Spherical Nanoparticle–Substrate Adhesion Interaction Simulations Utilizing Molecular Dynamics

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Abstract
From a molecular perspective, the fundamental rolling and sliding elasto-adhesion interactions between a spherical nano-particle and an elastic substrate is studied using a computational technique based on the Molecular Dynamics (MD) approach. Initially, the particle and the substrate were equilibrated individually at 300 K. The covalent bonds interactions between the atoms of the nanoparticle are modeled by constraining the atoms to stay together throughout the simulation. The temperature of the substrate atoms is regulated by periodically scaling to mimic the bulk substrate effect to minimize the effects of the finite substrate size. The intermolecular interaction between the particle and the substrate is defined by the Lennard–Jones (LJ) 12-6 potential. The total force–displacement curves of the 4.2 and 7.89 nm particles in the cases of particle being pushed normally towards the substrate and the particle pushed tangentially, while in adhesion with substrate, are obtained. The rolling resistance moment exhibited by the smaller nanoparticle (4.2 nm) is calculated from the force–displacement curve obtained from simulations and compared to the theoretical predictions based on a two-dimensional adhesion model. It is found that the moments as a function of the rotation angle $\theta$ are of the same order (3.64$\theta$ nN nm). The rolling and sliding force–displacement profiles when the nanoparticle is subjected to tangential load are also presented.

Keywords
Nanoparticle adhesion, molecular dynamics simulations, rolling resistance moment, rolling motion, sliding motion, nanoparticles

1. Introduction
The equilibrium of the particle–substrate system when a normal (out-of-plane) load is applied is well understood by several one-dimensional adhesion models. A uni-
A three-dimensional nanoparticle–substrate system was modeled for the presented computational investigation. The material of the particle and the substrate considered was silicon (diamond structure) with a lattice distance parameter of 0.543 nm. The simulations were performed with two different particle sizes, and the dimensions of the substrate were altered depending on the size of the particles to minimize the boundary effects. Prior to energy equilibration, the initial diameters of the two particles were 3 nm (Case 1) and 6 nm (Case 2), and the simulation domain se-
lected for 3 nm (Case 1) and 6 nm (Case 2) particles are 7 nm × 10 nm × 7 nm and 12 nm × 15 nm × 12 nm, respectively. The particle and the substrate domains were populated with atoms having a spacing of the lattice distance of silicon. The number of atoms in the substrate and the particle for Case 1 were 5070 and 712; for Case 2 were 14 876 and 5654, respectively. All the boundary atoms of the substrate were constrained by setting the external forces on these atoms to zero, except for the top atoms that are exposed to the particle. The simulation domain is selected to be periodic in the x-direction, so that the atoms leaving the boundary at the x-maximum would enter from the other side (x-minimum) of the boundary. Thus, the simulation domain could be smaller and, as a result, the number of atoms in the simulations is minimized.

3. Simulation Scheme

The atoms of the particle and the substrate were equilibrated to bring the system to its minimum energy configuration at a room temperature of 300 K. This equilibration was performed to ensure that the atoms were not far from their equilibrium at the specified temperature. In the present simulations, the atomic lattices for the particle and the substrate are equilibrated individually at 300 K. Two particle sizes were investigated to understand the effect of the particle size on their removal mechanisms. The computational scheme for the smaller (3 nm) and the bigger (6 nm) particles is explained as two cases below.

Case 1: The 3 nm particle was first displaced by 1.4 nm in the positive y-direction from its original position in order to be at a distance greater than the cut-off radius of the substrate. As a result, when the particle is pushed down towards the substrate, the initial force of adhesion between the particle and the substrate would be almost zero. At this position, the particle was equilibrated to its minimum energy configuration at 300 K using the NVE (constant volume (V), constant energy (E)) integration. In the NVE ensemble (also referred to as microcanonical), the system is isolated from changes in moles (N), volume (V) and energy (E) and updates the position and velocity for atoms in the group at each time step. The atom coordinates were rescaled for 150 000 steps with a constant time step of 0.008 fs. It was observed that at the end of the minimization process, the atoms rearranged to a configuration with expansion of particle diameter to 4.2 nm from its original diameter of 3.0 nm, and the shape of particle became closer to a perfect sphere. Then the substrate was equilibrated to its minimum energy configuration at the same temperature (300 K) for 10 000 steps with a time step of 0.001 fs. The temperature of the particle and the substrate was saved for every 200 steps. The equilibration temperature change as a function of the sample steps is depicted in Fig. 1.

Case 2: As the particle (6.0 nm) was larger in diameter, it was displaced by 2.0 nm in the positive y-direction from its initial position, and then the particle was equilibrated to its minimum energy configuration at 300 K using the NVE integra-
tion and rescaling the atom coordinates for 50,000 steps with a constant time step of 0.03 fs. It was observed that, at the end of the minimization process, the diameter of the particle expanded to 7.89 nm from 6.0 nm. Then the substrate was equilibrated to its minimum energy configuration at the same temperature (300 K) for 80,000 steps with a time step of 0.005 fs. The temperature data were saved for every 200 steps. The equilibration temperature change for Case 2 is summarized in Fig. 2. The before and after equilibration images of the 3.0 nm and the 6.0 nm particles are shown in Fig. 3. As a result of the temperature equilibration, as depicted, the shapes of both particles became closer to a perfect sphere.

Once the particle and the substrate were equilibrated to their minimum energy configurations, the atoms of the particle were constrained such that these atoms
always stayed together in the form of near-sphere to model the effect of the covalent bonds in between the particle atoms i.e., the inter-atomic forces due to the van der Waals attractive/repulsive forces between the nanoparticle atoms are neglected since the covalent bond strength is much higher than the van der Waals force by nearly two orders of magnitude.

The particle–substrate and the substrate atoms were made to interact by the 12-6 Lennard–Jones (LJ) pair potential given by:

$$\phi = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^6 - \left( \frac{\sigma}{r} \right)^{12} \right]$$, \hspace{1cm} (1)

where $\varepsilon$ and $\sigma$ are, respectively, the pair potential and the spacing between the atoms when the potential crosses the axis. In the simulations, the values of the parameters are taken as $\varepsilon = 0.4023$ kcal/mol, $\sigma = 0.3826$ nm [9] and the cut-off radius $r = 2.5\sigma$. The Lennard–Jones potential is the most common potential used to model the van der Waals adhesion/repulsion force between the particle and the substrate. The particle atoms were constrained to be rigid, and the NVE integration was removed from the particle and all the substrate atoms were integrated by NVE and rescaled to 300 K at every 5 steps. This process was to absorb the impact of the high speed particle approaching the substrate and also to model the behavior of the bulk substrate, to minimize the effects of the finite substrate size.

**Normal External Force:** The equilibrated rigid particle in both cases was then subjected to a constant velocity field in the direction of the substrate normal (the negative $y$-direction) to study the interactions of the particle and the substrate system due to adhesion. In this case, the equilibrium of the particle–substrate system is well understood by the one-dimensional adhesion models [1] and, therefore, the
comparison of the MD simulation results with the continuum mechanics models is possible. The velocity field was set to 0.045 nm/fs and the nanoparticle in Case 1 (4.2 nm) was pushed for 25,000 steps at a time step of 0.001 fs, while in Case 2 (7.89 nm), the nanoparticle was pushed for 30,000 steps. Note that the velocity used was very high compared to the speed of sound in the material, yet the time step was very short. The effective displacement of the particle per step was 0.000045 nm. The force acting on the particle due to the interactions in the vicinity of the distance given by the cut-off radius (0.956 nm) and the position of the lowest atom in the particle and the atoms on the upper surface of the substrate were saved for every 100 steps for Case 1 and 300 steps for Case 2 for further analysis. The positions of all the atoms of the substrate and the particle at every 200 steps for Case 1 and every 300 steps for the larger particle were saved for the visualization of motion of

**Figure 3.** The locations of the atoms of the particle in Case 1 (diameter 4.2 nm) (a) and Case 2 (diameter 7.89 nm) (b) before (top) and after (bottom) minimization.
the particle subjected to the normal force. The total normal component of equilibrium force ($F_{ad}$) acting on the particle due to interactions with the substrate and the separation distance between the particle and the substrate for the particle in Case 1 (4.2 nm) and Case 2 (7.89 nm) are shown in Fig. 4. The number of time steps and the size of the time step for equilibration were selected such that the maximum adhesion (attractive) force (Fig. 4) was within the pull-off force estimated from the JKR and DMT models, as expected from the adhesion map [1]; i.e., the pull-off force estimated from JKR and DMT theories was used as a norm to attain the current configuration. According to the adhesion map, the simulation carried out using the LJ potential lies in between the JKR and DMT models. The maximum force of adhesion for the 4.2 nm particle is 0.53 nN at a separation distance of 0.413 nm and
the maximum force of adhesion for the 7.89 nm particle is 0.81 nN at a separation distance of 0.396 nm. The three-dimensional image of the particle–substrate system for Cases 1 and 2 with the number of atoms in each case are depicted in Fig. 5.

Radial External Force: The equilibrated rigid particle in Case 1 was then moved by 1.1 nm (1.5 nm in case of the particle in Case 2) in the negative $x$-direction from the initial center of the particle and in $y$ by the equilibrium distance, which is the separation distance where the adhesion force is maximum, as illustrated in Fig. 4. The particle is subjected to the maximum adhesion force due to the substrate at this equilibrium point. The mode (rolling/sliding) of particle motion depends on the number and the location of the atoms which were subjected to an external load (velocity). In this investigation, the atoms selected were on the periphery of the particle with the minimum $x$-coordinate value and at the center of the particle in the $z$-direction.

To achieve rolling, the constant velocity was applied on the atom which had the minimum $x$-coordinate and at the center of the $y$- and $z$-coordinates for the particle in Case 1 and on the atom which had the minimum $x$-ordinate, slightly above the center of $y$-coordinate and at the center of the $z$-coordinate, for the particle in Case 2. Again the atoms of the substrate are rescaled throughout the simulation to mimic the elastic behavior of the bulk substrate. The simulation was run for 80,000 steps at a time step of 0.001 fs. The force on all the atoms and the position of the center of the particle at every 400 steps were obtained. The simulation was repeated
for a range of external velocities of 5 nm/fs, 100 nm/fs and 200 nm/fs for the particle in Case 1 and at 200 nm/fs and 1200 nm/fs for the particle in Case 2.

For studying the *sliding* motion of the particles, the constant velocity was applied at six pre-defined atoms for the Case 1 particle; at center and three atoms for the Case 2 particle, which are located on the periphery of the particle with the minimum

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**Figure 5.** The three-dimensional models of the particle–substrate systems in Cases 1 (top) and 2 (bottom), respectively.
x-coordinate. During sliding, the substrate atoms were rescaled as described above. The simulation was run for 80,000 steps at a time step of 0.001 fs. The force on all the atoms and the position of the center of the particle at every 400 steps were acquired. In all these simulations, the positions of all the atoms were saved for every 400 steps for visualization of the motion of the particle under external force. This simulation procedure was repeated for a range of external velocities of 5 nm/fs, 16.7 nm/fs and 100 nm/fs for the Case 1 particle and with velocities of 200 nm/fs, 1200 nm/fs (on one atom) and 400 nm/fs (on three atoms) for the Case 2 particle.

Also, a combination of rolling and sliding motion was achieved by exerting a uniform velocity field on two atoms of the particle in Case 2. One of the atoms was located slightly above the center of the $y$-coordinate and at the center of the $z$-coordinate for the larger particle and the other atom at the center of $y$- and $z$-coordinates and on the periphery of the particle with the minimum $x$-coordinate. A uniform velocity of 500 nm/fs was applied and the remaining parameters were kept the same as the previous cases.

4. Simulation Results

It is evident from Fig. 3 that, as anticipated, the particles became more spherical after the minimization process. The three-dimensional model of the particle–substrate system indicating the number of atoms for the Case 1 (4.2 nm) and the Case 2 (7.89 nm) particles are shown in Fig. 5. The total force experienced by the particle due to interaction with the substrate versus the separation distance between the particle and the substrate for the two cases is reported in Fig. 4. The maximum forces experienced in the simulations of adhesion for Case 1 and Case 2 are 0.5295 nN and 0.8153 nN, respectively. While the pull-off force estimations from the JKR theory for Case 1 and Case 2 are 0.4195 nN, 0.5581 nN and for DMT theory for Case 1 and Case 2 are 0.7888 nN and 1.0517 nN, respectively, assuming a work-of-adhesion value for the Si–Si system $W_A^* = 42.4$ mJ/m$^2$ calculated from the Hamaker constants reported in the literature [10]. The rolling and sliding of the particle in Case 1 when subjected to a constant velocity at two instances of time are shown in Fig. 6. The modes for the particle in Case 2 with an external velocity of 1200 nm/fs and 400 nm/fs for rolling and sliding, respectively, at two instances of time are depicted in Fig. 7. The total equilibrium force components in the $x$- and $y$-directions (represented by $F_x$ and $F_y$, respectively) acting on the particle and the relative displacement ($x_0$) of the center atom for the smaller particle and for the bigger particle when subjected to different levels of external velocities for the case of rolling and sliding are plotted in Figs 8 and 9, respectively. The slope of the curve (resisting the applied force) in the displacement range $x_0 = 10.05–10.65$ nm is determined to be $k = 0.82$ N/m (Fig. 8(c)). The work-of-adhesion calculated is then given by $W_A = k/6\pi = 43.7$ mJ/m$^2$ [6], which is in good agreement with the work of adhesion $W_A^* = 42.4$ mJ/m$^2$ [9]. Also, the rolling
resistance moment as a function of rolling angle $\theta$ approximated from simulations is $M = kr^2\theta = 3.64\theta$ nN nm and the theoretical prediction for rolling resistance moment $M^* = 6\pi W_A r^2\theta = 3.52\theta$ nN nm.

Comparing the equilibrium force curves due to rolling and sliding in Fig. 8, it is evident that the force due to sliding is almost constant while the force due to rolling varies as the particle rolls, which is possibly due to the variation in the contact area. The particle tries to resist the motion when it rolls as indicated by the force curve in the horizontal component of the equilibrium force and there is a repulsive force as observed from the vertical component of the equilibrium force. However, the equilibrium force for the particle in Case 2, shown in Fig. 9, indicates that the

![Figure 6](image_url)
force required for rolling, sliding and roll–slide are of the same order. Also, the force of interaction between the substrate and the particle is the same, irrespective of the applied external velocity, except that the displacement of the particle would vary, which implies that the particle would follow the same force–displacement curve. Note that for sliding the particle in Case 2, the atoms of the particle that were selected in each case were different and the velocities were different, yet the particle tends to follow the same sliding curve. Thus, the rolling and sliding profiles for the particles in Case 1 and Case 2 were determined along with rolling–sliding profile of the Case 2 particle. Also, the deformation of the particle would be small in these simulations as the particle motion is averaged in every time step as the particle is
Figure 8. The total force components in the $x$- and $y$-directions ($F_x$ and $F_y$) ((a) and (b) respectively) acting on the particle (Case 1) vs the relative displacement of the central atom of the particle ($x_0$). The dotted and solid lines represent the rolling and sliding of the particle, respectively, and (c) shows part of the curve in (a) in the range of $x_0 = 10.05–10.65$ nm. The slope of this curve obtained by linear curve fitting is 0.82464 N/m.

made rigid in order to mimic the covalent bond attraction between the atoms of the particle.

Comparing the normal and the tangential forces (Fig. 8(a) and 8(b)) experienced by the 4.2 nm particle, the order of the magnitude of both forces is the same. However, the order of the tangential force is two orders of magnitude lower than the normal force in case of the 7.89 nm particle. The rolling resistance moment for the 7.89 nm particle was determined to be similar to the 4.2 nm particle, but the rolling
resistance moment was one order of magnitude lower than the predicted value. The reason for this discrepancy is currently unclear and further studies to better understand the phenomena are underway.

5. Summary and Conclusions

Understanding the particle–substrate adhesion at molecular level is essential for nanoparticle removal and manipulation applications. In the reported computational investigation, using LAMMPS code, the elasto-adhesive interactions of two spherical silicon particles of different sizes (4.2 nm and 7.89 nm) were simulated. Initially, the particle and the substrate were equilibrated to their minimum energy configuration at 300 K individually in both cases. The particles were then pushed normally towards and parallel to the substrate. The total adhesion force due to the interaction of the particle and the substrate atoms within the cut-off radius was determined. The parameters for the minimization of the particle in both cases were selected such that this total force would stay within the limits of the pull-off force predicted from JKR and the DMT theories. The particles were displaced to the equilibrium point where the adhesion force was maximum. At this position, the particle was subjected to an external velocity in the tangential direction. The rolling, sliding and the combination of both were observed based on the locations and the number of atoms that were subjected to an external uniform velocity. The force–displacement profiles in all the above mentioned cases were obtained. The slope obtained from the rolling curve with peak negative force was used to calculate the rolling resistance moment and the calculated value was in good agreement with the theoretical predictions based on a two-dimensional model. It is also observed that the parti-
Figure 9. The total force components in the x- and y-directions ($F_x$ and $F_y$) ((a) and (b) respectively) acting on the particle (Case 2) vs the relative displacement of the central atom of the particle ($x_0$). The solid, dotted and the line with an asterisk (*) marker represent the rolling, sliding and rolling/sliding of the particle, respectively.

cle tends to follow the same profile as the force experienced by the particle due to the substrate, even though the external velocity in the tangential load is changed significantly. Thus, the total force profiles of the particle for rolling, sliding and
rolling/sliding modes are identified. The equilibrium force curves for the 4.2 nm particle indicated that the particle tends to exhibit resistance to motion in the course of rolling, while the force for sliding remains constant throughout the simulation. For the 7.89 nm particle, the equilibrium force for rolling, rolling/sliding and sliding remains almost the same. The particle motion profiles for the case of rolling, sliding and rolling/sliding were identified. A discrepancy in the order of magnitude of the tangential and normal forces and the rolling resistance moment for the bigger particle was observed and studies to understand the phenomena are underway.

References