Modeling the Dynamics of a Spiky Anisotropic Particle Over a Surface

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Modeling the Dynamics of a Spiky Anisotropic Particle Over a Surface

by

Darrel Qi-Jie Chew

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Abstract

Anisotropic particles have gained increasing interest due to their possible applications in biotechnology, such as for drug delivery, biosensing, and imaging. In particular, spiky particles have been shown to perform better than their smooth counterparts in terms of binding affinity and cellular uptake. However, these studies did not replicate the dynamic conditions of these particles in the bloodstream when interacting with other particles or surfaces, which could diminish their efficacy. This work focuses on modeling the dynamics of a spiky anisotropic particle relative to a surface given its DLVO interactions. The force and torque of the spiky particle is calculated using numerical differentiation methods, which are validated by comparing the numerically calculated force and torque of an ellipsoid with the analytically calculated force and torque.
Introduction

Increasing amounts of research have been done on the numerous applications of anisotropic particles in recent years. Janus particles have been investigated for use in imaging,\textsuperscript{1,2} sensing,\textsuperscript{3} and drug delivery\textsuperscript{4,5} due to their asymmetry allowing for more targeted and diverse interactions. Experimentally, spiky particles have specifically shown to have higher bio-affinity over their smoother counterparts;\textsuperscript{6,7} the mechanism behind this phenomena is less clear, although studies have indicated that the spikes could be able to penetrate cells to selectively release the biomolecule.\textsuperscript{8}

Less research has been conducted on the dynamics of anisotropic particles. A few of these works have focused on experimentally finding how these particles interact with surfaces and other particles in fluid flow,\textsuperscript{9} while computational fluid dynamics studies have been able to model single and pair particles with ellipsoidal shapes.\textsuperscript{10-13} However, much of this research is limited for anisotropic particles with more complex shapes. As a result, there has been a lack of research done on the dynamics of spiky particles, which is a critical characteristic to their efficacy and potential in applications.

In this study, we analyze a method to calculate the force and torque exerted on a spiky particle by a surface. This method is validated by applying it on ellipsoids and comparing the results to the analytically calculated force and torque. This method is then applied to spiky particles to calculate the force and torque and derive a better understanding of their dynamics.
Theory

In this work, spiky particles are modeled as having composite geometry with a spherical core and ellipsoidal spikes at locations corresponding to the vertices of either a regular tetrahedron, cube, octahedron, or dodecahedron. The surface of the spherical core and the spikes are generated using a refined mesh with a resolution smaller than 0.001 times the core radius. The spike mesh is rotated to the polyhedron vertex orientation, and the overlapping areas between the core and spikes are removed.

Particles are represented in terms of laboratory coordinates, where the particle is expressed relative to a fixed reference frame \((x, y, z)\), or in terms of particle coordinates, where the particle is expressed in terms of its own semi-axes \((x', y', z')\), as depicted in Figure 1. Euler angles \((\phi, \theta, \psi)\) are commonly used to define rotations between coordinate systems, where \(\phi\) is the polar angle, \(\theta\) is the azimuthal angle, and \(\psi\) is the rotor angle about the \(z'\) axis.

![Diagram of a spiky particle](image)

**Figure 1.** Representation of a spiky particle close to a surface. \((x, y, z)\) represents the laboratory coordinate system. The particle's axes \((x', y', z')\) are defined by rotating the fixed particle axes by the Euler angles \((\phi, \theta, \psi)\).
However, Euler angles suffer from singularities at certain orientations and take a lot of computing power because of the numerous amounts of trigonometric functions that are calculated for each rotation.\textsuperscript{14,15} Quaternions are an alternative to Euler angles that can express any rotation. They are defined as

\begin{align*}
q_0 &= \cos \left( \frac{\phi}{2} \right) \cos \left( \frac{\psi + \theta}{2} \right), \\
q_1 &= \sin \left( \frac{\phi}{2} \right) \cos \left( \frac{\psi - \theta}{2} \right), \\
q_2 &= \sin \left( \frac{\phi}{2} \right) \sin \left( \frac{\psi - \theta}{2} \right), \\
q_3 &= \cos \left( \frac{\phi}{2} \right) \sin \left( \frac{\psi + \theta}{2} \right),
\end{align*}

where \( q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1 \).\textsuperscript{16}

Surfaces in lab coordinates can be transformed into particle coordinates by

\[ \mathbf{H}' = \mathbf{A} \cdot \mathbf{H}, \]

where \( \mathbf{H}' \) is a surface in particle coordinates, \( \mathbf{H} \) is a surface in lab coordinates, and \( \mathbf{A} \) is the rotation transformation matrix, which is given by\textsuperscript{16}

\[ \mathbf{A} = \begin{pmatrix}
A_{11} & A_{12} & A_{13} \\
A_{21} & A_{22} & A_{23} \\
A_{31} & A_{32} & A_{33}
\end{pmatrix}. \]

For quaternions specifically, \( \mathbf{A} \) is represented as\textsuperscript{16}

\[ \mathbf{A} = \begin{pmatrix}
q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2(-q_1q_2 + q_0q_3) & 2(q_1q_3 + q_0q_2) \\
-2(q_1q_2 + q_0q_3) & q_0^2 - q_1^2 + q_2^2 - q_3^2 & 2(-q_2q_3 + q_0q_1) \\
2(q_1q_3 - q_0q_2) & -2(q_2q_3 + q_0q_1) & q_0^2 - q_1^2 - q_2^2 + q_3^2
\end{pmatrix}. \]

The DLVO interaction potential \( U \) between particles and surfaces is well defined in literature as\textsuperscript{17}

\[ U = U_e + U_v, \]

where $U_e$ represents the electrostatic potential and $U_v$ represents the van der Waals potential. These potentials are presented as:

$$U_e = -\frac{\kappa}{2\pi} Ze^{-\kappa h}, \quad (6)$$

$$U_v = \frac{A_H}{12\pi h^2}, \quad (7)$$

respectively, where $\kappa^{-1}$ is the Debye length, $h$ is the minimum separation distance between the particle and the surface, $A_H$ is the Hamaker constant, and $Z$ is given by:

$$Z = 64\pi \varepsilon_m \left(\frac{k_B T}{Z_v e}\right)^2 \tanh \left(\frac{Z_v e \psi_p}{4k_b T}\right) \tanh \left(\frac{Z_v e \psi_w}{4k_b T}\right), \quad (8)$$

where $k_B$ is Boltzmann’s constant, $T$ is absolute temperature, $e$ is electron charge, $\varepsilon_m$ is the medium dielectric constant, $Z_v$ is the electrolyte valence, $\psi_p$ is the particle potential, and $\psi_w$ is the wall surface potential. To apply these formulations to our system, the electrostatic and van der Waals potentials are calculated for each point in the mesh using the Surface Element Integration (SEI) method, which are summed to yield the DLVO potential.

The force exerted by the surface on the particle is given by

$$F = -\frac{\partial U}{\partial Z} = -\frac{\partial U}{\partial h}. \quad (9)$$

Since the spiky particles in this study are generated using a mesh, it is not possible to analytically determine the force. Since the force is only dependent on the separation distance, it is sufficient to use a forward finite difference to approximate the derivative. A major consideration when using numerical differentiation techniques is the short-range variation of the van der Waals interaction, i.e., if the step size is too large, the calculated
derivative will not be accurate, and if the step size is too small, the calculated derivative may have large roundoff errors.

The torque exerted by the surface on the particle is given by

\[
\mathbf{M} = -\frac{1}{2} \left( \frac{\partial U}{\partial q_0} \mathbf{q} + q_0 \frac{\partial U}{\partial \mathbf{q}} + \mathbf{q} \times \frac{\partial U}{\partial \mathbf{q}} \right),
\]

(10)

where the quaternion \( \mathbf{q} \) is expressed as

\[
\mathbf{q} = q_0 - i q_1 + j q_2 - k q_3.
\]

(11)

A second divided difference with an appropriate step size (10\(^{-7}\)–10\(^{-6}\)) can be used to accurately approximate the derivative.

Since analytical potentials are defined for ellipsoids, the numerical differentiation techniques for finding force and torque can be compared against the analytical values. The potential for an ellipsoid interacting with a plane surface is defined as

\[
U(z) = a Z e^{-\kappa(z-S_{z,min})} - \frac{a A_H}{6(z-S_{z,min})^3},
\]

(12)

where \( z \) is the distance between the particle center and the surface and \( S_{z,min} \) for an ellipsoid and \( a \) are defined as

\[
S_{z,min} = \sqrt{(r_x A_{13})^2 + (r_y A_{23})^2 + (r_z A_{33})^2},
\]

(13)

\[
a = \Gamma^{-\frac{1}{2}},
\]

(14)

where \( r_x, r_y, \) and \( r_z \) are the lengths of the semi-axes of the ellipsoid and \( \Gamma \) is the Gaussian curvature, which for an ellipsoid is defined as

\[
\Gamma = \frac{1}{r_x^2 r_y^2 r_z^2} \left( (r_x A_{13})^2 + (r_y A_{23})^2 + (r_z A_{33})^2 \right)^2.
\]

(15)
The minimum separation distance $h$ between the ellipsoid and the plane surface is defined as\textsuperscript{17}

\[ h = z - S_{z,\text{min}}. \]  

\[ (16) \]

$A_{13}, A_{23},$ and $A_{33}$ are defined in terms of quaternions, as defined in Eq. (4). The equation for the potential of an ellipsoid, Eq (12), can be directly differentiated to calculate force and torque to validate the numerical approach.
Results and Discussion

In this work, the core has radius $R = 0.5 \, \mu m$, and the spikes have semi-axes with lengths $r_x = r_y = 1 \, \mu m$ and $r_z = 5 \, \mu m$. The particles were modeled in a system with $T = 298 \, K$, $\varepsilon_m = 78 \varepsilon_0$, $z_v = 1$, $\psi_w = \psi_p = -0.025$, $\kappa^{-1} = 3.04 \, nm$, and $A_H = 20.57 k_B T$.

The proposed procedure for calculating the force and the torque of spiky particles was validated by comparing the force and torque of an ellipsoid calculated with numerical and with analytical differentiation.

The force was calculated by numerically differentiating the potential, Eq (12), with respect to separation distance. Figure 2 shows the effect of various step sizes on the forward finite difference to calculate the force on a sphere ($r_x = r_y = r_z = 1 \, \mu m$), prolate ($r_x = r_y = 1 \, \mu m, r_z = 3 \, \mu m$), oblate ($r_x = 1 \, \mu m, r_y = r_z = 3 \, \mu m$), and a triaxial ellipsoid ($r_x = 1 \, \mu m, r_y = 2 \, \mu m, r_z = 3 \, \mu m$) at a separation distance of $h = 5 \, nm$. All the panels show that a step size of $10^{-15} \, m$ is sufficient for determining the force on the particle. Figure 3 compares the numerical and analytical force of a triaxial ellipsoid using a step size of $10^{-15} \, m$. These results reinforce that this step size provides accurate values for the force as the particle moves between 1 to 100 nm away from the surface. Therefore, a step size of $10^{-15} \, m$ was used for future numerical force calculations.
Figure 2. Plot of the numerical approximation of force for a (a) sphere, (b) prolate, (c) oblate, and (d) triaxial ellipsoid as a function of step size. The analytical force is plotted as a baseline for comparison. The particles are at orientation $\phi = 30^\circ$, $\theta = 45^\circ$, and $\psi = 60^\circ$.

Figure 3. Plot of the force exerted by the surface on a triaxial ellipsoid as a function of $h$. The finite difference was calculated using a step size of $10^{-15}$ m. The particle is at orientation $\phi = 30^\circ$, $\theta = 45^\circ$, and $\psi = 60^\circ$. 
The torque was first validated by calculating the gradient of the potentials with respect to quaternions and comparing it to the analytical value. Figure 4 shows the effect of various step sizes on the second divided difference to calculate the gradient of the potential with respect to quaternions on a triaxial ellipsoid. The panels show that a step size of $10^{-7}$ is sufficient for getting the gradient with respect to quaternions. Figure 4 (b) and (c) show that a step size of $10^{-6}$ produces more accurate results for the gradient with respect to $q_1$ and $q_2$. Figure 4 (a) and (d) show that a step size of $10^{-6}$ quickly decreases the accuracy of

![Image of graphs showing the effect of step size on the gradient of potential](image)

Figure 4. Plot of the numerical approximation of the gradient of the potential with respect to (a) $q_0$, (b) $q_1$, (c) $q_2$, and (d) $q_3$ of a triaxial ellipsoid as a function of step size. The analytical gradient is plotted as a baseline for comparison. The particle is at orientation $\phi = 30^\circ$, $\theta = 45^\circ$, and $\psi = 60^\circ$. 
the gradient with respect to \( q_0 \) and \( q_3 \). Therefore, a step size of \( 10^{-7} \) was used for future numerical gradient calculations.

Figure 5 compares the numerical and analytical calculation for the gradient of the potential with respect to quaternions while changing \( \phi \). No physical qualities can be used to validate these plots; the torque exerted on a sphere by a surface should be zero, but the gradient of the potential with respect to one quaternion is just one component of that

![Figure 5](image)

Figure 5. Plot of the numerical approximation and analytical calculation of the gradient of the potential as a function of \( \phi \) for a (a) sphere, (b) prolate, (c) oblate, and (d) triaxial ellipsoid. The solid lines represent the analytical calculation, and marks are used to represent the numerical approximation. The colors represent which quaternion the gradient of the potential is calculated with respect to. The particles are at orientation \( \theta = 45^\circ \) and \( \psi = 60^\circ \).
calculation, so it can be nonzero. However, each panel does show that the numerical gradient is consistent with the analytical gradient. Figure 6 compares the numerical and analytical calculation for the torque exerted on the particle by the surface while changing $\phi$. Figure 6 (a) accurately shows that the torque exerted on a sphere is zero, and the error associated with the numerical method is on the order of $10^{-9}$. Figure 6 (b) and (c) show that the torque associated with the particle’s z-axis and x-axis respectively is zero regardless of the value of

Figure 6. Plot of the numerical approximation and analytical calculation of the torque (particle coordinates) as a function of $\phi$ for (a) sphere, (b) prolate, (c) oblate, and (d) triaxial ellipsoid. The solid lines represent the analytical calculation, and marks are used to represent the numerical approximation. Red represents the x-component of torque, green represents the y-component, and blue represents the z-component. The particles are at orientation $\theta = 45^\circ$ and $\psi = 60^\circ$. 
\(\phi\), which is expected due to the force being directed upwards from the surface. All the panels show that the torque at \(\phi = 0\) is zero, which corresponds to the particle axis perpendicularly aligned to the plane surface.

Figure 7 shows the force exerted by the surface on a particle with spikes corresponding with the vertices of a tetrahedron, cube, octahedron, and dodecahedron as a function of separation distance. The force sharply decreases for cubes and octahedrons as they move farther away from the surface, while it more slowly decreases for tetrahedrons and dodecahedrons.

Figure 8 shows the torques exerted by the surface on a spiky particle with spikes corresponding with the vertices of a tetrahedron, cube, octahedron, and dodecahedron as a function of \(\phi\). Figure 8 (a) shows that the tetrahedron appears to have a large shift in torque after a rotation of around 110°, which is approximately the bond angle in tetrahedral geometries. The cube in Figure 8 (b) has symmetrical components of torque as a function of \(\phi\) in the particle’s x-axis and y-axis and a very low torque in the particle’s z-axis. The

\[\text{Figure 7. Plot of the force exerted by the surface on a particle with spikes at the vertices of a tetrahedron, cube, octahedron, and dodecahedron as a function of separation distance. The particles are at orientation } \phi = 30^\circ, \theta = 45^\circ, \text{ and } \psi = 60^\circ.\]
octahedron in Figure 8 (c) also has symmetrical components of torque in the particle’s x-axis and y-axis and shows large shifts in torque at 45° and 135°. The dodecahedron in Figure 8 (d) has much more angular variability than the other polyhedrons, which may be attributed to its lack of symmetry when rotating about $\phi$.

Figure 8. Plot of the torque (particle coordinates) as a function of $\phi$ for a spiky particle with spikes at the vertices of a (a) tetrahedron, (b) cube, (c) octahedron, and (d) dodecahedron. Red represents the x-component of torque, green represents the y-component, and blue represents the z-component. The particles are at orientation $\theta = 45^\circ$, and $\psi = 60^\circ$. 
Conclusion

This work suggested and validated a way to calculate the force and torque exerted on a spiky particle using numerical differentiation to study the dynamics of spiky particles over a plane surface. The force calculation can be done using a forward difference, while the torque calculation fares better with a second divided difference. The force shows a similar decay as presented by other particle shapes; however, the torque shows a large angular variability, which requires further analysis for a better understanding.

In the future, it may be beneficial to calculate the interaction energy between a particle pair to calculate the interacting forces and torques using the same procedure presented in this work; additionally, it would be of interest to include the present results to simulate multiple spiky particles given their force and torque, incorporating hydrodynamic interactions to get a better sense of their dynamics near plane surfaces.
References


