Dynamics of Neutral and Charged Nanodiamonds in Aqueous Media Confined between Gold Surfaces under Normal and Shear Loading

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ABSTRACT: The dynamics of cubo-octahedral nanodiamonds (NDs) with three different surface treatments and confined in aqueous environments between gold surfaces under shear and normal loading conditions have been characterized via molecular dynamics (MD) simulations. The treatments consisted of carboxyl (−COO⁻) or amino (−NH₄⁺) groups attached to the NDs, producing either negatively or positively charged NDs, respectively, and hydrogen-terminated surfaces producing neutral NDs. Simulations were performed in the presence and absence of induced image charges to explore the impact of electrostatic interactions on friction and surface deformation. Significant deformation of the gold surfaces was observed for negatively charged NDs placed between gold surfaces under external loads that were sufficient to displace water from the contact. Rolling and relatively high friction levels were also observed for the negatively charged NDs under the same conditions. In contrast, the neutral and positively charged NDs exhibited sliding behavior with only minor deformation of the gold surfaces. The results suggest that the size of the surface functional group plays a major role in determining whether NDs slide or roll on solid contacts. Higher friction levels were also observed in conjunction with induced image charges in the gold contacts. The results demonstrate how surface functionalization and surface-induced charges can work in combination to profoundly influence tribological performance.

1. INTRODUCTION

The need for a new generation of efficient and eco-friendly lubricants has increased greatly in recent years, sparking major interest in nanoparticles as antifriction and antiwear additives. Published reports to date have been predominantly experimental in nature, with significant reductions in both friction and wear being commonly observed when nanoparticles are added. Cases where nanoparticles are detrimental to tribological performance are few in number, but it is unknown whether they are actually in the minority or if they are being under-reported. The detailed lubrication mechanisms underlying such beneficial or detrimental behaviors have yet to be completely understood.

A variety of potential lubrication mechanisms have been proposed. These include friction reductions through rolling contact, formation of protective antiwear films, self-repairing effects, and polishing. The mechanisms have not been established from a firm theoretical viewpoint, and the range of applicability for specific combinations reported to exhibit strong tribological performance has not been established. To better understand the lubricating mechanisms of nanoparticles at a fundamental level, a detailed picture of the nanoscale structure of the contacting interface is required. Classical molecular dynamics (MD) simulation provides a mean to explore the details of frictional processes at the atomic scale. We report such a study here, focusing on nanodiamonds (NDs) in aqueous suspensions and how surface functionalization and charge levels work in combination to determine tribological performance.

NDs are widely investigated as lubricant additives for both oil- and water-based systems because of their low cost, eco-friendliness, and ability to be synthesized on manufacturing scales. They moreover require far lower additive quantities than most nanoparticles to achieve similar friction reductions. Although the majority of ND experiments report improvements in friction and wear, detrimental effects have also been reported. In a recent set of experiments, for example, the tribological performance of positively and negatively charged NDs was measured by both nanoscale and macroscale methods for gold, stainless steel, and alumina contacts. The studies revealed that positively and negatively charged NDs exhibit significantly different tribological properties, and that surface charge and functionalization of NDs can significantly impact tribological performance.

We recently reported results from a MD study of negatively charged aqueous NDs near gold surfaces. The
simulations revealed a water layer containing counter ions present between the negative NDs and the surface that was not present for the positive NDs. The resulting closer proximity of the positive ND to the surface, as well a lack of cancellation of electrostatic interactions, resulted in stronger adhesion and friction levels for the positively charged NDs with respect to the negatively charged NDs. The results were consistent with experimental results and provided valuable information on the impact of NDs in hydrodynamic and/or mixed contact regimes of lubrication where direct contact between the solid contacts is eliminated in whole or in part by the intervening lubricant. Particularly notable was the sensitive interplay between surface functional groups and surface charge in determining the system’s tribological behavior.

Although there are many MD simulations in the literature that have reported on the impacts of nanoparticles on surface friction, the majority of them consider dry sliding conditions while ignoring the potential influence of electrostatics of nanoparticles near the sliding surfaces. References and for example, reported MD simulations of dry friction levels for ND tips sliding on iron, silicon, and carbon-based surfaces. References and explored dry friction of carbon-based nanoparticles confined in sliders. Very few investigations studied the frictional characteristics of nanoparticles in liquid suspensions.

All-atom MD simulations were employed here to explore how NDs with different surface treatments confined in aqueous media between gold surfaces would behave under sliding conditions and impact the system’s tribological properties. The study focused on the boundary regime of lubrication, where external loads are sufficiently strong to produce direct solid contact. In this case, NDs prevent the counter surfaces from direct contact but may lead to surface deformation, friction, sliding, and/or rolling behavior depending on the nature of the interfacial interactions. The simulations were of cubo-octahedral NDs with different charged surface functional groups confined between sliding gold surfaces loaded with varying levels of external forces in aqueous environments. For consistency with experimental results and our prior simulation, NDs were modeled with either carboxyl (−COO⁻) or amino (−NH₄⁺) groups attached to their surfaces. Because ionizable sites can override the effects of transfer doping, electron transfer between the solvent and hydrogen termination of NDs was not considered in our model. The electrostatic interactions between the gold surface and the NDs, counter ions, and water solvent were modeled with a charge equilibration scheme that produces induced charges on the metal. To separate the effects of interface electrostatic interactions on the tribological performance of the NDs from other interface interactions, simulations were carried out with and without the charge equilibration scheme.

2. METHODOLOGY

The details of the simulations, including the system setup, the force model, the simulations, and the codes used for each are given in this section.

2.1. Simulation Setup. The atomic simulation is illustrated in Figure 1. It consisted of two identical gold slabs, one of which was fixed, while the other was slid at a constant velocity parallel to the interface. A cubo-octahedral ND with a ~4 nm apex-to-apex diameter immersed in water was placed between the two surfaces (Figure 1), preventing direct contact. The ND was free to move with no artificial constraints. The gold slabs consisted of rigid layers (1, 4) and deformable layers (2, 3), with the deformable layers in contact with the ND. The atoms in the deformable layers were unconstrained and could move freely due to the interatomic forces, while the relative atom positions in the rigid layers were fixed. A normal load was imposed on the lower rigid layer, and the upper rigid layer (rigid layer 1) was assigned a constant sliding velocity in the X-direction. The layers were not allowed to rotate. The upper rigid layer (rigid layer 1) was immobile except in the X-direction, and the lower rigid layer (rigid layer 4) was immobile except in the Z-direction. The gold was modeled as a face-centered cubic lattice with a lattice constant of 4.08 Å. Each slab consisted of three layers of atoms in their respective rigid layers and six layers of atoms in the deformable layers, with exposed {111} surfaces. The NDs contained 14 facets with a total of 496 surface atoms, 8 {111} facets, and 6 {100} facets. The surface carbon atoms on the {100} facets were dimer reconstructed based on the reported
results. The simulations were performed on negatively charged, positively charged, and neutral NDs. For negatively and positively charged NDs, 48 surface carbon atoms were randomly chosen and bonded to an ionized carboxyl (−COO\(^{-}\)) or amino group (−NH\(_{3}\)\(^{+}\)), respectively. The remaining surface carbon atoms were terminated by hydrogen. This density of ionized functional groups is associated with a \(\zeta\)-potential of approximately 45 mV, roughly matching values employed in experimental studies. For neutral NDs, the surface carbon atoms were terminated with hydrogen only. To maintain system charge neutrality, 48 Na\(^{+}\) or Cl\(^{-}\) counter ions were added to the solvent for the simulations of the negative or positive NDs, respectively. Here, our simulation electronneutral setup follows a similar approach to that reported in Ref 48, which demonstrates that after sufficient equilibration only a ratio of counter ions will be finally attached to nanoparticle surfaces in the electronneutral system (balanced by counter ions). The nanoparticles’ surface, therefore, has an effective charge equal to the net charges of the surface functional group minus the net charges of the attached counter ions. In our work, we employ a similar approach to estimate the required density of ionized functional groups required to establish the desired surface effective charges in static conditions. The density of ionized functional groups is associated with a \(\zeta\)-potential of approximately 45 mV (desired surface effective charges), roughly matching values employed in experimental studies in static conditions. The motion of the slider may also potentially impact the nanodiamond’s effective surface charges. We therefore also examine and discuss the nanodiamond’s effective surface charges (\(\zeta\)-potential) under friction motion. The systems were maintained in a cubic box with dimensions 79.95 \(\times\) 80.78 \(\times\) 80.00 Å\(^3\) containing water molecules with a 1.0 g/cm\(^3\) bulk density. The explicit number of water molecules ranged from about 6700 to about 6950 in different simulation cases. Periodic boundaries were used in the two directions perpendicular to the sliding direction, and a fixed boundary was used in the normal direction.

### 2.2. Molecular Dynamics Simulation

These simulations used the LAMMPS code with a time step of 1 fs. The temperature was maintained at 298 K via the Nose–Hoover thermostat. The water interatomic forces were simulated with the TIP3 model with the addition of a nonbonded field. The induced charges in the gold slabs were modeled using a similar approach to that reported in Ref 48, which demonstrates that after sufficient equilibration only a ratio of counter ions will be finally attached to nanoparticle surfaces in the electronneutral system (balanced by counter ions). The nanoparticles’ surface, therefore, has an effective charge equal to the net charges of the surface functional group minus the net charges of the attached counter ions. In our work, we employ a similar approach to estimate the required density of ionized functional groups required to establish the desired surface effective charges in static conditions. The density of ionized functional groups is associated with a \(\zeta\)-potential of approximately 45 mV (desired surface effective charges), roughly matching values employed in experimental studies in static conditions. The motion of the slider may also potentially impact the nanodiamond’s effective surface charges. We therefore also examine and discuss the nanodiamond’s effective surface charges (\(\zeta\)-potential) under friction motion. The systems were maintained in a cubic box with dimensions 79.95 \(\times\) 80.78 \(\times\) 80.00 Å\(^3\) containing water molecules with a 1.0 g/cm\(^3\) bulk density. The explicit number of water molecules ranged from about 6700 to about 6950 in different simulation cases. Periodic boundaries were used in the two directions perpendicular to the sliding direction, and a fixed boundary was used in the normal direction.

#### Table 1. Parameters for the Lennard-Jones Potential and Coulombic Interaction

| Element | \(q\) (e units) | \(\sigma\) (Å) | \(\epsilon\) (eV) |
|---------|-----------------|---------------|-----------------|
| H       | 0.417           | 0.4000        | 0.001995        |
| O       | −0.834          | 3.1507        | 0.006596        |
| Na\(^{+}\) | 1.000          | 2.4393        | 0.003792        |
| Cl\(^{−}\) | −1.000         | 4.4777        | 0.001544        |
| Au      | 2.6290          | 2.2942        |                 |

*Previously reported and updated every twenty steps using a Python code external to LAMMPS.*

#### 2.3. Simulation Procedure

The system was first equilibrated for 1000 ps without applying an external load. A load was then gradually applied to the lower rigid layer (rigid layer 4) for 500 ps. The pressure was controlled by applying a constant uniform normal force to the atoms in the lower rigid layer (rigid layer 1) at constant load and a constant velocity of 10 m/s. During the sliding simulations, the heat generated by shearing of the molecules was dissipated via the Nose–Hoover thermostat. The evolution of friction was tracked by monitoring the average resistance of the two rigid layers. Sliding simulations were performed for positively charged, negatively charged, and neutral NDs with loads of 333.3, 666.7, and 1000.0 MPa. To separate the effects of electrostatic interactions from those of the functional groups and nonbonding adhesion, the simulations were carried out in both the presence and absence of surface-induced charges. A total of 18 sliding simulations were performed in this study.

#### 3. RESULTS AND DISCUSSION

In a previous study, we reported the results from MD simulations of negatively and positively charged aqueous NDs near gold surfaces. The simulations revealed a water layer containing counter ions present between the negative NDs and the surface that was not present for the positive NDs. This resulted in stronger adhesion and friction levels for the positively charged NDs with respect to the negatively charged NDs. In this study, the frictional properties of NDs confined between gold surfaces under normal and shear loading are analyzed. The results indicate that different surface treatments can have a substantial impact on tribological properties.

#### 3.1. Contact States and ND Deformation in Sliding Contacts

Illustrated in Figure 2 are atomic configurations from the simulations, as viewed from the Y-direction under different load levels at the initial time of each simulation. Black and gold atoms, respectively, represent the rigid and deformable layers. Under the applied load, the gold slabs remain separated from each other by the ND, consistent with literature reports of ND’s ability to prevent asperity contact. In all cases, there is an ordered layering of the water near the gold surface, in agreement with prior studies. The neutral NDs show a preference for facet contact with the surface under all loads. Under low load (333.3 MPa), the water layer remains between the ND facet and the surface. Simulations under increasing loads showed that the water layer is removed starting at a load of about 433 MPa.
Figure 2. Illustration of the initial contact states of NDs between sliding gold surfaces viewed from the Y-direction under different loads. The sliding velocity is 10 m/s. Gold and black colored atoms on the surface represent the deformable layers and rigid layers, respectively. The red and blue spheres represent carbon and hydrogen atoms, respectively, the brown spheres represent the solvated counter ions, the white rods represent water molecules, and the green and yellow spheres represent the surface functional groups.

Figure 3. Morphology of lower slabs after 2000 ps, color-coded in grayscale according to the position on the z-axis. $V = 10$ m/s, $P = 666.7$ MPa.
(17.12 eV/Å) for neutral NDs. For positive NDs, facet contact is established under low and middle loads (333.3 and 666.7 MPa), while the interface switches to apex contact under high load (1000.0 MPa). As with the neutral NDs, for positive NDs, the water layer between the facet and surface remains up to a load of about 373 MPa (14.75 eV/Å). For negative NDs, at a load of 333.3 MPa, there is a preference for apex contact and no interfacial water layer. Additional simulations showed that the water is present below a much lower load of 67 MPa (2.65 eV/Å). This is because the apex contact has a much smaller contact area compared to the facet contact, and therefore less energy is required to displace the water layer in the apex contact. In contrast, both the positive NDs and the neutral NDs favor contact between the facet and the surface. The different sizes of surface functional groups may explain the difference; the larger size of the −COO− groups on the negative NDs causes their facets to be more irregular and could enable apex contact when confined under load. Because the size of the −NH+ group is between −H and −COO−, positive NDs’ behaviors fall between neutral NDs and negative NDs. The contact state of positive NDs could, therefore, be expected to transition from facet contact (like neutral NDs) under low/mid load to apex contact (like negative NDs) under high load. Here, we also notice that frictional motion potentially impacts the ND’s effective surface charges. We use an approach similar to that reported in Ref 48 to estimate the associated ζ-potential of charged NDs during the friction motion. When the surface-induced charges are included, the ζ-potential of positively charged NDs ranges from 40.33 to 64.50 mV, while that of negatively charged NDs ranges from 30.11 to 49.39 mV. When the surface-induced charges are not included, the ζ-potential of positively charged NDs ranges from 35.37 to 73.81 mV, while that of negatively charged NDs ranges from 35.37 to 53.51 mV. This result indicates that the carboxyl (−COO−) group of negatively charged NDs has a stronger ability to capture counter ions than the amino (−NH+ ) group of positively charged NDs. The larger partial charge of the oxygen atom site and the larger size of the carboxyl (−COO−) group are responsible for the stronger electrostatic attachment ability. The inclusion of the surface-induced charges may have limited ability to enhance the attachment of counter ions. Due to the high fluctuation in the measured values, the effect of surface-induced charges is not however definitively confirmed by the simulation results.

Illustrated in Figure 3 is the morphology of the lower sliding surface against the charged NDs (positive and negative charged, respectively) after sliding for 2000 ps in the absence (left panels) and presence (right panels) of surface-induced charges. For negative NDs, there is substantial deformation in both cases, with more atoms deformed when the surface-induced charges are included. Similar results were observed for positive NDs, with the exception that far fewer atoms are deformed. Literature studies have suggested that NDs can exert a polishing effect on materials, particularly in the boundary lubrication regime of direct asperity contact.12,70,71 While the results presented here are not directly comparable because the surfaces were smooth at the simulation start, they do demonstrate that surface treatments can influence the wear and polishing rates by the NDs. This result suggests that friction and tribological performance can be influenced by surface charges and functionalization of NDs.

| Load (MPa) | Neutral ND (with) | Neutral ND (without) | Positive ND (with) | Positive ND (without) |
|-----------|------------------|----------------------|-------------------|-----------------------|
| 333.3     | 4                | 3                    | 9                 | 109                   |
| 666.7     | 7                | 15                   | 51                |                       |
| 1000.0    | 63               | 411                  | 557               |                       |
|           | 37               | 159                  | 275               |                       |

*Cases with apex contact are highlighted.*

Generally, surface deformation increases with increasing applied load. In addition, for each case, the presence of surface-induced charges also increases the surface deformation. This result is not surprising because the presence of surface-induced charges introduces more electrostatic interaction between the ND and surface. This, in turn, makes atoms in a deformable layer to be more “sticky”, as shown in our previous work,36 and more easily deformed while sliding against NDs. Comparing apex contact cases (highlighted) with facet contact cases (unhighlighted), it is obvious that apex contact cases are more sensitive to the presence of surface-induced charges. The presence of surface-induced charges will lead to more serious deformation than the absence of surface-induced charges. Apex contact helps the NDs to squeeze out the shielding water layer and cut into the sliding surface. This enhances the induced charge effect and causes more surface damage.

### 3.2. Rolling and Sliding Behavior of NDs in Sliding Contact

Plotted in the bottom sections of Figure 4 are the cumulative rolling angles of the NDs from their initial states versus simulation time under various applied loads. The slope of the lines reflects the ND angular velocities. These results show the rolling state of the NDs during the sliding process. Plotted in the upper sections of Figure 4 are the relative ND sliding speeds versus simulation time. The two interfaces slide at a constant speed of 0.1 Å/ps. For the pure sliding case, the relative sliding speed will be close to 0.1 Å/ps. The relative sliding speed is calculated as the sum of relative sliding speed against the top and bottom surfaces. These plots indicate the friction mechanism of the various NDs. From these results, the rolling states of NDs are heavily dependent on the applied load. Figure 4a–e, for example, shows that the neutral and positive NDs exhibit almost no rolling, and therefore almost pure sliding, under the low and middle loads (P = 333.3, 666.7 MPa), regardless of whether surface-induced charges are involved. For Figure 4d, there is a slight rotation at the initial period; this is because the sliding system is not tightly confined and the contacted facet has a chance to slip to its proximal facet. The system then maintains facet contact and keeps sliding during the whole process. Under high load (P = 1000.0 MPa), the positive NDs start to roll continuously (Figure 4f), while neutral NDs begin to flip randomly (Figure 4c). This is due to the deformation of the contacted surface under high load, which breaks the ND–gold sliding contact. Negative NDs exhibit behaviors that are quite different from the others (Figure 4g–i). In the absence of surface-induced charges, the negative NDs exhibit similar rolling and sliding speeds (about 0.07 Å/ps) under all loads studied. While taking account of surface-induced charges, the motion of negative NDs is switching from minor rolling to a combination of sliding and
rolling. The rolling speed increases as the normal load increases, while the relative sliding speed decrease from 0.0988 to 0.0893 Å/ps. Similar mechanisms of mixed sliding and rolling motion of spherical nanoparticles in asperity contacts have been reported in experimental studies. A possible explanation is that the enhanced induced charge effect in apex contact will resist the rolling motion of negative NDs, while the induced charge effect will keep the facet contact and sliding motion of neutral and positive NDs.

Figure 4. Relative sliding speed (upper section) and the cumulative rolling angle (bottom section) of NDs from their initial state versus simulation time. The blue lines represent the results of simulations that take account of the surface-induced charges. The red dashed lines represent the results of simulations without involving the surface-induced charges. (a)–(c) Neutral NDs at loads of 333.3, 666.7, and 1000.0 MPa, respectively. (d)–(f) Positively charged NDs at loads of 333.3, 666.7, and 1000.0 MPa, respectively. (g)–(i) Negatively charged NDs at loads of 333.3, 666.7, and 1000.0 MPa, respectively.
Figure 5. Friction force versus simulation time under various applied loads in the presence and absence of surface-induced charges. The average friction forces are plotted on the right vertical axis. The blue dashed lines represent results under load 333.3 MPa. The red lines represent results under load 666.7 MPa. The yellow dot dash lines represent results under load 1000.0 MPa. (a) Neutral NDs with induced charges (left) and without induced charges (right). (b) Positively charged NDs with induced charges (left) and without induced charges (right). (c) Negatively charged NDs with induced charges (left) and without induced charges (right).

Table 3. Summarized Average Friction Force and Friction Coefficient Values (Friction Unit: eV/Å)

| case               | friction | error | coeff | friction | error | coeff | friction | error | coeff |
|--------------------|----------|-------|-------|----------|-------|-------|----------|-------|-------|
| neutral ND (with)  | 0.251    | 0.134 | 0.0187| 1.371    | 0.443 | 0.0510| 2.121    | 0.583 | 0.0526|
| neutral ND (without)| 0.231    | 0.128 | 0.0172| 1.197    | 0.520 | 0.0445| 2.013    | 0.509 | 0.0499|
| +ND (with)         | 1.126    | 0.221 | 0.0837| 1.811    | 0.592 | 0.0674| 3.534    | 0.605 | 0.0877|
| +ND (without)      | 1.013    | 0.262 | 0.0754| 1.450    | 0.477 | 0.0539| 3.195    | 0.479 | 0.0792|
| −ND (with)         | 4.743    | 0.784 | 0.3529| 8.003    | 1.206 | 0.2977| 10.235   | 1.505 | 0.2538|
| −ND (without)      | 1.105    | 0.299 | 0.0822| 2.088    | 0.492 | 0.0777| 3.416    | 0.607 | 0.0847|
3.3. Friction. Plotted in Figure 5 is the friction force versus simulation time under various applied loads in the presence and absence of surface-induced charges. The average friction forces are listed at the right axis of each plot. Fluctuations in friction forces are large, but overall trends are clearly evident in the data. Average friction forces, errors, and friction coefficient values are summarized in Table 3. In general, the friction force increases as the applied load increases. It tends to increase slightly when surface-induced charges are present for positive and neutral NDs (Figure 5a,b), but increases by nearly four times larger for negative NDs (Figure 5c) when surface-induced charges are present. In our previous work, a series of simulations showed that the surface-induced charges can increase the surface adhesion strength and the positive NDs have much stronger adhesion strength than negative NDs. Based on Figures 2 and 3, facet contact can be formed for neutral and positive NDs, and this sliding contact will be enhanced while the surface electrostatic interactions with the induced charges are involved. For negative NDs, apex contact is formed due to the relatively larger size of the \(-\text{COO}^-\) groups. Without the induced charges, the friction process is a similar combination of rolling and sliding motion due to apex contact, regardless of applied loads. After taking account of the surface electrostatic interactions with the surface-induced charges, the surface adhesion gives rise to a resistance of rolling, with friction arising from a mix of rolling—polishing and sliding—cutting—polishing. Because our simulations start with an atomically smooth surface, deformations will always increase friction. The facet sliding observed here for neutral and positive NDs (Figure 5a,b) therefore exhibits lower friction than that observed for negative NDs. The rolling and sliding motion of negative NDs without induced charges, meanwhile, leads to higher friction levels in association with surface deformation, and the mix of rolling polishing and sliding cutting polishing effect of negative NDs with induced charges leads to even higher friction levels (Figure 5c).

Fluctuations in the friction force and sliding speed similar to that observed here have also been reported in studies of dry friction. The same studies also show similar trends and magnitudes in friction values. Previous studies of dry contacts also identified surface deformation caused by carbon-based nanoparticles confined between sliding surfaces. In a study by Hu et al., they simulated dry friction of spherical NDs confined by sliding iron surfaces and estimated a friction coefficient of about 0.12 at a load of 500 MPa and 0.19 at a load of 1000 MPa. In Ewen et al., they also simulated dry friction of NDs confined by iron surfaces and showed that the friction coefficient ranges from about 0.03 to about 0.50 within a load range of 1000–5000 MPa. In the current work, we investigated the tribological performance of NDs with different surface treatments in aqueous suspensions. Generally, the simulations show lower friction in the hydrodynamic regime (facet contact), but higher friction in the contact bounded regime (apex contact). Without taking account of the electrostatic interaction with surface-induced charges, the friction coefficient varies from about 0.02 to about 0.08 for the different cases (Table 3). After taking account of the electrostatic interaction with surface-induced charges, for neutral and positive NDs, there is a slight increase of about 10% in the friction coefficient, while the friction coefficient increases by nearly four times and reaches a range of about 0.25–0.35 for negative NDs (Table 3).

4. CONCLUSIONS

A series of MD simulations of NDs were carried out in an aqueous environment between two sliding gold interfaces to better understand the effect of induced charge and surface functional group on friction and wear in this work. To study the influence of surface-induced charges on friction and wear, the simulations were carried out both with and without a model that includes these contributions to the interatomic forces. Because of the complexity and added computational burden associated with including these types of electrostatic forces, they are often neglected in simulations of this type. Therefore, the results reported here not only lend new insights into nanoparticle-surface dynamics but also help to guide how future studies should be carried out.

The simulations show that the ND-surface contact orientation, mechanisms of NP dynamics under shear, and surface wear all depend on the surface functional groups, as well as the load and inclusion of surface-induced charges. The neutral NDs show a preference for facet-surface contact under all loads. For positive NDs, facet contact occurs for loads through about 666.7 MPa, while the interface switches to apex contact under a higher load of \(\sim 1000\) MPa. For negative NDs, even at the load of 333.3 MPa, there is a preference for apex contact.

The rolling and sliding dynamics of NDs, as well as the degree of surface damage, was also shown to depend on surface functionalization and load. In general, the friction and number of displaced surface atoms increase with increasing load. Surface-induced charges have a relatively small effect on friction for positive and neutral NDs, but they increase friction nearly four times for negative NDs. Except for the neutral NDs at the lowest two loads (333.3 and 666.7 MPa) and the positive ND at the lowest load of 333.3 MPa, the inclusion of surface-induced charges increases the number of displaced surface atoms by a factor of about 2. At loads below about 666.7 MPa, both the neutral and positive NDs show primarily sliding dynamics under shear, which transitions to a rolling and sliding (neutral ND) or rolling motion (positive ND) as loads increase to 1000.0 MPa. In contrast, negative NDs show sliding or rolling dynamics with or without the induced charges, respectively, at the loads of 333.3 MPa. As load is increased, the negative NDs simulated with induced charges show a combination of rolling and sliding. In all cases, rolling dynamics, which is associated with a preference for apex contact compared to facet contact, leads to more displaced surface atoms.

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Notes
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