

Article

Unveiling the Lubrication Mechanism of Graphene Coating on PEEK: A Molecular Dynamics Study Under Dry Friction and Seawater

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Abstract

Graphene coatings have considerable potential to improve the tribological performance of polyetheretherketone (PEEK) under dry friction conditions. For PEEK components operating in marine environments, direct exposure to seawater introduces water molecules and dissolved ions into the sliding interface, which may alter interfacial interactions and lubrication behavior. However, how seawater alters the lubrication mechanism and protective effect of graphene at the PEEK interface remains poorly understood. To address this issue, molecular dynamics simulations were performed to compare PEEK with and without graphene under dry and seawater conditions, thereby revealing the interfacial deformation and molecular response. The results show that graphene preserved the structural integrity of PEEK, reduced its tangential displacement by more than 99%, and decreased the shear stress transmitted into the polymer matrix by approximately 85% to 90%. In the absence of graphene, seawater reduced the tangential mean square displacement of PEEK by approximately 20%, while increasing the normal mean square displacement by about 17%, indicating that seawater redistributed part of the polymer motion from tangential dragging toward normal and local molecular rearrangement. The combined analysis shows that graphene mainly limits the penetration of sliding loads into PEEK, whereas seawater regulates the direction and spatial distribution of the remaining deformation. This work provides a molecular basis for the design of graphene-protected PEEK interfaces in marine friction applications.

Keywords: MD simulation; seawater; PEEK; graphene; friction



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1. Introduction

Polymer-based materials have garnered significant attention in tribological applications due to their exceptional strength-to-weight ratio, inherent corrosion resistance, and design flexibility [1,2]. Among them, polyetheretherketone (PEEK) stands out as a high-performance thermoplastic that exhibits outstanding thermal stability, mechanical robustness, and superior wear resistance, making it an ideal candidate for critical components such as bearings, seals, and gears in aerospace, automotive, and marine engineering [3–5]. Despite these advantages, the practical application of pristine PEEK in harsh sliding environments is often constrained by its relatively high friction coefficient and severe adhesive/abrasive wear under high contact pressures and elevated temperatures [6,7].

Consequently, enhancing the tribological performance of PEEK without compromising its bulk properties remains a pivotal challenge in surface engineering.

Surface modification, particularly the deposition of solid lubricant coatings, has been established as an effective strategy to tailor the friction and wear behavior of polymers [8,9]. Layered materials such as MoS₂ have been widely studied as solid lubricants because their weak interlayer interactions facilitate shear during friction [10]. Under comparable loading conditions, atomistic simulations have revealed distinct deformation and wear responses of MoS₂ and graphene coatings [11,12]. Among these layered materials, graphene has attracted considerable attention because of its high mechanical strength and low interlayer shear resistance [13].

Recent experimental studies have demonstrated that incorporating graphene as a coating or filler can significantly reduce the coefficient of friction (COF) and wear rate of polymer matrices [14–16]. For example, Bashandeh et al. [17] demonstrated that the addition of graphene nanoplatelets to polymer coatings effectively reduced both the friction coefficient and wear rate under dry sliding conditions, highlighting the lubricating potential of graphene in solid-lubricant composite systems. Chih et al. [18] reported that graphene nanoplatelet (GNP) coatings on ultra-high-molecular-weight polyethylene (UHMWPE) significantly reduced friction by up to 40% compared to the pristine polymer under dry sliding conditions. This improvement is primarily attributed to the formation of a protective transfer film at the sliding interface and the facile interlayer sliding of graphene sheets, which effectively diminishes the direct contact between the counterface and the polymer substrate.

However, the majority of existing research on graphene-reinforced PEEK composites has been conducted under ambient or dry sliding conditions, with a predominant focus on macroscopic experimental observations. The microscopic mechanisms governing the lubricating action of graphene coatings, especially under complex service environments, remain poorly understood [19]. In particular, marine environments introduce a distinct set of interfacial physicochemical interactions [20]. Water molecules and dissolved ions in seawater can enter the sliding interface, potentially altering the adhesion strength between the graphene coating and the PEEK substrate, modifying the charge distribution at the contact zone, and even inducing tribochemical reactions [21,22]. Within nanoscale sliding contacts, confined water molecules can participate directly in the local frictional response rather than acting solely as a surrounding medium [23]. These environmental factors are expected to fundamentally alter the tribological response of the graphene coating compared to dry conditions. Currently, a systematic molecular-scale comparison of the lubrication efficacy of graphene coatings on PEEK under dry sliding versus seawater-lubricated conditions is conspicuously absent in the literature.

Molecular dynamics (MD) simulation [24,25] offers a powerful computational tool to probe the atomic-scale evolution of friction interfaces, providing dynamic insights into energy dissipation, atomic migration, and structural transformation that are inaccessible through conventional experiments. Recent developments such as Normal Dynamics have further expanded the available approaches for atomistic simulation by reformulating atomic motion in reciprocal space and enabling selective sampling to reduce computational cost in suitable systems [26]. In view of the unresolved mechanisms of graphene lubrication on polymer surfaces, especially under different environments, MD simulation is used here to examine the interfacial response directly.

In this work, we construct a sliding contact model of a graphene coating on a PEEK substrate and investigate its tribological behavior under four conditions: with and without graphene under dry and seawater conditions. This comparative framework enables the effects of graphene and seawater on the interfacial response of PEEK to be distinguished.

Our aim is to reveal the microscopic lubrication mechanism of graphene, clarify how seawater modifies its protective effect, and evaluate the environmental dependence of the graphene coating. These findings provide a molecular basis for the design of PEEK-based components in marine and other demanding applications.

2. Materials and Methods

2.1. Force Fields and Interatomic Potentials

All molecular dynamics (MD) simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS, 22 July 2025) [27]. A hybrid pair_style was used to describe the different interactions in the system. The PEEK polymer was modeled using the OPLS-AA (Optimized Potentials for Liquid Simulations All-Atom) force field [28–30], which has been widely validated for aromatic polymers. Water molecules were described by the TIP4P/2005 model [31], while Na^+ and Cl^- ions were parameterized using the OPLS force field to ensure consistency with the aqueous environment [32]. The interfacial interactions between the organic/inorganic components (PEEK–graphene, graphene–Fe, and PEEK–Fe) were described by the Interface Force Field (IFF) [33], which is specifically designed to accurately capture non-bonded interactions at organic–inorganic interfaces. Graphene’s intramolecular C–C bonds and angle interactions were modeled using the adaptive intermolecular reactive empirical bond order (AIREBO) potential [34], which properly accounts for the covalent bonding network within the graphene sheets. The Fe substrate was modeled using the embedded atom method (EAM) potential [35], suitable for describing metallic bonding in the iron lattice. Lorentz–Berthelot mixing rules were applied for all cross-interactions between dissimilar atom types. Long-range electrostatic interactions were evaluated using the particle–particle particle–mesh (PPPM) method with a tolerance of 1.0×10^{-4} [36]. A cutoff distance of 10.0 Å was applied to the van der Waals interactions and the real-space contribution of the Coulombic interactions, consistent with previous TIP4P/2005-based molecular dynamics simulations [37], while the remaining long-range electrostatic contribution was treated using PPPM.

2.2. Model Construction

The simulation model consisted of four distinct components: a PEEK substrate, a graphene coating, a seawater layer, and an Fe counterface (Figure 1). The PEEK block was constructed with dimensions of approximately $100 \text{ Å} \times 60 \text{ Å} \times 35 \text{ Å}$, containing 10 repeating units per chain with a total of 8 polymer chains, using the amorphous builder in the PACKMOL (version 21.2.3) package [38]. The graphene layer, composed of 2 stacked monolayers with dimensions matching the PEEK surface, was placed directly on top of the PEEK substrate. The seawater layer contained TIP4P/2005 water molecules and Na^+/Cl^- ions at a salinity of approximately 3.5 wt%, providing a simplified representation of natural seawater [39,40]. A layer approximately 1 nm thick was positioned above the graphene coating to represent the nanoconfined aqueous environment at the sliding interface. The Fe counterface, consisting of a body-centered cubic (BCC) lattice oriented along the (001) plane, was placed above the seawater layer. The four systems are denoted as SW-Gr/PEEK, SW-PEEK, Dry-Gr/PEEK, and Dry-PEEK, where SW and Gr represent seawater and graphene, respectively.

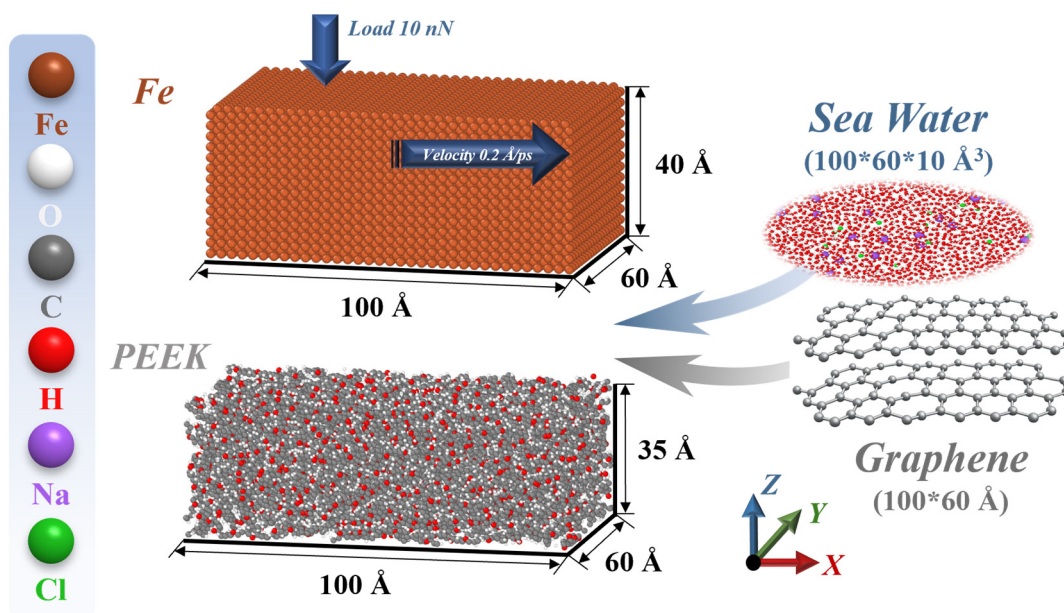


Figure 1. Schematic of the MD simulation models.

2.3. Simulation Protocol

All simulations were performed under periodic boundary conditions in the x and y directions, with a fixed boundary in the z direction. The initial configuration was energy-minimized using the conjugate gradient algorithm. The system was then heated from 10 K to 300 K over 100 ps using a Langevin thermostat with the microcanonical (NVE) ensemble, followed by 100 ps of equilibration in the isothermal–isobaric (NPT) ensemble at 300 K and 1 atm using a Nosé–Hoover thermostat and barostat. During equilibration, the PEEK substrate and Fe counterface were rigidly constrained.

For the friction simulations, the bottom layers of the PEEK substrate and the top layer of the Fe counterface were fixed to serve as the supporting base and sliding driver, respectively. A constant normal load of 10 nN was applied to the Fe counterface, while the middle portion of the PEEK substrate and the seawater layer were maintained at 300 K using a Nosé–Hoover thermostat. Frictional energy generated near the sliding interface was transferred to these mobile regions and dissipated through the thermostat, which acted as a thermal reservoir to prevent artificial heat accumulation in the finite simulation cell. Sliding was initiated by moving the Fe counterface along the x direction at a constant velocity of 0.2 Å/ps for 500 ps. The 500 ps friction period was used to resolve the short-time response of the interface, including load transfer, molecular motion, and structural deformation within the time scale accessible to atomistic molecular dynamics simulation, rather than to represent the complete long-term viscoelastic response of bulk PEEK.

3. Results

3.1. Macroscopic Deformation and Spatial Evolution of PEEK During Friction

Figure 2 compares the average COF of the four systems during the steady friction stage. Dry-PEEK exhibited the highest average COF of approximately 0.67, which decreased to about 0.13 after the introduction of graphene. Under seawater conditions, the average COF decreased from approximately 0.28 for SW-PEEK to only about 0.02 for SW-Gr/PEEK. Accordingly, graphene reduced the average COF by approximately 81% under dry conditions and by more than 90% in seawater. Seawater also reduced the friction response of PEEK in both the presence and absence of graphene, indicating that the aqueous environment further facilitates interfacial sliding. The pronounced decrease in COF after introducing

graphene is consistent with the displacement and stress responses discussed below, suggesting that graphene effectively limits the transmission of tangential motion and shear loading into the PEEK substrate.

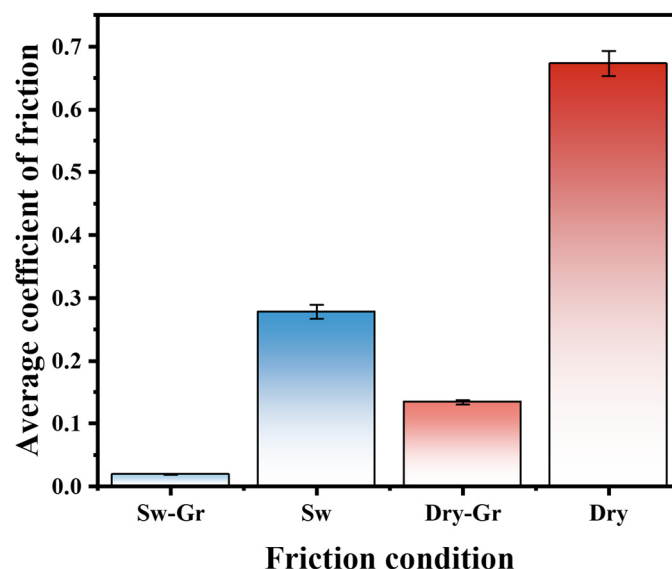


Figure 2. Average COF of the four systems during steady friction.

Figure 3 shows the final configurations of the PEEK surface under seawater and dry conditions with and without the graphene interlayer. As shown in Figure 3a, the SW-Gr/PEEK system largely retained the initial block-like morphology of the PEEK substrate, while the graphene sheet extended approximately 53.5 Å beyond the original edge. The absence of pronounced forward pile-up indicates that the continuous graphene layer accommodated a considerable portion of the tangential displacement through interfacial sliding and in-plane deformation, thereby limiting the direct transfer of shear motion into the PEEK matrix. In Figure 3b, removing graphene led to substantial forward displacement and upward accumulation of the PEEK chains, producing a wedge-shaped deformation region with an inclination angle of approximately 49°. This morphology suggests that direct interaction with the counterface transferred the sliding motion into the polymer, causing chain dragging and simultaneous redistribution in the tangential and normal directions.

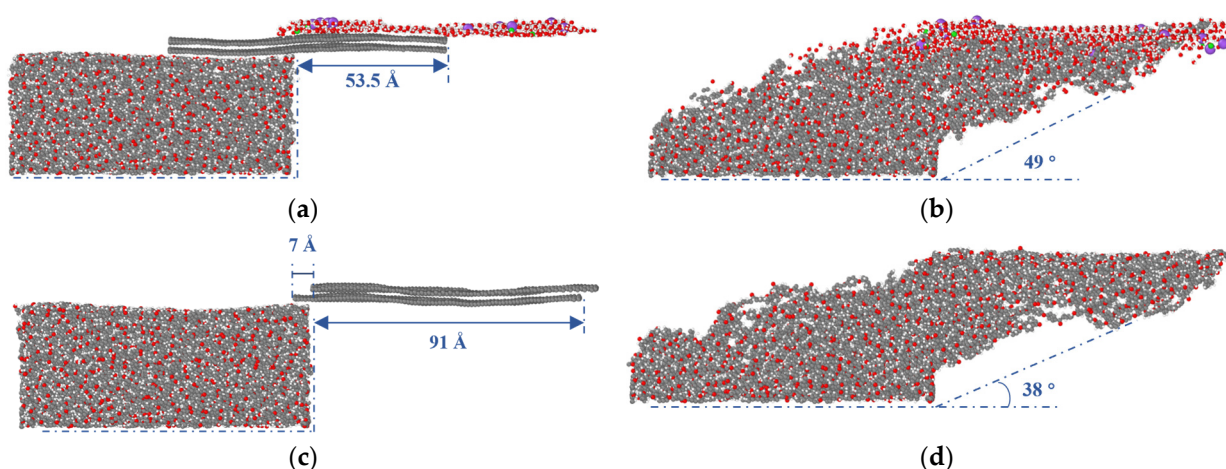


Figure 3. Final configurations and deformation characteristics of the PEEK: (a) SW-Gr/PEEK, (b) SW-PEEK, (c) Dry-Gr/PEEK, and (d) Dry-PEEK.

Under dry conditions, Figure 3c shows that the graphene sheet extended approximately 91 Å and exhibited an upward deflection of about 7 Å near the original PEEK edge. Compared with SW-Gr/PEEK, the extension distance increased by approximately 70.1%. Equivalently, seawater reduced the dragged graphene length by about 41.2%. Without interfacial water, the more direct interaction between graphene and PEEK allowed the friction-induced traction to propagate farther along the graphene sheet. The local upward deflection reflects partial separation caused by competition between interfacial adhesion and tangential pulling. As shown in Figure 3d, the Dry-PEEK system also developed a pronounced forward pile-up, but its inclination angle was approximately 38°, which was 11° lower than that of SW-PEEK. The steeper deformation front in seawater therefore does not necessarily indicate a larger total deformation; instead, it suggests that seawater altered the partitioning of polymer motion by promoting more localized upward rearrangement, whereas the dry interface produced a broader and flatter region dominated by forward chain dragging.

Figure 4 shows the evolution of the mean square displacement (MSD) of PEEK in the friction and normal directions. The MSD reflects the combined contribution of the overall translation and local rearrangement of the PEEK chains. As shown in Figure 4a, the MSD in the friction direction increased continuously in the two systems without graphene, particularly after approximately 100 ps. At 500 ps, the X-direction MSD reached approximately $1.40 \times 10^3 \text{ Å}^2$ for Dry-PEEK and $1.12 \times 10^3 \text{ Å}^2$ for SW-PEEK. The presence of seawater therefore reduced the tangential displacement by approximately 20%, indicating that the confined liquid partially weakened the direct dragging of PEEK by the counterface. Water molecules accommodated part of the relative motion through interfacial rearrangement, thereby decreasing the proportion of sliding displacement transmitted directly into the polymer matrix. In contrast, the X-direction MSD of the two graphene-containing systems remained below approximately 1.1 Å^2 throughout the friction process, as shown more clearly in the inset of Figure 4a. The final values were approximately 1.0 Å^2 for Dry-Gr/PEEK and 0.6 Å^2 for SW-Gr/PEEK. The continuous graphene sheet therefore acted as an interfacial sliding plane that accommodated tangential displacement while limiting the long-range translation and internal dragging of the PEEK chains. The lower MSD of SW-Gr/PEEK than that of Dry-Gr/PEEK further indicates that seawater reduced the residual motion transmitted across the graphene-PEEK interface.

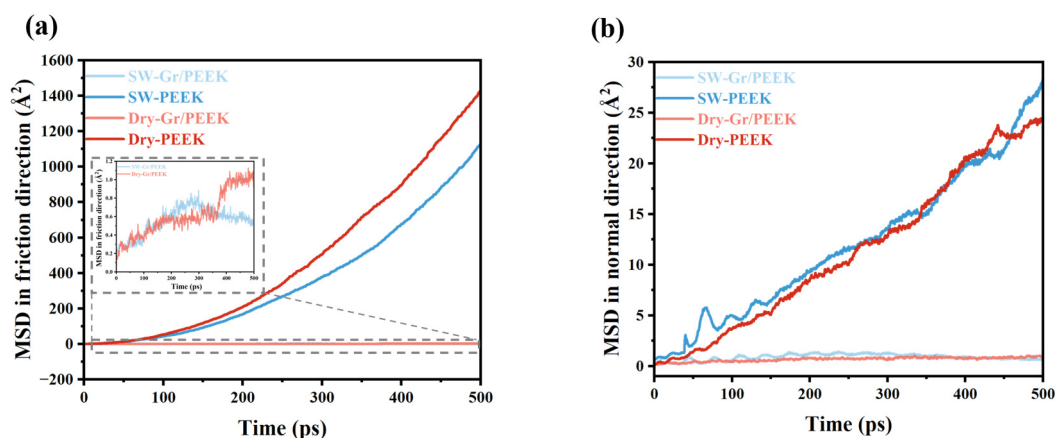


Figure 4. Evolution of the MSD of PEEK in the (a) friction and (b) normal directions.

As shown in Figure 4b, the normal MSD exhibited a different trend. In the absence of graphene, the Z-direction MSD of SW-PEEK showed pronounced oscillations during the initial stage and subsequently increased to approximately 28 Å^2 at 500 ps, whereas that of Dry-PEEK reached approximately 24 Å^2 . Thus, although seawater reduced the tangential

MSD by approximately 20%, it increased the final normal MSD by approximately 17%. This directional difference indicates that seawater did not simply suppress the mobility of PEEK. Instead, it redistributed part of the sliding-induced motion from continuous tangential dragging to normal compression, recovery, and upward chain rearrangement. This behavior is consistent with the steeper pile-up region observed for SW-PEEK in Figure 3b. In the systems with graphene, the normal MSD remained close to $1 \text{ \AA}^2$, representing a reduction of more than 96% relative to the systems without graphene. Graphene therefore restricted not only the tangential translation of PEEK but also the normal rearrangement of the polymer chains. By separating the PEEK matrix from direct interaction with the counterface and accommodating interfacial displacement through its own deformation and sliding, graphene confined the structural response to a narrower interfacial region and prevented the large-scale displacement observed in the unprotected PEEK systems.

Figure 5 shows the evolution of the PEEK center of mass (COM) in the friction and normal directions, which distinguishes the collective translation of the polymer matrix from the atomic-scale mobility characterized by the MSD in Figure 4. As shown in Figure 5a, the COM displacement increased continuously in the two systems without graphene. At 500 ps, Dry-PEEK exhibited a displacement of approximately $52.5 \text{ \AA}$, whereas the corresponding value for SW-PEEK was approximately $44.5 \text{ \AA}$. The presence of seawater therefore reduced the collective tangential translation of PEEK by approximately 15.2%. This reduction indicates that molecular rearrangement within the confined seawater layer accommodated part of the relative sliding motion and weakened the direct mechanical coupling between the counterface and the PEEK chains. Nevertheless, the continuously increasing displacement of SW-PEEK shows that seawater alone was insufficient to prevent the sliding motion from propagating into the polymer matrix. In contrast, the COM displacements of SW-Gr/PEEK and Dry-Gr/PEEK remained close to $0 \text{ \AA}$ throughout the friction process, with fluctuations generally confined within approximately $0.5 \text{ \AA}$. Compared with the corresponding systems without graphene, the collective tangential motion of PEEK was suppressed by more than 99%. The continuous graphene sheet therefore separated the PEEK matrix from direct tangential dragging and accommodated the imposed displacement through interfacial sliding and its own in-plane deformation. This markedly restricted the conversion of counterface motion into coherent translation of the polymer, consistent with the preserved block-like morphology observed in Figure 3a,c.

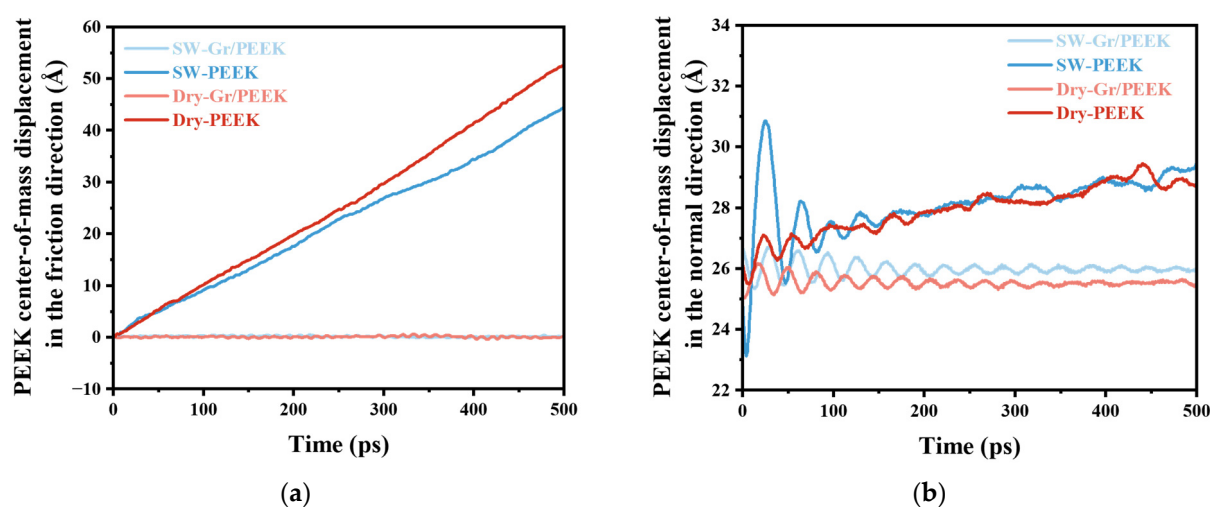


Figure 5. Evolution of the PEEK center of mass in the (a) friction and (b) normal directions.

As shown in Figure 5b, the normal COM position exhibited a markedly different response. SW-PEEK underwent the strongest initial oscillation, decreasing to

approximately 23 Å and subsequently reaching a transient peak of about 30.8 Å within the first 30 ps. The oscillation gradually decayed, after which its COM increased to approximately 29.3 Å at 500 ps. Dry-PEEK showed a smaller initial fluctuation and reached a final position of approximately 28.8 Å. The final COM position of SW-PEEK was therefore about 0.5 Å higher than that of Dry-PEEK, indicating that seawater reduced the tangential dragging of PEEK while promoting a greater proportion of normal rearrangement. The pronounced initial fluctuation arose from the rapid redistribution of water molecules and polymer chains under the applied normal load, while the subsequent upward shift corresponded to the development of the steeper pile-up structure shown in Figure 3b. The normal COM positions of SW-Gr/PEEK and Dry-Gr/PEEK stabilized at approximately 26.0 and 25.5 Å, respectively, after the initial damped oscillations. These values were approximately 3.3 Å lower than those of the corresponding systems without graphene at the end of sliding. By preventing direct penetration and dragging of the counterface into the PEEK surface, graphene confined the normal structural adjustment to the interfacial region and limited the upward redistribution of the polymer chains.

Figure 6 shows the number-density distributions of PEEK along the normal direction. As shown in Figure 6a, the lower boundary of PEEK in the SW-Gr/PEEK system remained at approximately 10 Å throughout the simulation. The dense region near the upper surface initially oscillated between approximately 38 and 42 Å. Its oscillation gradually weakened, and the upper boundary stabilized near 39–40 Å after about 150 ps. The overall thickness of the PEEK layer therefore remained close to 30 Å. The initial oscillation reflects the compression and recovery of the surface chains under the normal load, while graphene limited this adjustment to the region close to the sliding interface. As shown in Figure 6b, SW-PEEK exhibited a broader density distribution near the upper surface. The upper boundary rapidly expanded from approximately 40 Å to nearly 45 Å during the initial stage and subsequently remained close to this position. Compared with SW-Gr/PEEK, the thickness occupied by PEEK increased by approximately 5 Å, corresponding to an increase of about 17% relative to its initial thickness. Without graphene, the motion imposed by the counterface was transferred directly into the polymer, causing the surface chains to move upward and occupy a wider region along the normal direction. The rapid expansion during the initial stage also indicates that the seawater layer promoted local molecular rearrangement under the applied load, although it reduced the continuous tangential motion of PEEK, as observed in Figures 4 and 5.

As shown in Figure 6c, the density evolution of Dry-Gr/PEEK was similar to that of SW-Gr/PEEK. The upper boundary underwent several oscillations during the initial stage and then stabilized near 39–40 Å, while the lower boundary remained at approximately 10 Å. The nearly constant distance between the two boundaries indicates that the PEEK matrix retained its original thickness during dry sliding. Although the graphene sheet extended farther along the friction direction under dry conditions, its continuous coverage prevented this motion from producing substantial upward migration of the underlying PEEK chains. As shown in Figure 6d, the upper boundary of Dry-PEEK gradually shifted from approximately 40 Å to 44–45 Å as sliding proceeded. Different from the rapid and relatively dispersed expansion observed in SW-PEEK, the upward movement in Dry-PEEK developed progressively and produced a more concentrated, dense region near the upper boundary. In the absence of both seawater and graphene, direct interaction with the counterface continuously transferred tangential traction into the PEEK matrix. The surface chains were therefore dragged forward and progressively accumulated in the normal direction, consistent with the broad pile-up structure in Figure 3d and the continuously increasing center-of-mass displacement in Figure 5a.

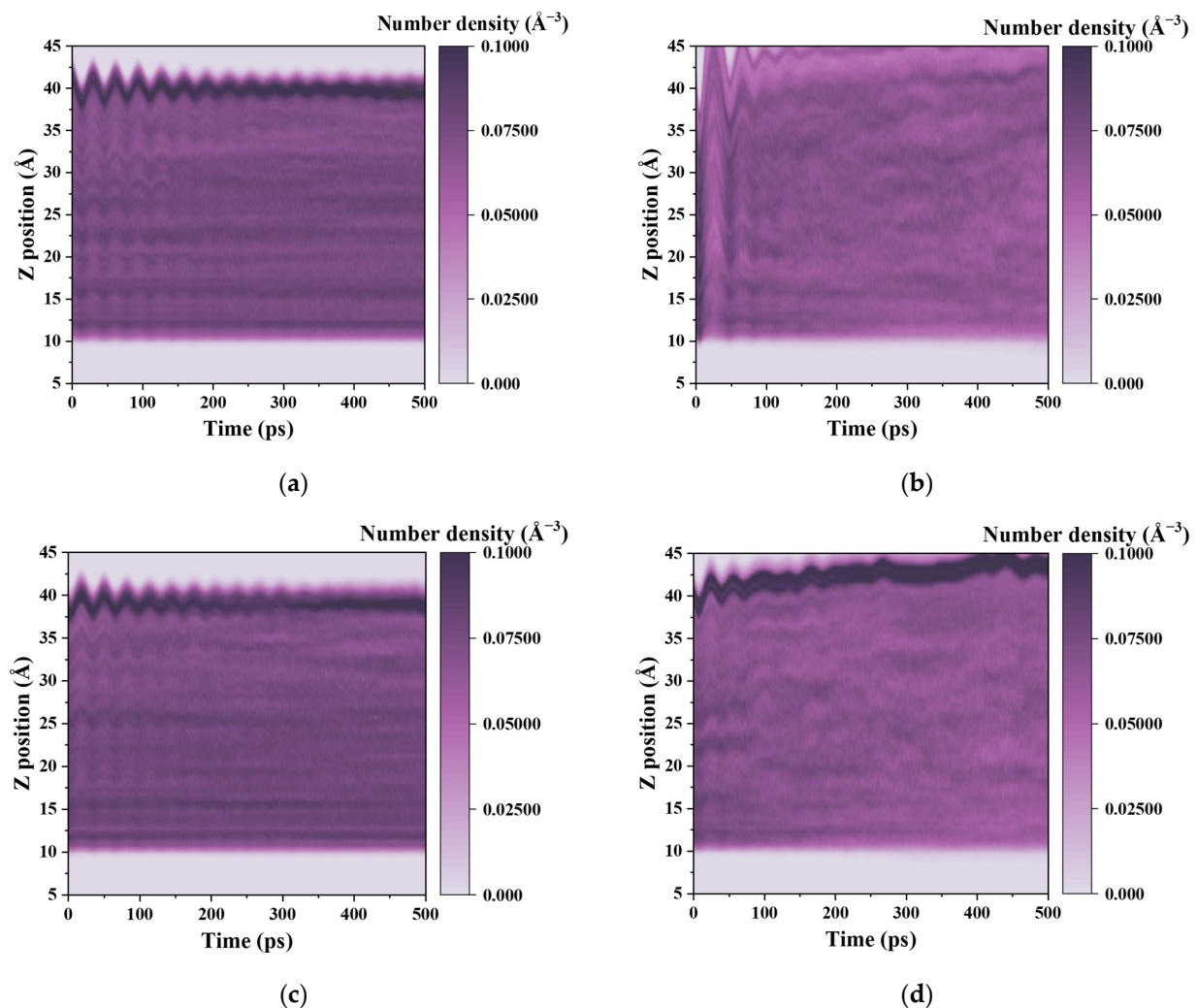


Figure 6. Evolution of the PEEK number density along the normal direction in (a) SW-Gr/PEEK, (b) SW-PEEK, (c) Dry-Gr/PEEK, and (d) Dry-PEEK.

3.2. Microscopic Stress Transfer and Molecular Response of PEEK

Figure 7 shows the evolution of the normal stress, shear stress, and von Mises stress of PEEK during friction. As shown in Figure 7a, σ_{xx} underwent pronounced oscillations during the initial adjustment stage and gradually approached a relatively stable range after approximately 100 ps. During 200–500 ps, the average σ_{xx} values of Dry-PEEK and SW-PEEK were approximately 0.40 and 0.33 GPa, respectively. The introduction of seawater therefore reduced σ_{xx} by about 18% in the absence of graphene. For Dry-Gr/PEEK and SW-Gr/PEEK, the corresponding values decreased to approximately 0.18 and 0.12 GPa. Graphene reduced the stress transmitted along the sliding direction by approximately 56% under dry conditions and 63% in seawater. This reduction indicates that graphene accommodated a considerable portion of the tangential displacement through its in-plane deformation and interfacial sliding, thereby limiting the transmission of friction traction into the PEEK matrix. The lower σ_{xx} of SW-Gr/PEEK further suggests that molecular rearrangement in seawater weakened the residual mechanical coupling across the graphene and PEEK interface.

As shown in Figure 7b, σ_{zz} exhibited strong transient oscillations during the initial stage, particularly in SW-PEEK. Its value first decreased to approximately -0.95 GPa and then increased to nearly 0.48 GPa within the first several tens of picoseconds. These oscillations gradually decayed, and the four systems converged to approximately 0.10 – 0.16 GPa after about 150 ps. Thus, seawater and graphene mainly changed the initial

accommodation of the applied load rather than the final average normal stress. The stronger transient response of SW-PEEK reflects the rapid compression and redistribution of the confined seawater and PEEK chains, consistent with the pronounced normal motion observed in Figures 5b and 6b.

Figure 7c shows a clearer difference in the transmission of shear stress. The average τ_{xz} values of Dry-PEEK and SW-PEEK were approximately 0.15 and 0.13–0.15 GPa during the stable stage. In contrast, the values in the systems with graphene remained mainly between 0 and 0.03 GPa. Graphene therefore reduced the shear stress within PEEK by approximately 85–90%. This substantial reduction explains why SW-Gr/PEEK and Dry-Gr/PEEK showed almost no collective translation in Figure 5a. Rather than being transferred directly into the polymer chains, most of the relative displacement was accommodated near the graphene interface. Seawater alone produced only a moderate decrease in τ_{xz} , indicating that the liquid layer weakened direct dragging but could not completely isolate PEEK from the applied shear motion.

As shown in Figure 7d, graphene reduced the von Mises stress of PEEK by approximately 46% under dry conditions and 60% in seawater. Meanwhile, seawater reduced the von Mises stress by only about 11% without graphene, whereas the reduction reached approximately 35% when graphene was present. The lower combined stress in SW-Gr/PEEK indicates that seawater and graphene acted at different positions in the load transmission process: graphene restricted the entry of shear traction into PEEK, while seawater reduced the residual interaction and molecular constraint at the protected interface.

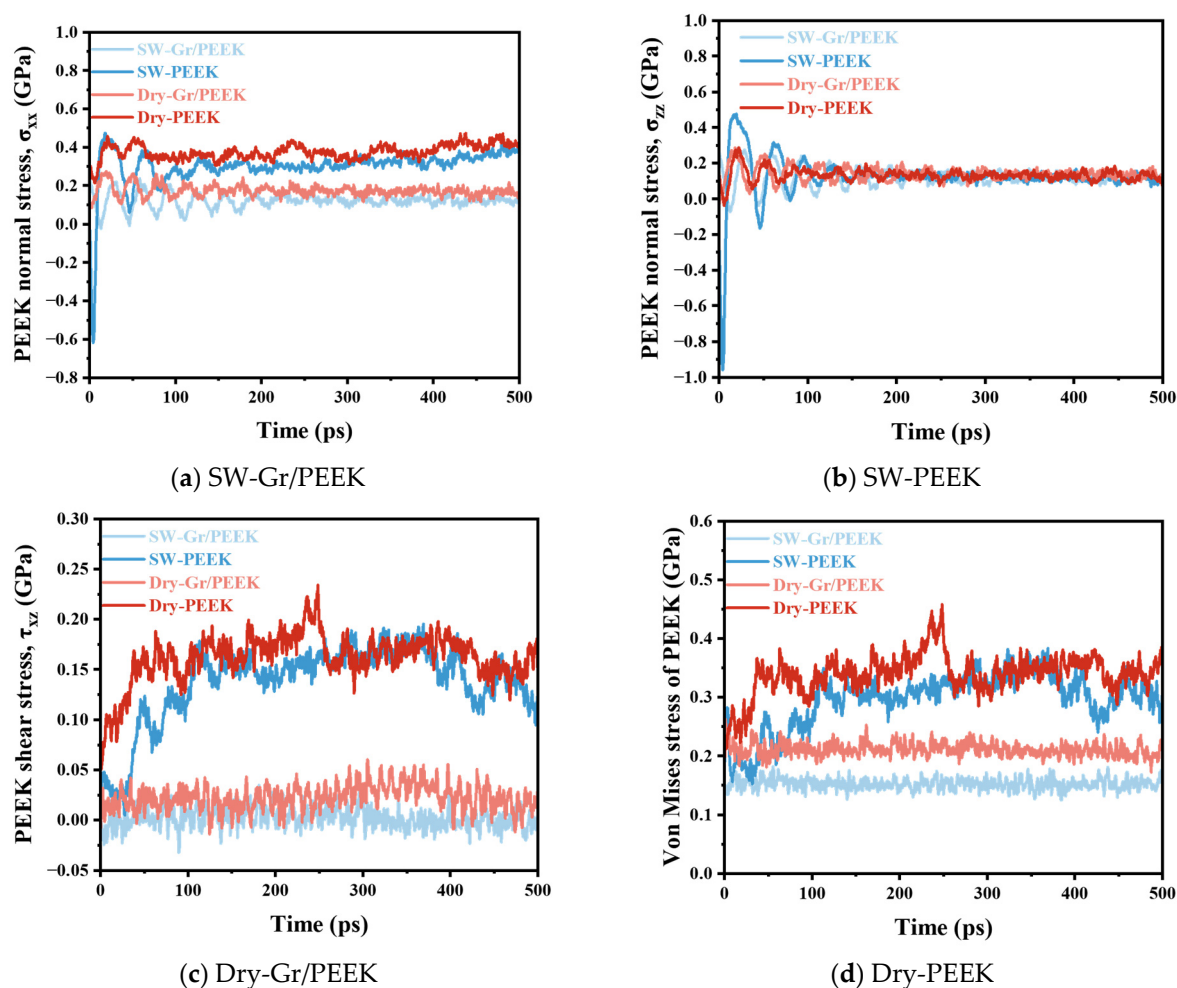


Figure 7. Evolution of the stress response of PEEK during sliding: (a) normal stress σ_{xx} , (b) normal stress σ_{zz} , (c) shear stress τ_{xz} , and (d) von Mises stress.

Figure 8 shows the spatial distributions of shear strain in PEEK after friction. As shown in Figure 8a, most of the SW-Gr/PEEK matrix remained in the low strain range, while isolated regions with strain values approaching 8–10 were dispersed throughout the polymer. The absence of continuous high-strain bands indicates that graphene prevented the shear deformation from propagating over a large area. However, the scattered high-strain sites suggest that the presence of seawater introduced local variations in interfacial slip and chain mobility, allowing a small portion of the deformation to enter the PEEK matrix through discrete regions. Figure 8b shows a substantially broader shear strain distribution in SW-PEEK. Compared with SW-Gr/PEEK, the deformation was no longer limited to isolated sites but extended throughout most of the PEEK matrix. Without graphene, the relative motion of the counterface was transferred directly into the polymer chains. Meanwhile, seawater increased the local mobility of the chains and facilitated their relative rearrangement, causing the applied shear displacement to be accommodated through distributed internal deformation rather than purely through coherent translation.

As shown in Figure 8c, Dry-Gr/PEEK exhibited the lowest and most uniform shear strain. This result agrees with the low τ_{xz} and von Mises stress observed in Figure 7. Under dry conditions, the continuous graphene layer accommodated the sliding displacement through its own extension and interfacial motion, while limiting both the magnitude and spatial penetration of shear deformation into PEEK. In Figure 8d, Dry-PEEK displayed a heterogeneous strain field composed of a low-strain background. Compared with SW-PEEK, the high-strain regions were less uniformly distributed and appeared as more concentrated clusters. The direct contact between the counterface and PEEK generated strong local dragging and caused deformation to accumulate preferentially along specific chain groups. This localized response is consistent with the relatively high shear and von Mises stresses in Figure 7 and the broad forward pile-up observed in Figure 3d. The comparison between Figure 8b,d therefore indicates that seawater redistributed the shear deformation from concentrated regions into a more spatially dispersed chain rearrangement, although it did not prevent substantial deformation when graphene was absent.

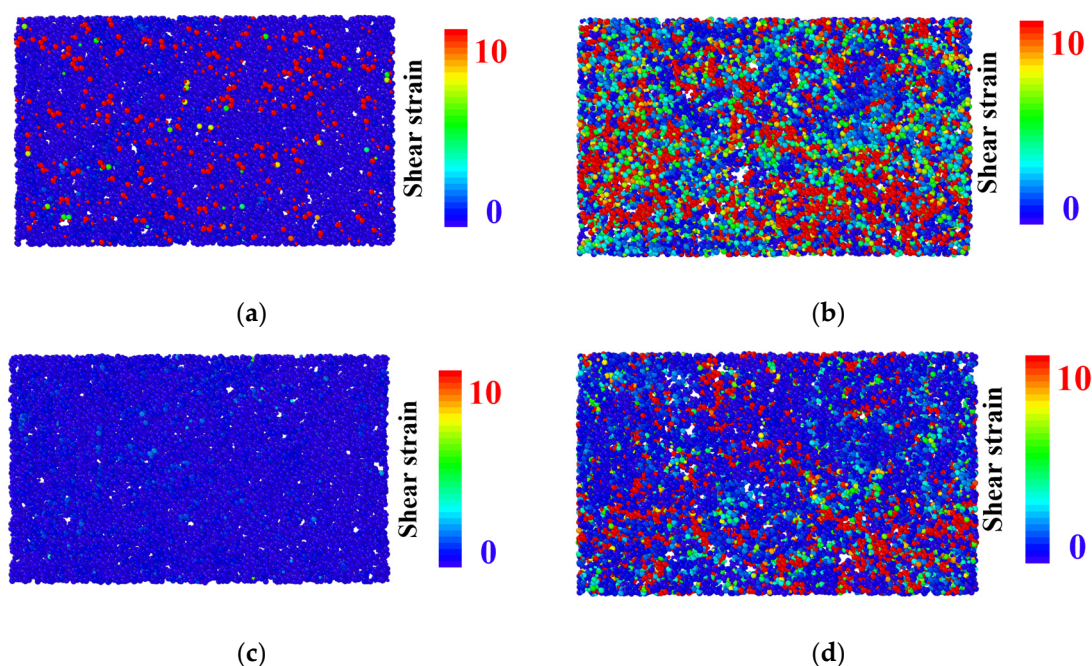


Figure 8. Shear strain distributions in PEEK: (a) SW-Gr/PEEK, (b) SW-PEEK, (c) Dry-Gr/PEEK, and (d) Dry-PEEK.

Figure 9 shows the evolution of the kinetic, potential, bond, and angle energies of PEEK during friction. As shown in Figure 9a, the kinetic energies of SW-PEEK and Dry-PEEK decreased rapidly during the initial stage and gradually stabilized at approximately 554–558 eV after about 150 ps. The two systems with graphene reached lower values of approximately 538–543 eV during the same period, corresponding to a reduction of about 14–17 eV, or approximately 2.5–3.0%, relative to the systems without graphene. The lower kinetic response indicates that graphene restricted the transfer of sliding motion into the PEEK matrix and reduced the dynamic activity of the polymer chains. By contrast, the similar steady values of SW-PEEK and Dry-PEEK suggest that seawater alone mainly altered the direction and spatial distribution of chain motion rather than substantially changing its overall kinetic contribution.

As shown in Figure 9b, the four systems occupied clearly different potential energy ranges. During the stable stage, SW-Gr/PEEK and SW-PEEK remained at approximately –2620 and –2650 eV, respectively, while Dry-PEEK stabilized near –2690 eV. Dry-Gr/PEEK exhibited the lowest potential energy, decreasing from approximately –2945 to –2985 eV during sliding. Its final value was about 295 eV lower than that of Dry-PEEK. This large difference should not be interpreted solely as greater thermodynamic stability. Instead, it indicates that direct contact with graphene produced a distinct interaction environment and conformational state within PEEK. The much smaller difference between SW-Gr/PEEK and SW-PEEK suggests that seawater weakened the direct interaction between graphene and PEEK and allowed the interfacial chains to adopt less constrained configurations.

Figure 9c shows that the bond energies of SW-PEEK and Dry-PEEK gradually converged to approximately 755 eV after the initial relaxation. The corresponding value of SW-Gr/PEEK was approximately 748 eV, about 7 eV lower than that of SW-PEEK. A more pronounced decrease occurred in Dry-Gr/PEEK, whose bond energy declined from approximately 737 eV to nearly 720 eV and remained about 35 eV below that of Dry-PEEK. These differences indicate that graphene, particularly under dry conditions, reduced the extent to which the imposed deformation was accommodated through bond stretching. The friction displacement was instead increasingly accommodated by changes in chain geometry and interfacial motion.

As shown in Figure 9d, the angle energy provides complementary evidence for this change in the deformation mode. SW-Gr/PEEK maintained the lowest angle energy at approximately 940 eV, whereas SW-PEEK and Dry-PEEK generally remained within approximately 950–956 eV. In contrast, Dry-Gr/PEEK exhibited an angle energy of approximately 1033–1042 eV, which was about 80–90 eV higher than that of Dry-PEEK during the stable stage. The simultaneous decrease in bond energy and increase in angle energy indicates that direct contact with graphene under dry conditions redirected the internal response of PEEK from bond stretching toward bond angle variation, chain bending, and conformational adjustment. When seawater was present, interfacial molecular rearrangement relieved part of this geometric constraint, thereby preventing the similarly large increase in angle energy observed in Dry-Gr/PEEK.

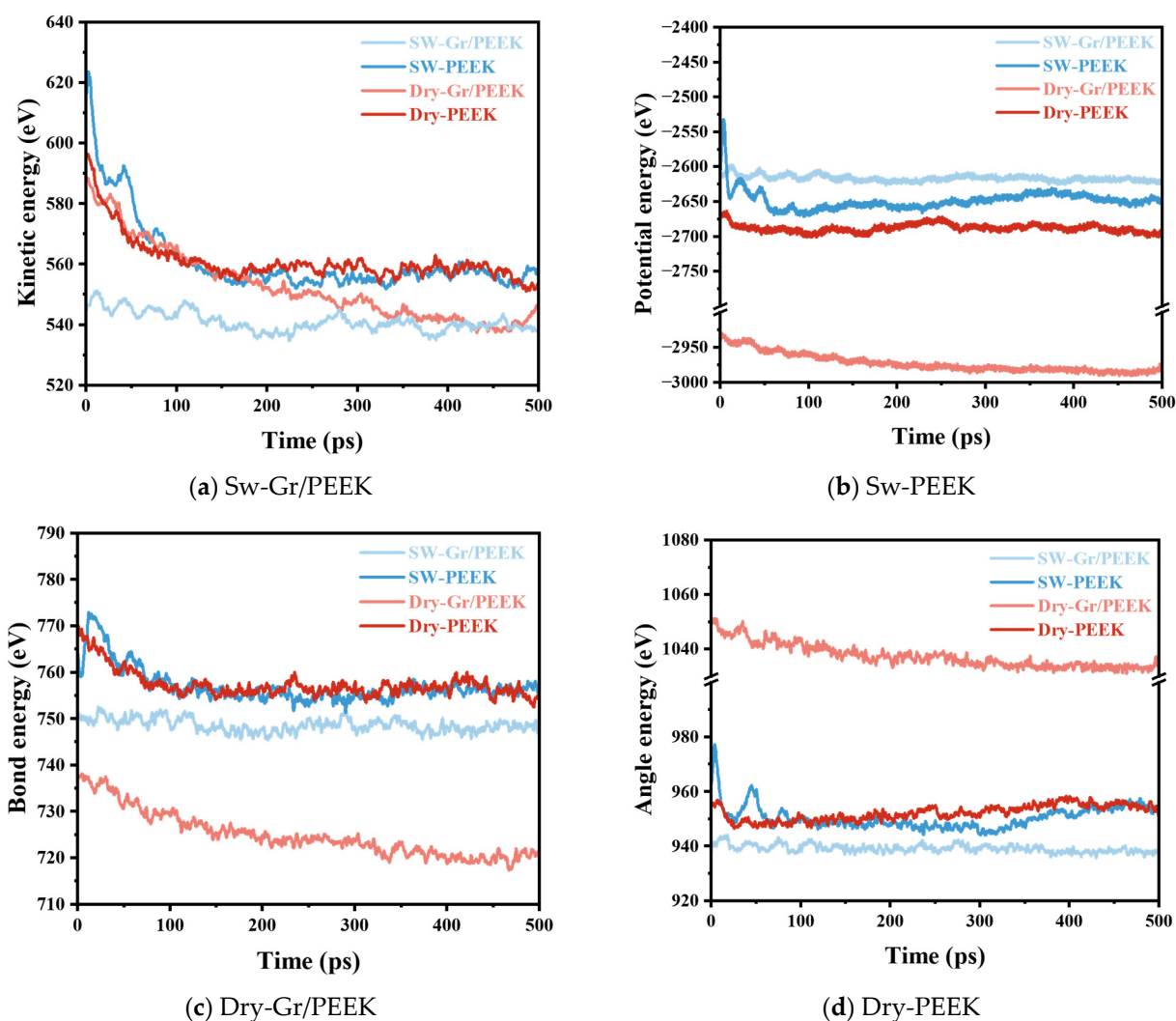


Figure 9. Evolution of the (a) kinetic, (b) potential, (c) bond, and (d) angle energies of PEEK during friction.

Figure 10 shows the evolution of the radius of gyration (R_g) distributions of the PEEK chains during friction. As shown in Figure 10a, the main distribution bands in SW-Gr/PEEK remained nearly unchanged throughout the 500 ps sliding process. Most of the chains were concentrated in the lower radius range, while several additional bands remained at larger radii without pronounced upward migration. The variation in the dominant bands was generally limited to approximately 1–2 Å. This stable distribution indicates that graphene restricted the transmission of friction displacement into the PEEK matrix, thereby preventing sustained chain stretching. The slight broadening of several bands reflects limited local rearrangement induced by the seawater environment rather than large-scale conformational extension. As shown in Figure 10b, SW-PEEK exhibited a substantially broader and more dynamic distribution. Several trajectories initially located below approximately 10 Å gradually shifted toward 20–24 Å as friction proceeded, while the low-radius region also became increasingly diffuse. The increase of more than 10 Å for these chains indicates progressive extension and orientation under the combined action of tangential dragging and normal redistribution. Without graphene, the motion of the counterface was transferred directly into the polymer matrix. Seawater reduced the coherent translation of PEEK, as shown in Figures 4 and 5, but allowed the imposed displacement to be accommodated through more dispersed chain rearrangement, resulting in multiple conformational evolution paths.

In Figure 10c, Dry-Gr/PEEK also retained a series of nearly horizontal distribution bands. The dominant low-radius region remained concentrated throughout sliding, and the bands at larger radii showed only limited fluctuations. Compared with SW-Gr/PEEK, the distribution was slightly more concentrated, indicating that the dry graphene interface imposed stronger geometric constraints on the underlying PEEK chains. This constraint limited extensive chain extension, although the energy results in Figure 9 show that part of the local response was accommodated through bond angle variation and chain bending. As shown in Figure 10d, Dry-PEEK displayed several pronounced trajectories extending from below approximately 10 Å to above 20 Å. The distribution in the low-radius region also broadened progressively, indicating that the chain response became increasingly nonuniform during sliding. Compared with SW-PEEK, the extending trajectories in Dry-PEEK were relatively concentrated and developed along several distinct paths. Direct interaction between the counterface and PEEK therefore caused deformation to accumulate preferentially in specific chain groups, producing simultaneous chain stretching, orientation, and forward dragging. This concentrated conformational evolution is consistent with the localized high-shear-strain regions in Figure 8d and the higher stress response observed in Figure 7.

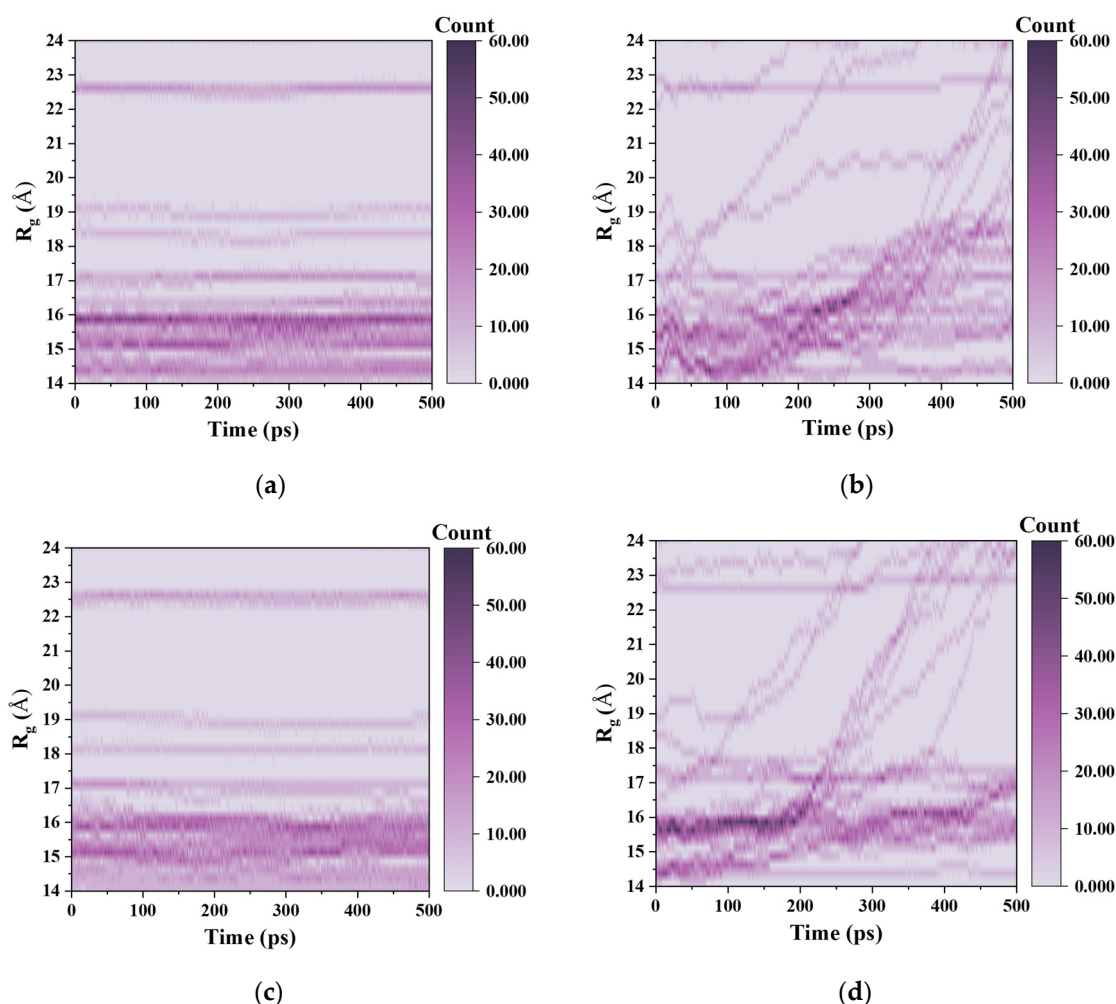


Figure 10. Evolution of the R_g distributions of PEEK chains during friction: (a) SW-Gr/PEEK, (b) SW-PEEK, (c) Dry-Gr/PEEK, and (d) Dry-PEEK.

Figure 11 shows the distribution of PEEK atomic velocities as a function of position along the normal direction. As shown in Figure 11a, the dominant distribution in SW-Gr/PEEK was concentrated in the low-velocity range, mainly below approximately 2 Å/ps.

Only a limited number of inclined trajectories extended toward higher velocities. This relatively compact distribution indicates that graphene restricted the transfer of sliding motion into the PEEK matrix, while seawater introduced only limited local fluctuations in chain activity. As shown in Figure 11b, SW-PEEK exhibited a substantially broader velocity distribution. Multiple trajectories extended from the low-velocity region toward approximately 8–10 Å/ps and covered a wide range of normal positions. Without graphene, the motion imposed by the counterface was transferred more directly into the polymer, causing different chain groups to undergo distinct dynamic responses. The broad and intersecting trajectories indicate that seawater promoted dispersed molecular rearrangement rather than a uniform translation of the PEEK matrix, consistent with the widespread shear strain and diverse conformational evolution observed in Figures 8b and 10b.

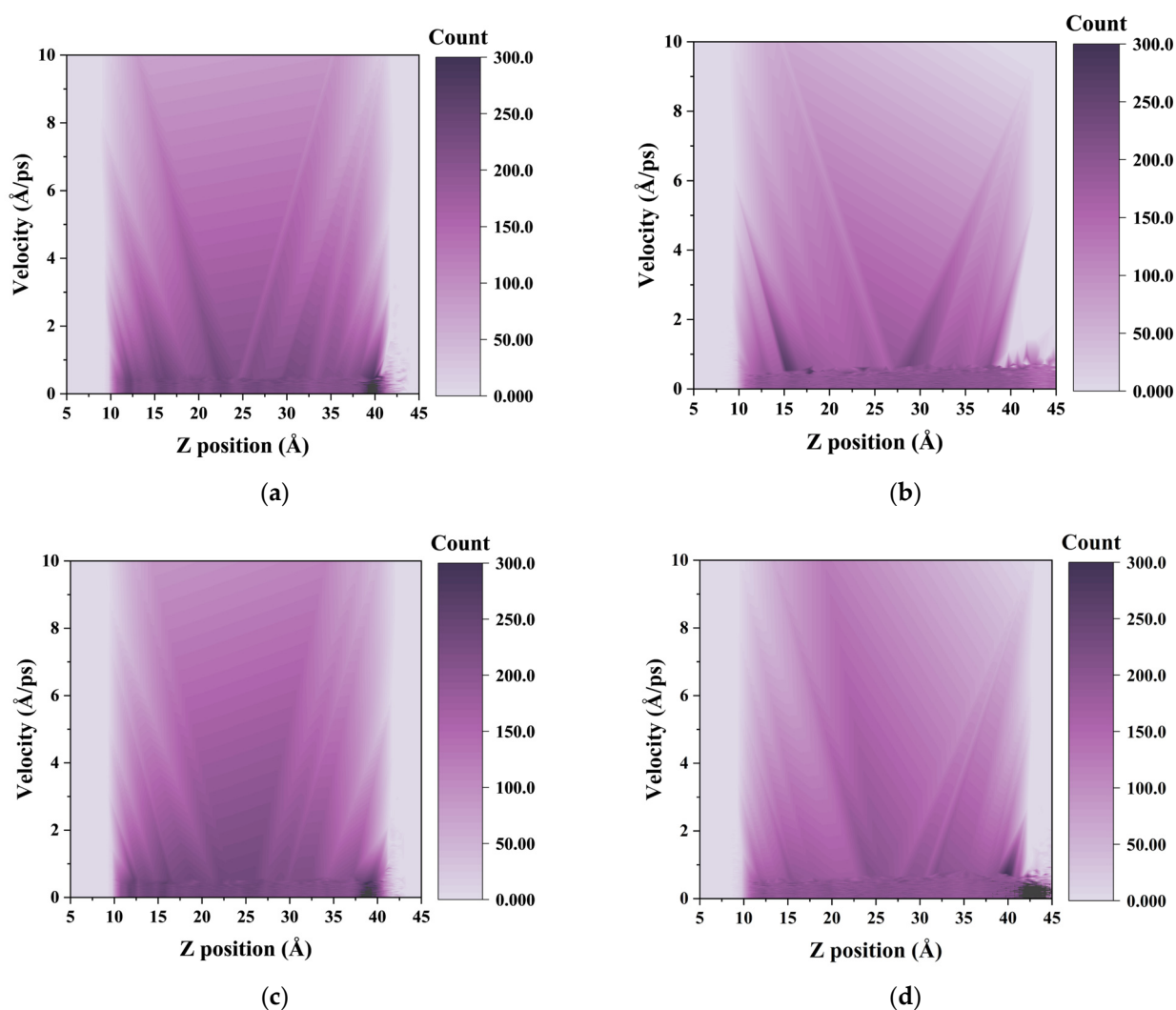


Figure 11. Distribution of PEEK atomic velocities along the normal direction during friction: (a) SW-Gr/PEEK, (b) SW-PEEK, (c) Dry-Gr/PEEK, and (d) Dry-PEEK.

As shown in Figure 11c, the velocity distribution of Dry-Gr/PEEK remained mainly concentrated below approximately 2 Å/ps, and the high-velocity trajectories were less pronounced than those in the systems without graphene. The more confined distribution agrees with the low shear stress and stable radius of gyration observed for this system. Under dry conditions, graphene accommodated the imposed displacement through its own extension and interfacial motion, thereby limiting the dynamic excitation of the underlying PEEK chains. As shown in Figure 11d, Dry-PEEK also developed several

inclined trajectories extending toward approximately 9 Å/ps. Compared with SW-PEEK, these trajectories were relatively concentrated along several distinct paths, suggesting that the motion was preferentially transferred to specific chain groups. Direct contact with the counterface therefore caused localized dragging and nonuniform chain motion, which correspond to the concentrated shear strain regions and chain extension identified in Figures 8d and 10d. The comparison among the four systems shows that graphene primarily confines the magnitude and penetration of polymer motion, whereas seawater changes its spatial distribution and promotes more dispersed local rearrangement.

4. Conclusions

All-atom molecular dynamics simulations were used to investigate how seawater, acting as an interfacial lubricant, and graphene, serving as a protective solid coating, influence load transfer, deformation, and molecular responses in PEEK during friction. The main conclusions are as follows:

- (1) Graphene suppressed the macroscopic deformation of PEEK. Without graphene, SW-PEEK and Dry-PEEK formed pile-up regions with inclination angles of approximately 49° and 38°, whereas the graphene-containing systems retained a relatively intact morphology. Seawater reduced the graphene extension from 91 to 53.5 Å, indicating that graphene blocked deformation propagation into PEEK while seawater shortened the transmission range of interfacial traction.
- (2) Seawater and graphene regulated different components of polymer motion. Graphene reduced the tangential center-of-mass displacement of PEEK by more than 99%. Without graphene, seawater reduced the tangential center-of-mass displacement and mean square displacement by approximately 15.2% and 20% but increased the normal mean square displacement by about 17%, showing that seawater redirected part of the motion from tangential dragging to normal rearrangement.
- (3) Graphene altered the load transfer pathway within PEEK. It reduced σ_{xx} by approximately 56–63%, τ_{xz} by 85–90%, and the von Mises stress by 46–60%. This occurred because graphene accommodated relative displacement near the interface, whereas seawater mainly redistributed shear deformation from concentrated regions into a more dispersed strain field.
- (4) The interfacial conditions determined how PEEK accommodated deformation at the molecular scale. Graphene lowered the kinetic energy by approximately 2.5–3.0%, while Dry-Gr/PEEK exhibited a bond energy about 35 eV lower and an angle energy 80–90 eV higher than Dry-PEEK. Together with the increase in radius of gyration exceeding 10 Å in the systems without graphene, these results show that graphene shifted the PEEK response from chain translation and stretching toward chain bending and local conformational adjustment.

Future work will consider seawater salinity as an independent parameter to determine how variations in ionic concentration influence interfacial molecular organization, load transfer, and the lubrication behavior of graphene-protected PEEK.

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