 $\text{\AA}$ for graphene), which also contributes to more favorable interactions. On the other hand, PVP-PVDF interaction in the case of graphene is more favorable than PVP-graphene and PVDF-graphene [interaction energy has a

negative sign; it is the most negative energy, ~ -45 kJ/mol, Fig. 3(a)]. Comparing PVP-graphene and PVDF-graphene interaction energies, PVP monomer binder guides adsorption and molecular planarity on graphene (PVP-graphene interaction energy value less positive than PVDF-graphene, more favorable interaction, and thus higher affinity between PVP and the 2D surface than between PVDF and the 2D surface). In graphite surface [Fig. 3(b)], no difference in PVP-PVDF monomer binder interaction energy value is observed with respect to graphene (~ -45 kJ/mol). Likewise, comparing PVP-graphite and PVDF-graphite interaction energies, PVP monomer binder also guides adsorption and molecular planarity on the graphite surface. Therefore, PVP:PVDF monomer binder blend over graphite surface leads to a more effective adsorption (higher affinity) from the viewpoint of interaction energy and densification upon adsorption.

The structuring of considered PVP and PVDF molecules in the first adsorbed layer on both 2D surfaces in comparison with bulk PVP and PVDF is analyzed through the radial distribution functions (RDFs) reported in Fig. 4. As shown in Fig. 4(a), PVP and PVDF molecules in the first adsorbed layer show a more ordered structure in comparison with bulk PVP and PVDF, as shown by the increase in intensities of the reported RDFs, leading to a solid-like structure for

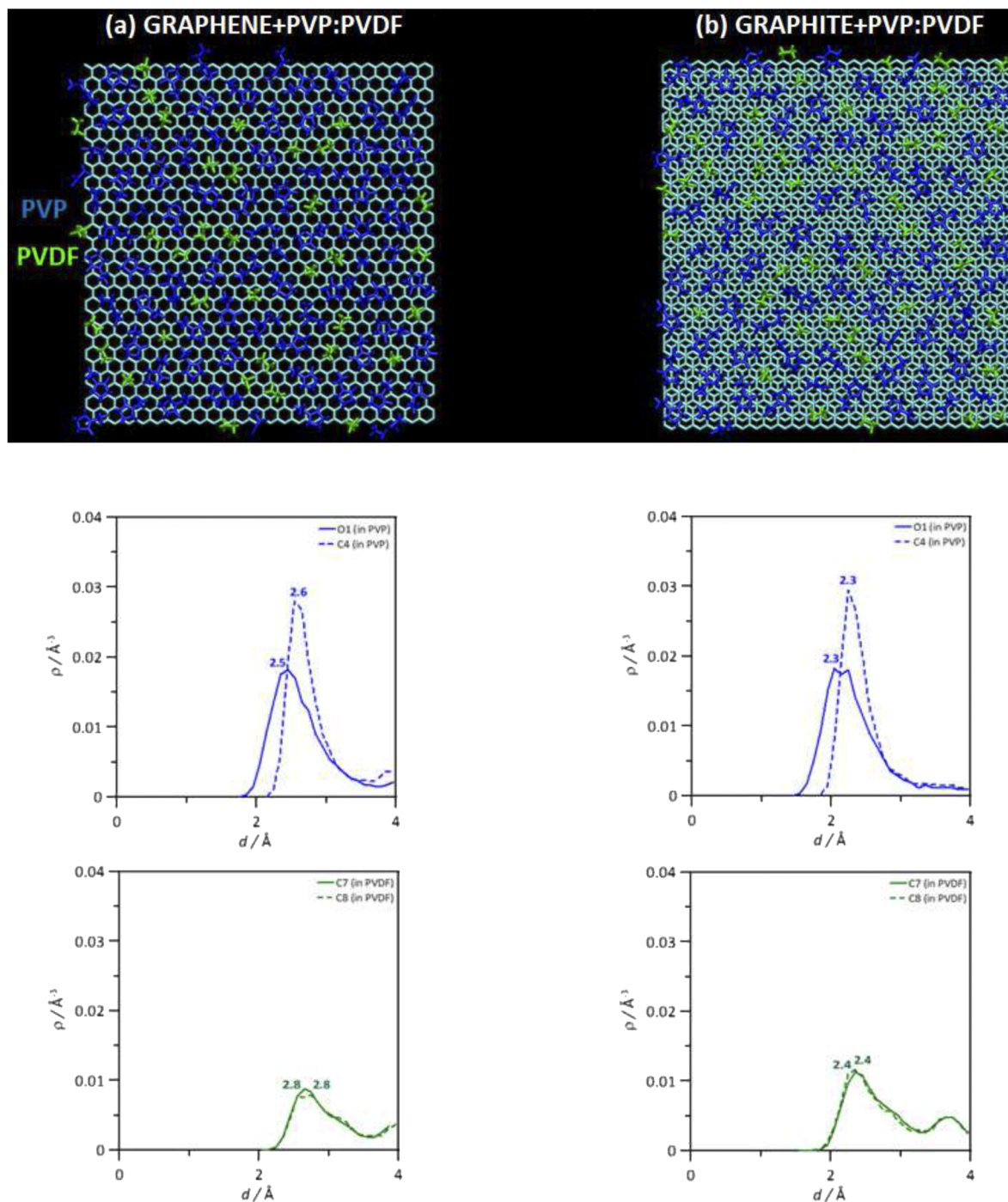


FIG. 2. Distribution of molecules on top of graphene/graphite sheet for the first adsorbed layer in (a) GRAPHENE+PVP:PVDF and (b) GRAPHITE+PVP:PVDF interfaces at 293 K. The first adsorbed layer is defined according to the density profiles reported in Fig. 1 ($d < 4 \text{\AA}$). Plot at the bottom of each column shows number density profiles for the reported atoms in PVP and PVDF in the first adsorbed layer showing parallel (planar) arrangement of PVP and PVDF molecules regarding graphene/graphite surface. Atom labeling as in Table S1.

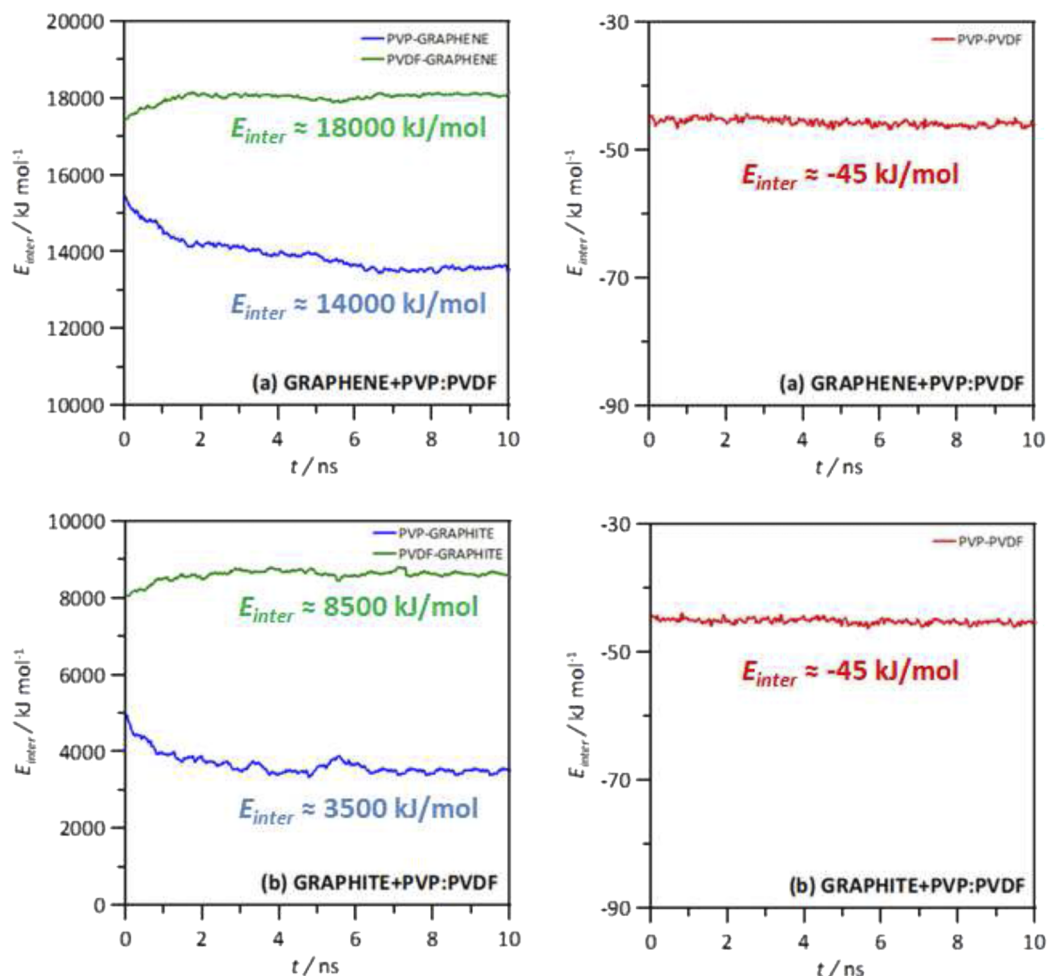


FIG. 3. Simulation time evolution of interaction energy (Electrostatic + Lennard-Jones) between PVP and graphene/graphite (blue color), PVDF and graphene/graphite (green color), and PVP-PVDF (red color) molecules for (a) GRAPHENE+PVP:PVDF and (b) GRAPHITE+PVP:PVDF interfaces.

the layer in direct contact with graphene. Nevertheless, the position of the maxima for the peaks in RDFs (at 7.0 and 10.6 Å for PVP-PVP; at 4.5 and 9.2 Å for PVDF-PVDF; at 5.4 and 9.8 Å for PVP-PVDF) remains constant upon adsorption, and thus the mechanism of interaction between PVP, PVDF, and PVP-PVDF molecules is the same both in the bulk phase and in the first adsorbed layer. Regarding graphite surface [Fig. 4(b)], PVP and PVDF molecules in the first adsorbed layer also show a more ordered structure in comparison with bulk PVP and PVDF, and the mechanism of interaction between PVP, PVDF, and PVP-PVDF molecules is the same both in the bulk phase and in the first adsorbed layer. Therefore, PVP:PVDF monomer binder blends not only bind to both graphene and graphite surfaces tight but also preserve their interaction integrity and keep the monomer binder blend properties stable at the interfaces. Furthermore, the presence of both graphene and graphite surfaces does not induce any alterations in the interaction mechanisms of the PVP:PVDF monomer binder blend. Thus, the binder blend maintains its stable properties at the interfaces,

ensuring tight binding to both surfaces while preserving the integrity of their interactions. The only difference between graphene and graphite is that PVP and PVDF molecules in the first adsorbed layer and in the bulk phase show a slightly more ordered structure in the graphite than in the graphene [slightly more intense peaks in Fig. 4(b) than in Fig. 4(a)]. This is probably because increasing the number of carbon layers in graphite compared to graphene also increases the van der Waals-type forces with the monomer binder, leading to stronger interactions followed by larger ordering.

The reported RDFs allow the calculation of PVP and PVDF molecules in the solvation spheres around another type of PVP and PVDF molecules as reported in Table II. The reported results reveal a decrease in the number of molecules around each type of molecule for all the considered pairs for graphene and graphite cases on going from the bulk phase to the first adsorbed layer. The main difference between graphene and graphite surfaces is that there is a significant increase in the total number of molecules around the first solvation sphere for the PVP-PVDF pair in the first adsorbed layer for graphite

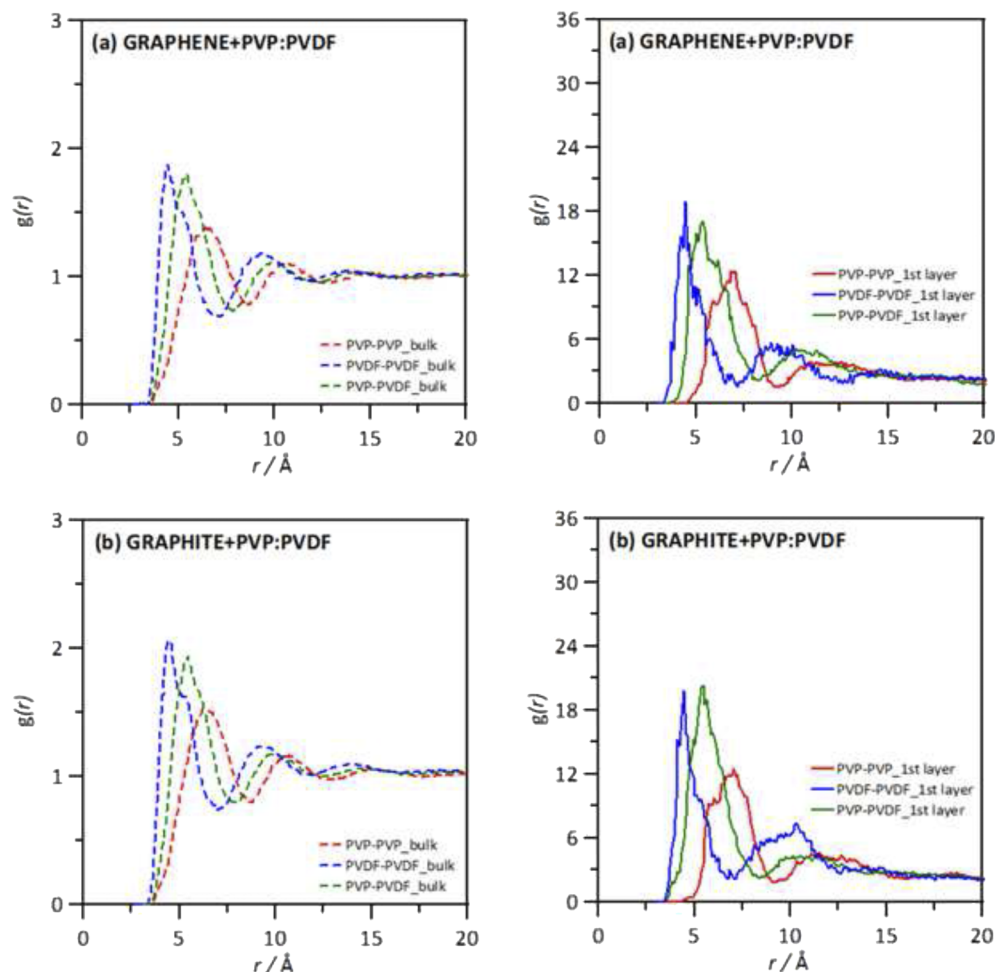


FIG. 4. Center-of-mass RDFs, $g(r)$, for the reported molecular pairs (PVP, N1 atom; PVDF, C7 atom) for (a) GRAPHENE+PVP:PVDF and (b) GRAPHITE+PVP:PVDF interfaces. The first adsorbed layer is defined according to the density profiles reported in Fig. 1 ($d < 4$ Å). All values are at 293 K. Atom labeling as in Table S1.

compared with graphene (2.5 vs 1.6), which agrees with the higher RDF intensity of the PVP-PVDF pair in the first adsorbed layer for graphite compared with graphene reported in Fig. 4. This can be justified due to the higher concentration of PVDF molecules adsorbed on the graphite for the first layer than on the graphene [Fig. 1(b) vs Fig. 1(a)].

As recently reported in a paper from our group,²⁷ PVP-PVDF monomer binder blend develops H-bond type interactions, so the analysis of hydrogen bonding in MD simulations considering PVP-PVP, PVDF-PVDF, and PVP-PVDF interactions is another important parameter to consider (Table III). For the analysis of hydrogen bonding in MD simulations, the frequently used geometrical criterion of 3.5 Å and 60° for donor-acceptor (PVP/PVDF) distance and angle, respectively, is used. The reported results reveal a decrease in the number of H-bonds formed (on average) for all the considered pairs for graphene and graphite cases on going from the bulk phase to the first adsorbed layer due to the appearance of PVP-2D surface and PVDF-2D surface interactions in the first adsorbed

layer, causing PVP-PVP, PVDF-PVDF, and PVP-PVDF interactions to weaken and resulting in a lower number of H-bonds. The main difference between graphene and graphite surfaces is that in the first layer of PVP and PVDF molecules adsorbed on graphite, more H-bonds are formed between the two species than on graphene. More H-bonds between PVP-PVDF will lead to other species such as electrolytes not interacting as easily with monomer binder blends for lithium-ion batteries devices applications.

B. PVP:PAA monomer binder blend on graphene/graphite interfaces

The adsorption of PVP:PAA monomer binder blend on graphene and graphite surfaces is analyzed in this section. In the same DFT simulation study mentioned previously,²⁷ our group showed that PVP:PAA monomer binder blend is also physisorbed onto the graphene surface with -14.12 kJ/mol interaction energy,

TABLE II. Number of molecules, N , in the first solvation sphere (defined according to results in Fig. 4) for the reported pairs for (a) GRAPHENE+PVP:PVDF and (b) GRAPHITE+PVP:PVDF interfaces. All values are at 293 K.

(a) GRAPHENE+PVP:PVDF	
Pair	N
PVP-PVP (bulk)	7.8
PVP-PVP (1st layer)	3.9
PVDF-PVDF (bulk)	4.7
PVDF-PVDF (1st layer)	0.8
PVP-PVDF (bulk)	6.6
PVP-PVDF (1st layer)	1.6
(b) GRAPHITE+PVP:PVDF	
Pair	N
PVP-PVP (bulk)	8.0
PVP-PVP (1st layer)	3.6
PVDF-PVDF (bulk)	4.5
PVDF-PVDF (1st layer)	1.1
PVP-PVDF (bulk)	6.7
PVP-PVDF (1st layer)	2.5

showing parallel arrangement and with monomer binder molecules placed at ≈ 3 Å. Therefore, the structure of the adsorbed PVP:PAA monomer binder blend on graphene (and graphite) was first analyzed through the number density profiles in a perpendicular direction to the 2D surfaces, Fig. 5. Results in Fig. 5(c) show that

adsorption of PVP:PAA monomer binder blend on graphene leads to densification and layering with an oscillatory damped behavior. The region 15 Å above graphene is characterized by three adsorption layers for PVP (peaks [1], [3], and [4], separated by a less-dense layer, peak [2], between [1] and [3]), and three adsorption layers for PAA molecules (peaks [1], [2], and [3]), with a very intense first adsorption layer. The maxima of peak [1] (with PVP and PAA monomer binder molecules placed at 2.6 and 2.5 Å, respectively, regarding graphene surface) strongly agrees with the DFT results reported by our group recently,²⁷ where monomer binder molecules were found to be located at ≈ 3 Å. In the first adsorption layer, there is a slightly larger concentration for PAA than PVP (number for enrichment is 1.1). The area under peak [1] for PAA is 0.0102 Å^{-2} and for PVP is 0.0092 Å^{-2} . Furthermore, PAA molecules are placed slightly closer to the graphene surface in comparison with PVP. In addition, there is a great competition between PVP and PAA molecules in the remaining adsorbed layers, with PAA roughly closer to the surface than PVP. The parallel arrangement of PVP and PAA molecules in the first adsorbed layer is confirmed in Fig. 6(c), being placed in different regions on top of the graphene surface. In the case of graphite [Fig. 5(d)], the reported results also show that adsorption of PVP:PAA monomer binder blend leads to a highly structured region above the graphite surface, with three adsorption layers for PVP (peaks [1], [3], and [4], separated by a less-dense layer, peak [2], between [1] and [3]), and three adsorption layers for PAA molecules (peaks [1], [2], and [3]), with a very intense first adsorption layer [1]. In [1], there is a slightly larger concentration for PVP than PAA (number for enrichment is 1.1). The area under peak [1] for PVP is 0.0115 Å^{-2} and for PAA is 0.0104 Å^{-2} . Furthermore, PAA molecules are placed slightly closer to the graphite surface in comparison with

TABLE III. Average number of hydrogen bonds per PVP/PVDF molecule, N_H , for the reported atomic pairs (donor–acceptor) in (a) GRAPHENE+PVP:PVDF and (b) GRAPHITE+PVP:PVDF interfaces, with 3.5 Å and 60° as donor–acceptor distance and angle as hydrogen bonding criteria. The first adsorbed layer is defined according to the density profiles reported in Fig. 1 ($d < 4$ Å). All values are at 293 K. Atom labeling as in Table S1.

(a) GRAPHENE+PVP:PVDF	
Pair	N_H
PVP(C2)-PVP(O1) (bulk)	0.071 (1000 total molecules of PVP)
PVP(C2)-PVP(O1) (1st layer)	0.046 (76 total molecules of PVP)
PVDF(C7)-PVDF(F1) (bulk)	0.083 (1000 total molecules of PVDF)
PVDF(C7)-PVDF(F1) (1st layer)	0.015 (35 total molecules of PVDF)
PVDF(C7)-PVP(O1) (bulk)	0.168 (1000 total molecules of PVP)
PVDF(C7)-PVP(O1) (1st layer)	0.061 (76 total molecules of PVP)
(b) GRAPHITE+PVP:PVDF	
Pair	N_H
PVP(C2)-PVP(O1) (bulk)	0.071 (1000 total molecules of PVP)
PVP(C2)-PVP(O1) (1st layer)	0.040 (75 total molecules of PVP)
PVDF(C7)-PVDF(F1) (bulk)	0.083 (1000 total molecules of PVDF)
PVDF(C7)-PVDF(F1) (1st layer)	0.028 (45 total molecules of PVDF)
PVDF(C7)-PVP(O1) (bulk)	0.165 (1000 total molecules of PVP)
PVDF(C7)-PVP(O1) (1st layer)	0.092 (75 total molecules of PVP)

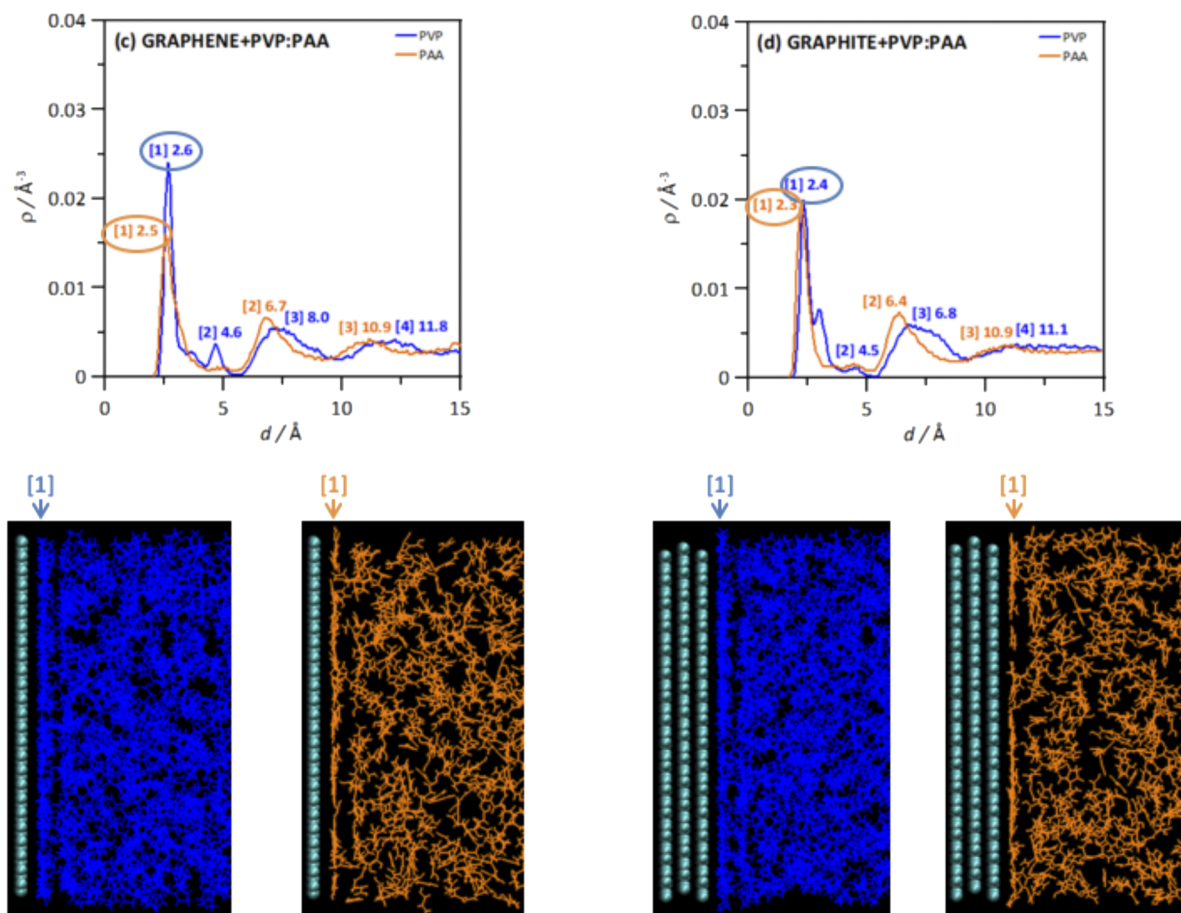


FIG. 5. Number density profiles for the centers of mass of PVP (N1 atom) and PAA (C8 atom) molecules in a perpendicular direction to graphene/graphite for (c) GRAPHENE+PVP:PAA and (d) GRAPHITE+PVP:PAA. Graphene/graphite is placed at $d = 0$. All values are at 293 K. The numbers inside each panel show the d ($\text{\AA}$) corresponding to the maxima. Atom labeling as in Table S1.

PVP, as the maxima at 2.3 and 2.4 $\text{\AA}$ show. In all the adsorbed layers, there is a great competition between PVP and PAA, with PAA roughly closer to the surface than PVP. As in the case of graphene, the concentration for PAA molecules on graphite is similar (number for enrichment is 1, the area on graphite is $0.0104 \text{ \AA}^{-2}$ and on graphene is $0.0102 \text{ \AA}^{-2}$). The planar arrangement of PVP and PAA molecules on graphite in the first adsorbed layer is confirmed in Fig. 6(d), being placed in different regions on top of the graphite surface. However, the reported results on graphite also show some differences in comparison with graphene. A first adsorbed layer is formed by PVP and PAA molecules, with a slightly larger concentration for PVP molecules than on graphene case (number for enrichment is 1.3). The area under peak [1] for PVP on graphite is $0.0115 \text{ \AA}^{-2}$ [Fig. 5(d)] and on graphene is $0.0092 \text{ \AA}^{-2}$ [Fig. 5(c)]. Likewise, PVP and PAA molecules are placed slightly closer to the graphite surface in comparison to the graphene surface [2.3 and 2.4 $\text{\AA}$ for the first maxima reported in Fig. 5(d) vs 2.5 and 2.6 $\text{\AA}$ for the first maxima reported in Fig. 5(c)]. For the rest of the adsorbed layers, this behavior is also observed. Therefore, PVP:PAA monomer

binder blend adsorption from graphite surface leads to better results in terms of slightly higher concentration of PVP and PAA molecules in the first layer and closer interactions.

The kinetics of the development of adsorption layers for PVP:PAA monomer binder blend on both 2D surfaces considered in this work is analyzed through the time evolution of PVP and PAA-graphene/graphite interaction energies reported in Fig. 7. Adsorbed layers are developed in 5 ns both for graphene and graphite surfaces, which show that the structure of adsorbed layers is developed more slowly (slow kinetics compared with the PVP:PVDF monomer binder blend case, 2.5 times slower). This slow adsorption is guided mainly by the much lower affinity of PVP molecules for both 2D surfaces compared with PAA; this effect is quantified by the PVP/PAA-graphene/graphite interaction energies reported in Fig. 7, which are much less favorable for PVP than for PAA in both 2D (the difference is very significant). Comparing graphite with graphene, the PAA-graphite interaction energy is a great deal more favorable [$\sim -3500 \text{ kJ/mol}$ for graphite, Fig. 7(d), and $\sim -2500 \text{ kJ/mol}$ for graphene, Fig. 7(c), much more negative value,

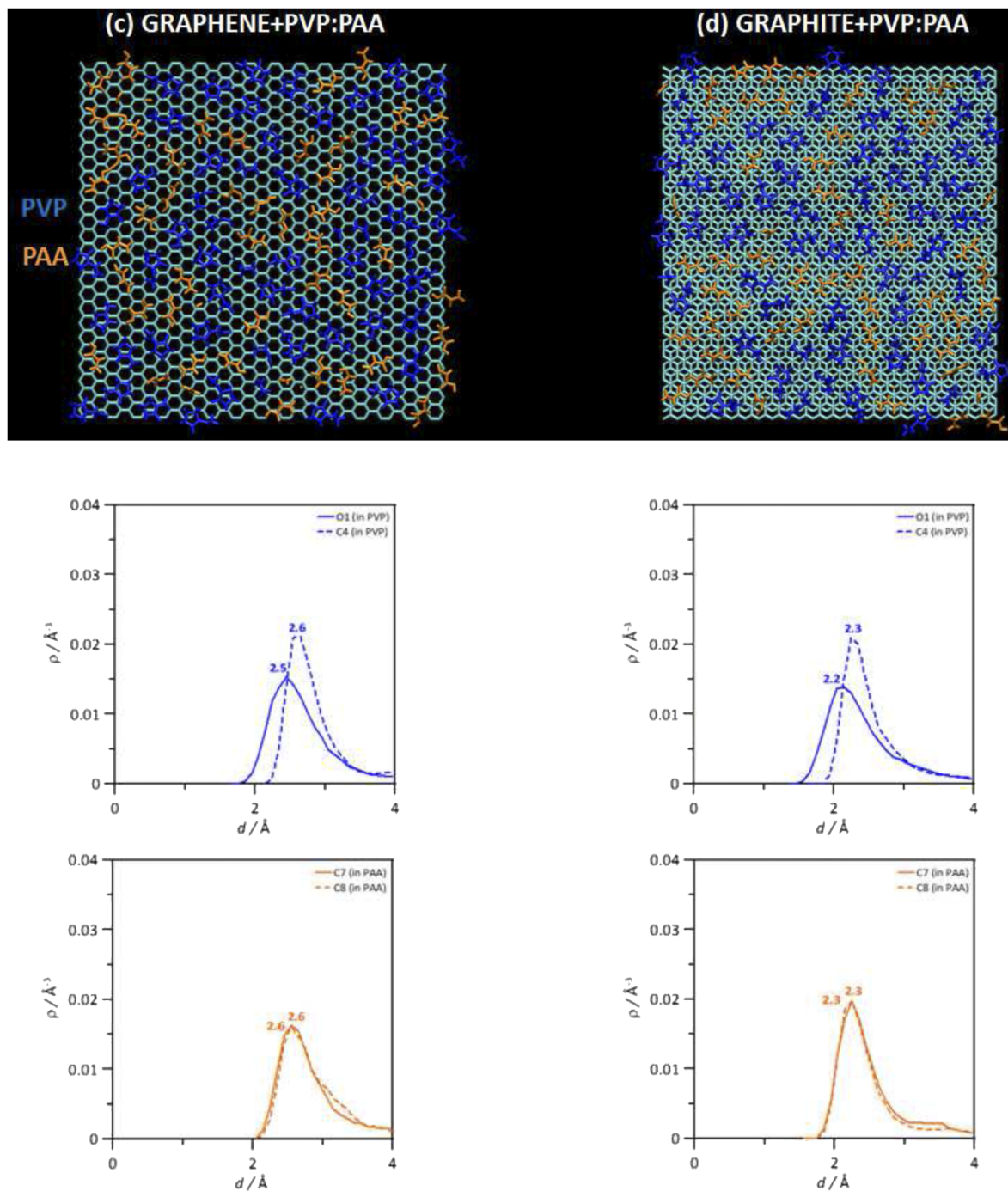


FIG. 6. Distribution of molecules on top of graphene/graphite sheet for the first adsorbed layer in (c) GRAPHENE+PVP:PAA and (d) GRAPHITE+PVP:PAA interfaces at 293 K. The first adsorbed layer is defined according to the density profiles reported in Fig. 5 ($d < 4 \text{\AA}$). Plot at the bottom of each column shows number density profiles for the reported atoms in PVP and PAA in the first adsorbed layer showing parallel (planar) arrangement of PVP and PAA molecules regarding graphene/graphite surface. Atom labeling as in Table S1.

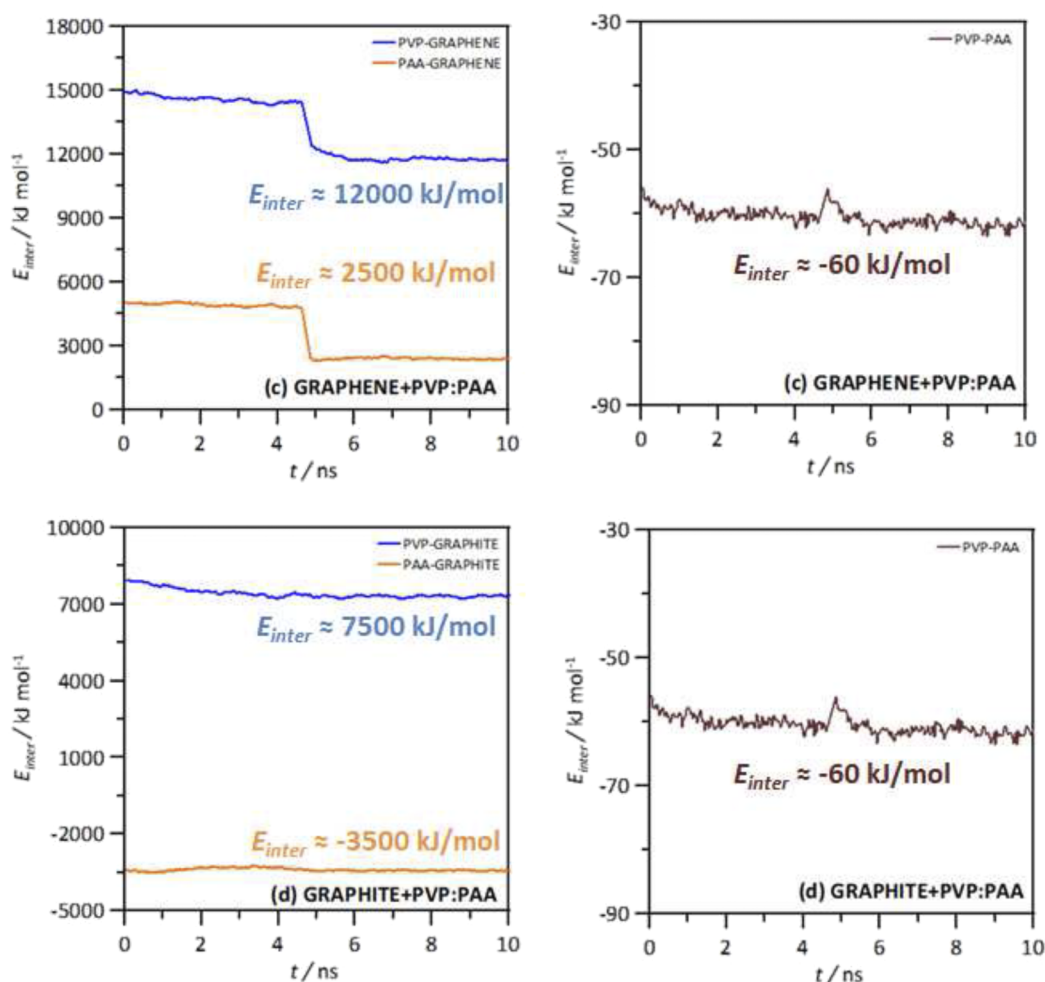


FIG. 7. Simulation time evolution of interaction energy (Electrostatic + Lennard-Jones) between PVP and graphene/graphite (blue color), PAA and graphene/graphite (orange color), and PVP-PAA molecules (dark red color) for (c) GRAPHENE+PVP:PAA and (d) GRAPHITE+PVP:PAA interfaces.

stronger interaction and thus higher affinity], and PVP-graphite interaction energy is around two times as favorable [$\sim 7500 \text{ kJ/mol}$ for graphite, Fig. 7(d), and $\sim 12000 \text{ kJ/mol}$ for graphene, Fig. 7(c)], so PVP/PAA-graphite interactions are more favorable when compared with graphene; it should be remarked that density profiles reported in Fig. 5 showed that PAA and PVP molecules are placed at shorter distances of graphite than graphene (2.3 and $2.4 \text{ \AA}$ for graphite vs 2.5 and $2.6 \text{ \AA}$ for graphene), which also contributes to more favorable interactions. On the other hand, PVP-PAA interaction in the case of graphene is more favorable than that of PVP-graphene and PAA-graphene [interaction energy has a negative sign; it is the most negative energy, $\sim -60 \text{ kJ/mol}$, Fig. 7(c)]. Comparing PVP-graphene and PAA-graphene interaction energies, PAA monomer binder guides adsorption and molecular planarity on graphene (PAA-graphene interaction energy value less positive than PVP-graphene, more favorable interaction, and thus higher affinity between PAA and the 2D surface than between PVP and the 2D surface). In the graphite surface [Fig. 7(d)], no

difference in PVP-PAA interaction energy value is observed with respect to graphene ($\sim -60 \text{ kJ/mol}$). Likewise, comparing PVP-graphite and PAA-graphite interaction energies, the PAA monomer binder also guides adsorption and molecular planarity on graphite surface (in graphite is even more relevant than in graphene due to the large differences in energy, very negative sign vs very positive sign). Therefore, PVP:PAA monomer binder blend over graphite surface leads to more effective adsorption (higher affinity) from the viewpoint of interaction energy and densification upon adsorption.

The structuring of considered PVP and PAA molecules in the first adsorbed layer on both 2D surfaces in comparison with bulk PVP and PAA is analyzed through RDFs reported in Fig. 8. As shown in Fig. 8(c), PVP and PAA molecules in the first adsorbed layer show a more ordered structure in comparison with bulk PVP and PAA, as shown by the increase in intensities of the reported RDFs, leading to a solid-like structure for the layer in direct contact with graphene as in the PVP:PVDF monomer binder blend.

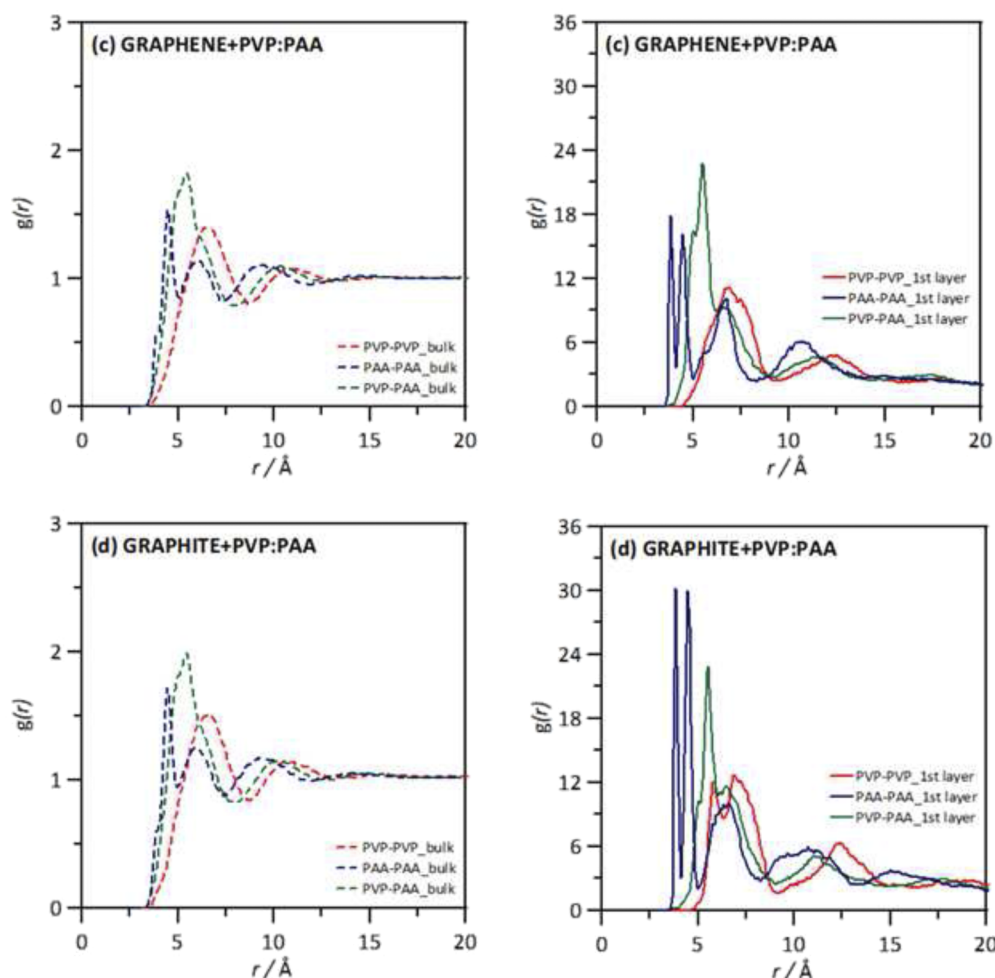


FIG. 8. Center-of-mass RDFs, $g(r)$, for the reported molecular pairs (PVP, N1 atom; PAA, C8 atom) for (c) GRAPHENE+PVP:PAA and (d) GRAPHITE+PVP:PAA interfaces. The first adsorbed layer is defined according to the density profiles reported in Fig. 5 ($d < 4$ Å). All values are at 293 K. Atom labeling as in Table S1.

Nevertheless, the position of maxima for the peaks in RDFs (at 6.5 and 10.8 Å for PVP-PVP; at 4.5, 6.1 and 9.3 Å for PAA-PAA; at 5.4 and 10.3 Å for PVP-PAA) remains constant upon adsorption, and thus the mechanism of interaction between PVP, PAA, and PVP-PAA molecules is the same both in the bulk phase and in the first adsorbed layer. Regarding graphite surface [Fig. 8(d)], PVP and PAA molecules in the first adsorbed layer also show a more ordered structure in comparison with bulk PVP and PAA, and the mechanism of interaction between PVP, PAA, and PVP-PAA molecules is the same both in the bulk phase and in the first adsorbed layer. Moreover, the PVP:PAA monomer binder blends not only bind to both 2D surfaces tight but also preserve their interaction integrity and keep the monomer binder blend properties stable at the interfaces. In addition, the presence of both 2D surfaces does not cause any changes in the interaction mechanisms of the PVP:PAA monomer binder blend. This indicates that the binder blend maintains its stable properties at the interfaces, ensuring tight binding to both surfaces while preserving the integrity of their interactions. The only

difference between graphene and graphite is that PVP and PAA molecules in the first adsorbed layer and in the bulk show a more ordered structure in graphite than in graphene [more intense peaks in Fig. 8(d) than in Fig. 8(c), especially in the first adsorbed layer]. This is probably because increasing the number of carbon layers in graphite compared to graphene also increases the van der Waals-type forces with the monomer binder, leading to stronger interactions followed by larger ordering.

The reported RDFs allow the calculation of PVP and PAA molecules in the solvation spheres around another type of PVP and PAA molecules as reported in Table IV. The reported results reveal a decrease in the number of molecules around each type of molecule for all the considered pairs for both graphene and graphite surfaces on going from the bulk phase to the first adsorbed layer. No significant difference is inferred in the total number of molecules around the first solvation sphere for the PVP-PAA pair in the first adsorbed layer for graphene compared with graphite (3.0 vs 2.9), which agrees with the similar RDF intensity of the PVP-PAA pair in the first

TABLE IV. Number of molecules, N , in the first solvation sphere (defined according to results in Fig. 8) for the reported pairs for (c) GRAPHENE+PVP:PAA and (d) GRAPHITE+PVP:PAA interfaces. All values are at 293 K.

(c) GRAPHENE+PVP:PAA	
Pair	N
PVP-PVP (bulk)	7.9
PVP-PVP (1st layer)	2.9
PAA-PAA (bulk)	1.0
PAA-PAA (1st layer)	0.4
PVP-PAA (bulk)	6.5
PVP-PAA (1st layer)	3.0
(d) GRAPHITE+PVP:PAA	
Pair	N
PVP-PVP (bulk)	8.0
PVP-PVP (1st layer)	3.0
PAA-PAA (bulk)	1.0
PAA-PAA (1st layer)	0.6
PVP-PAA (bulk)	6.6
PVP-PAA (1st layer)	2.9

adsorbed layer for graphite compared with graphene reported in Fig. 8. This can be justified because the total number of PVP and PAA molecules adsorbed on the graphite for the first layer is similar to the total number of molecules adsorbed on the graphene [Fig. 5(d) vs Fig. 5(c)].

As reported in a paper from our group recently,²⁷ the PVP-PAA monomer binder blend develops H-bond type interactions, so analysis of hydrogen bonding in MD simulations considering PVP-PVP, PAA-PAA, and PVP-PAA interactions is another important parameter to consider (Table V). The reported results reveal a decrease in the number of H-bonds formed (on average) for all the considered pairs for graphene and graphite cases on going from the bulk phase to the first adsorbed layer, except the PAA-PAA pair for graphite, where there is an increase. This is mainly due to the appearance of PVP-2D surface and PAA-2D surface interactions in the first adsorbed layer, causing PVP-PVP, PAA-PAA, and PVP-PAA interactions to weaken and resulting in a lower number of H-bonds. The main difference between graphene and graphite surfaces is that in the first layer of PVP and PAA molecules adsorbed on graphite, more H-bonds are formed between PAA molecules, but less H-bonds are formed between the two species (PVP and PAA) than on graphene. More H-bonds between PVP-PAA will lead to other species such as electrolytes not interacting as easily with monomer binder blends for lithium-ion battery device applications.

C. PVP:PVDF/PVP:PAA monomer binder blends on graphene and graphite interfaces (comparison)

In this section, a joint comparison of the results obtained in this adsorption process of both monomer binder blends on graphene and graphite surfaces is made to try to elucidate which of them could be more suitable in binding electrodes during battery manufacturing, depending on the 2D surface to be used.

The dynamic properties of PVP, PVDF, and PAA monomers are analyzed through the self-diffusion coefficients, D (Table VI), calculated from the corresponding Mean Square Displacements

TABLE V. Average number of hydrogen bonds per PVP/PAA molecule, N_H , for the reported atomic pairs (donor-acceptor) in (c) GRAPHENE+PVP:PAA and (d) GRAPHITE+PVP:PAA interfaces, with 3.5 Å and 60° as donor-acceptor distance and angle as hydrogen bonding criteria. The first adsorbed layer is defined according to the density profiles reported in Fig. 5 ($d < 4$ Å). All values are at 293 K. Atom labeling as in Table S1.

(c) GRAPHENE+PVP:PAA	
Pair	N_H
PVP(C2)-PVP(O1) (bulk)	0.057 (1000 total molecules of PVP)
PVP(C2)-PVP(O1) (1st layer)	0.028 (56 total molecules of PVP)
PAA(O2)-PAA(O3) (bulk)	0.255 (1000 total molecules of PAA)
PAA(O2)-PAA(O3) (1st layer)	0.210 (47 total molecules of PAA)
PAA(O2)-PVP(O1) (bulk)	0.653 (1000 total molecules of PVP)
PAA(O2)-PVP(O1) (1st layer)	0.546 (56 total molecules of PVP)
(d) GRAPHITE+PVP:PAA	
Pair	N_H
PVP(C2)-PVP(O1) (bulk)	0.060 (1000 total molecules of PVP)
PVP(C2)-PVP(O1) (1st layer)	0.033 (57 total molecules of PVP)
PAA(O2)-PAA(O3) (bulk)	0.263 (1000 total molecules of PAA)
PAA(O2)-PAA(O3) (1st layer)	0.353 (55 total molecules of PAA)
PAA(O2)-PVP(O1) (bulk)	0.655 (1000 total molecules of PVP)
PAA(O2)-PVP(O1) (1st layer)	0.445 (57 total molecules of PVP)

TABLE VI. Self-diffusion coefficients (calculated from MSDs using Einstein's equation), D , for PVP, PVDF, and PAA molecules in (a) GRAPHENE+PVP:PVDF, (b) GRAPHITE+PVP:PVDF, (c) GRAPHENE+PVP:PAA, and (d) GRAPHITE+PVP:PAA bulk interfaces at 293 K. Values are calculated for corresponding centers of mass.

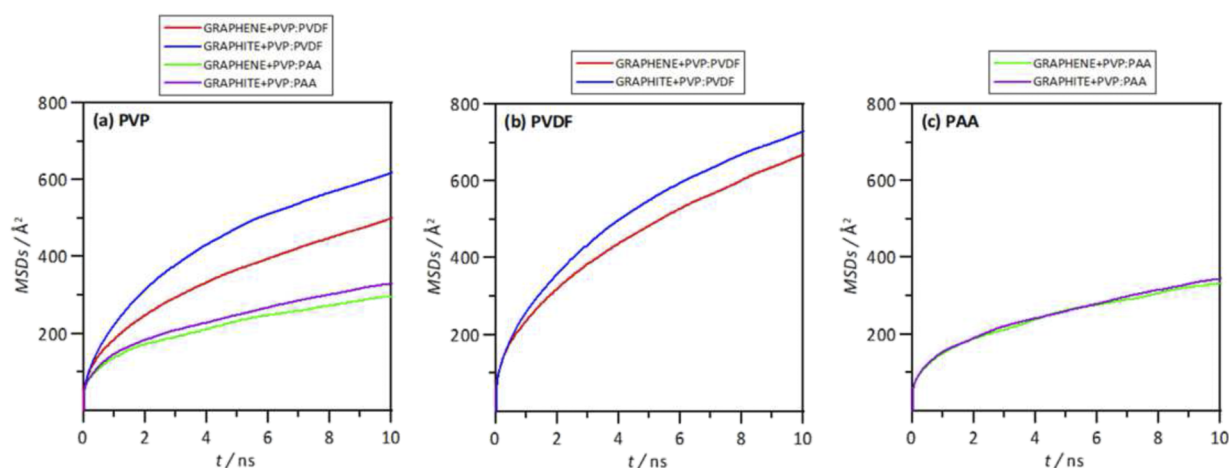
(a) GRAPHENE+PVP:PVDF	
Molecule	$10^{-6} D \text{ (m}^2 \text{ s}^{-1}\text{)}$
PVP	3.53
PVDF	4.87
(b) GRAPHITE+PVP:PVDF	
Molecule	$10^{-6} D \text{ (m}^2 \text{ s}^{-1}\text{)}$
PVP	4.29
PVDF	5.45
(c) GRAPHENE+PVP:PAA	
Molecule	$10^{-6} D \text{ (m}^2 \text{ s}^{-1}\text{)}$
PVP	3.32
PAA	3.81
(d) GRAPHITE+PVP:PAA	
Molecule	$10^{-6} D \text{ (m}^2 \text{ s}^{-1}\text{)}$
PVP	2.53
PAA	2.65

(MSDs) and the Einstein's equation. Calculated values of MSDs are reported in Fig. 9, showing proper, fully diffusive behavior, which was also verified through log-log plots of MSDs vs time leading to slopes in the 0.98–1 range. The reported results show that PVP and

PVDF monomers in the PVP:PVDF monomer binder blend have a higher molecular mobility than PVP and PAA monomers in the PVP:PAA monomer binder blend on both graphene and graphite surfaces. The ordering of diffusion rates for PVP, PVDF, and PAA on both graphene and graphite surfaces is PVP (PVP:PVDF monomer binder blend) > PVP (PVP:PAA monomer binder blend); PVDF (PVP:PVDF monomer binder blend) > PAA (PVP:PAA monomer binder blend). This demonstrates that the structure of adsorbed layers of the PVP:PVDF monomer binder blend on graphene and graphite is developed more quickly in comparison with PVP:PAA (faster kinetics for the PVP:PVDF blend than for PVP:PAA), in agreement with the E_{inter} behavior reported in Figs. 3 and 7.

In the case of graphene, the PVP:PAA monomer binder blend gives better results than PVP:PVDF from the viewpoint of interaction energies (much favorable interactions), densification upon adsorption (stronger competition between PVP and PAA molecules in all adsorbed layers), more ordered structure (higher intensities of the RDFs for all molecular pairs in PVP:PAA monomer binder blend both in the bulk and in the first adsorbed layer), and much more H-bonds formed between monomer binder species (the PVP:PAA monomer binder will not allow other species such as the electrolyte to interact as easily with graphene surface). It is also true that the PVP:PAA monomer binder blend gives worse results than PVP:PVDF from the kinetic viewpoint (slower kinetics). However, overall, the PVP:PAA blend is considered to be more suitable in binding electrodes during battery manufacturing over graphene surface.

In the case of graphite, the PVP:PAA monomer binder blend also gives better results than PVP:PVDF from the viewpoint of interaction energies (much favorable interactions, specially PAA-graphite compared with PVDF-graphite), densification upon adsorption (stronger competition between PVP and PAA molecules in all adsorbed layers), more ordered structure (higher intensities of the RDFs for all molecular pairs in PVP:PAA monomer binder blend both in the bulk and in the first adsorbed layer) and much

**FIG. 9.** Mean square displacements, MSDs, for (a) PVP, (b) PVDF, and (c) PAA molecules in GRAPHENE+PVP:PVDF, GRAPHITE+PVP:PVDF, GRAPHENE+PVP:PAA, and GRAPHITE+PVP:PAA bulk interfaces at 293 K.

more H-bonds formed between monomer binder species (PVP:PAA monomer binder will not allow other species such as the electrolyte to interact as easily with graphite surface). It is also true that PVP:PAA blend gives worse results than PVP:PVDF from the kinetic viewpoint (slower kinetics). However, overall, the PVP:PAA monomer binder is also considered to be more suitable in binding electrodes during battery manufacturing over graphite surface.

Finally, comparing both surfaces for PVP:PAA monomer binder blend (as explained in detail in Sec. III B), graphite gives better results than graphene from the viewpoint of interaction energies, densification upon adsorption, and more ordered structure. Similar H-bonds are formed between monomer binder blend species in both surfaces (so PVP:PAA monomer binder blends will not allow other species such as the electrolyte to interact as easily with graphite). Therefore, PVP:PAA monomer binder blends on graphite surface would be the best option (among those studied in this work) for the design of battery-optimized energy devices.

IV. CONCLUSIONS

The behavior of two different mixtures of monomers of PVP-based battery binders (PVP:PVDF and PVP:PAA) at graphene and graphite interfaces was studied using MD simulations, and the best performing monomer binder blend (PVP:PAA) and carbon-based material (graphite) from the viewpoint of interaction energies, densification upon adsorption, and more ordered structure has been identified accordingly for the design of battery-optimized energy devices. The ordered structure of the adsorbed PVP, PVDF, and PAA layers on graphene and graphite surfaces is influenced by the competition between enthalpy and entropy.^{36–40} The enthalpic contribution to the adsorption process comes from the formation of intermolecular interactions between the PVP/PVDF/PAA monomer binder and the 2D surface, which can be either attractive or repulsive in nature. In the case of PVP-graphene/graphite, PVDF-graphene/graphite, and PAA-graphene intermolecular interaction energies, E_{inter} , all of them have a positive sign, so these interactions are repulsive. However, in the case of PAA-graphite intermolecular interaction energy, E_{inter} , it has a negative sign, so this interaction is attractive (is the most favorable one and thus there is higher affinity between PAA monomer binder and graphite surface). On the other hand, the conformational entropy of the PVP, PVDF, and PAA chains is reduced when they are adsorbed on graphene and graphite surfaces because they lose their freedom to move and explore different conformations (as demonstrated by the formation of planar arrangements of PVP, PVDF, and PAA monomeric molecules regarding graphene/graphite surface in the first adsorbed layer). Other important properties such as electrical conductivity, which is important for computationally guided discovery of novel materials with desired electrical properties, or the selection of the optimal ratio of monomer binder blends in the electrode, also crucial to facilitate the electrochemical reactions that are necessary to deliver electrical energy, have not been considered in this work because they were not the priority objective. In any case, they should be considered in future works for more realistic applications. Monomer binder blends are strongly adsorbed on both 2D surfaces adopting parallel arrangements regarding the surfaces, leading to layering and solid-like densification from both PVP:PVDF and PVP:PAA

monomer binder blends. In the case of PVP:PVDF, four adsorption layers of both PVP and PVDF monomer binders on graphene and graphite surfaces following an oscillating damping behavior for number density profiles were formed, with PVP and PVDF occupying different regions on top of the graphene and graphite and with PVP molecules placed slightly closer to the 2D surfaces in comparison with PVDF. The interfaces of PVP:PAA monomer binder blend were characterized by three adsorption layers of both PVP and PAA monomer binder on graphene and graphite surfaces, also following an oscillating damping behavior, with PVP and PAA molecules occupying different regions on top of the 2D surfaces and with PAA placed slightly closer in comparison with PVP. The adsorption of PVP:PVDF monomer binder blend is guided by the higher affinity of PVP molecules for both surfaces compared with PVDF. However, in PVP:PAA monomer binder blend, this adsorption process is guided by the much higher affinity of PAA molecules for both surfaces compared with PVP. Furthermore, the structure of adsorbed layers of PVP:PVDF monomer binder blend on graphene and graphite is developed more quickly in comparison with PVP:PAA (faster kinetics for PVP:PVDF monomer binder blend than for PVP:PAA). These presented MD results complemented the previous DFT studies carried out by our group recently²⁷ and contributed to understand in depth the main nanoscopic features of relevant interfacial regions involving some monomer binder blends and different carbon-based materials such as graphene and graphite. The effect of a blend of commonly used binders on carbon-based materials is essential for obtaining tightly bound anode and cathode active materials in LIBs in order to design battery-optimized energy devices.

SUPPLEMENTARY MATERIAL

The systems used for molecular dynamics simulations considering the interfaces of interest are presented in the supplementary material (Table S1).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Alberto Gutiérrez: Formal analysis (equal); Methodology (equal); Software (equal); Writing – original draft (equal); Writing –

review & editing (equal). **Santiago Aparicio**: Conceptualization (equal); Resources (equal). **Alexandra Pekarovicova**: Conceptualization (equal); Investigation (equal). **Qingliu Wu**: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Resources (equal). **Mert Atilhan**: Conceptualization (equal); Data curation (equal); Methodology (equal); Project administration (equal); Resources (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article [and its supplementary material].

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