Analyzing structural and tribological characteristics of different materials at micro- and nano-level using molecular dynamics simulations: An overview

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Abstract. This review paper presents structural and tribological characterization of various materials at micro- and nano-level using molecular dynamics simulation. The investigated computational methods of molecular dynamics simulation are briefly explained. Molecular dynamics is the most accurate theoretical model to speculate motions at molecular level and are mainly used to study chemical and mechanical behavior of various phenomena with tribological properties like friction, wear and self-lubrication properties. The dynamics of transformation of structure, microstructure and composition with mechanical and chemical performances of different composites are reviewed. The mechanisms of friction, wear and self-lubricating behavior are analyzed for self-lubricating materials using available MD software models, LAMMPS being easily available and having low computational cost is the most widely used modeling software. These models are used to study and compare properties at micro and nano-level because in the first place friction and wear need to be controlled at molecular level. This paper is intended to render molecular dynamics simulation which is utilized to study the dynamics of various parameters of atoms and molecules in various phases at molecular level of different materials with main focus on friction and self-lubricating materials. The main focus behind this review is to present the potential and competence of computational modeling methods to envisage behavior and performance of different models at molecular level.

1. Introduction
The molecular level structure plays an influential role to generate new materials with control over significant properties required for specific applications. To understand and conduct molecular level analysis, need for a tool or computational method arises which is fulfilled by molecular simulation methods, such as, molecular dynamics, molecular mechanics, quantum mechanics and Monte Carlo [1]. In order to determine the time dependent parameters like position, velocity and direction of atoms and molecules in solids, liquids and gases the method of molecular dynamics is utilized [2]. Molecular dynamics models determine mechanical and chemical performance along with friction, wear and self-lubrication behavior [3]. With the growth of science and technology the significance of these methods increase. The dynamic characteristic features of the microstructure that take place during sliding are manifested by molecular dynamic simulations which are not exhibited by experiments. The various methods are employed to conduct simulations at molecular level.

1.1 Methods
The methods briefly described below have merits and demerits which are used in selecting the most appropriate technique as per the requirement and need of application.

1.1.1 Quantum mechanical (QM) method
In quantum mechanics the particles are considered as wave functions at molecular level, this method resolves Schrodinger’s equation in many-particle system [1, 3, 4]. Schrodinger’s equation that relates the motion of electrons and nuclei is as;
\[ H \psi = E \psi \]  
(1)

\[ H = E_k + E_p \]  
(2)

Here \( E_k \) and \( E_p \) represent kinetic and potential energy respectively. The wave function depends on 3N-coordinates in 3D system and in molecular level, existence of small particles make it difficult to resolve and apply equations. The exponential growth in time with increase in number of particles makes it difficult and impracticable for complicated models regardless of being a very accurate model.

1.1.2 Molecular mechanics (MM) method

This computational method is established to develop models based on classical mechanics where atoms in molecules are considered as mass particles which take part in force fields, bonds between molecules are treated as springs and the potential energy function is the sum of individual functions for bond stretching, angle bending, torsional energies, and non-bonding interactions\[3, 4\]. This method is used for large molecules but different force-fields are required for different kinds of atoms.

1.1.3 Monte Carlo (MC) method

This iterative method simulates N fixed number of particles at absolute temperature T, in a fixed volume V of system. MC method repeats random sampling to obtain the desired results by moving particles into a new position to reduce the system potential \[3\]. The simulation gets accurate as the number of random sampling increases. This method is easily implied but is applicable for systems near equilibrium configurations only which means MC method cannot be used in systems possessing time-dependent (dynamic) properties.

1.1.4 Molecular dynamics (MD) method

Molecular dynamics (MD) simulation technique for examining the physical movements of atoms and molecules which are permitted to interact for span of fixed time providing an overview of dynamics of the system \[4\]. This method determines the motion of particles (atoms and molecules) in solid, liquid and gas models which gives the detailed account of change in position, velocities and orientation with time, thereby following motion of molecules and describing real motion using molecular beam \[5\] or spectroscopic \[6\] methods. The interactions between particles in the system and system-environment are taken into consideration. The MD simulations is an effective and competent technique for micro-, meso- and nano-scale modeling \[2, 3\]. Molecular dynamics is divided into two categories namely first-principles molecular dynamics (FPMD) and classical molecular dynamics (CMD). FPMD simulations are based on properties and laws of quantum mechanics, is highly accurate but the computational cost for large systems is relatively high which makes it difficult to implement. CMD simulations are based on Newton’s equation to calculate position, velocity, structure, orientation and properties of the large system particles \[2, 3\]. Alder et al., in 1957 came up with the first paper and evolved the classical molecular dynamics \[7\]. The equation of motion for large body system is given by;

\[ F_i = m_i \frac{d^2 \mathbf{r}_i(t)}{dt^2} \]  
(3)

The procedure for conducting molecular dynamics simulation is as, (1) Preparation of sample with molecular topography; (2) Selection and initialization of system by assigning position and velocities to individual particles; (3) Computation of interactions between system particles by assigning boundary conditions and calculated interatomic forces on each particle which is given by potential energy function; (4) Integrating Newton’s equation of motion to move atoms and determining required length of time; (5) Reinstate molecular geometry and compute energy, temperature, pressure, velocity, etc. and save configurations \[2, 8\]
2. Friction, wear and lubrication behavior using MD simulations

Tupper et al.,[9] performed MD simulation for tribological , structural properties and studied frictional force of self-assembled monolayers using alkanethiols on gold. The simulations revealed that during compression of film there occurs transformation of structure which leads to self-assembling property of monolayer and the energy dissipations in these systems occurs due to swaying of the tilt angles formed. Joyce et al. [10], Chen and Israelachvili [11] performed IFM measurements and the investigations agreed with the study performed by MD simulations. Shimizu et al.,[12] performed MD simulations for atomic-scale stick-slip phenomena of AFM and observed the affect of cantilever spring forces. The research concluded stick-slip of surfaces have influence on stick-slip of spring force indicating the edge of MD simulations in determining spring forces. Robbins and Muser [13] presented computer simulations of tribological properties in understanding the mechanisms of friction, wear and friction at molecular level analyzing the complete dynamics of particles. They investigated the various spheres of tribological performances. Jabbarzadeh et al.,[14] simulated process of lubrication alongside the asperities and used molecular dynamics to study the properties and characteristics of regime of lubrication film obtained. The two linear chains of different sizes are simulated to study influence of size of molecules on the behavior of lubricant film. The molecular dynamics simulation revealed shear stress improved and normal stress vary near the asperities with size of molecules influencing the properties. Jeng [15] studied molecular dynamics of atomic-scale friction for various sliding systems using conditions like abrasive and non-abrasive wear. Li et al.,[16] used MD simulations to compare and analyze coating structure and growth dynamics of diamond-like-coating (DLC) synthesized by ion-beam assisted deposition method using C2 molecules as deposition projectiles and Ar ions as assistance projectiles with varying impact energy of Ar from 10 to 100 eV. As the flux is increased and impact energy is moderate, there is enough mobility in the atoms near collision cascade region to obtain dense and smooth coating which has better adhesion level. Kim et al.,[17] conducted friction experiments and simulations for steel and aluminium using tribotester for explosive friction and MD simulations for dynamic simulations. Both the researches suggested that nanostructures are formed within short duration of high velocity sliding. MD simulations revealed that the mechanism behind vorticity of generated cluster nanostructures is due to formation of eddies at the interface along with intermixing of materials producing nanocrystalline grain size layer of tribomaterial. Thenanostructure formed is affected by the interface hardness, chemical composition, orientation properties and size of grain boundaries.

2.1 MD Simulation of two bodies and influence of third body between two interacting surfaces

Yang et al.,[18] analyzed characteristics of sliding friction behavior of hemisphere placed on solid rectangular plane at nanoscale to study dynamics of contact area and force of friction using MD simulations. The simulations depicted the position, displacement, migration and accumulation of atoms, adherence of atoms along with change in structure and deformation of sphere, wear rate and sliding friction force with increase in depth of contact. As the contact depth increases the frictional force increases upto a certain limit, thereby remains steady during sliding and wear rate of sphere also increases. Virkhovetsev et al.,[19] presented the MD simulations for nanoindentation process of square, conical and spherical indenters on titanium crystal and investigated that the structure of the crystals deforms and behaves in accordance to the different forms and geometry of indenters. The maximum force on system was observed in case of spherical indenter possessing largest deformation in crystal atoms. Hu et al.,[20] performed simulation for frictional performance and mechanisms determining tribological behavior of diamond and silicon dioxide nanoparticles placed between iron blocks. Thus simulation results demonstrated that frictional force, deformations and temperature changes were enhanced by incorporating nanoparticles at low load (500MPa) and low velocity (10 m/s) withstanding loads for short period of time. By increasing the load (1000MPa) and velocity (500m/s), the behavior of diamond varied slightly but silicon dioxide crumbled which lead to deformation of nanoparticle in short duration of time thereby forming transfer layers. Hu et al.,[21] used MD simulation to investigate the mechanism and compare the boundary lubricant film properties of base oil (n-octane) and Cu nanoparticle confined between upper and lower walls. The results depicted improved load-carrying capacity of film incorporating nanoparticle as compared to base oil. The simulation revealed the properties exhibited by the lubricant film with Cu as nanoparticle was due to formation of adsorption layer which helps in development of well ordered, compact particle and
due to deformation of nanoparticle which is responsible for improved load-bearing capacity. Hu et al.,[22] simulated and compared the influence of Cu nanoparticle on friction behavior during sliding between two Fe blocks, moving with 10m/s velocity and 500 MPa applied load using MD simulations. The incorporated nanoparticle reduced the internal molecular deformation thereby reducing friction which otherwise can be seen without using Cu nanoparticle. The results exhibited the formation of lubrication films and transfer films at lower and higher velocities respectively. Ewen et al.,[23] performed simulation of carbon nano diamonds (CNDs) and carbon nano onions (CNOs) placed between two Fe blocks to study the effect of incorporation of nanoparticles on friction and wear behavior. The study includes influence of CNDs and CNOs with variations in nanoparticle coverage, sliding velocity and normal load. The presence of nanoparticles exhibits 75% reduction in friction which is found optimum with experimental observations.

2.2 Simulations of Self-lubricating materials and composites

MD computing and simulations revealed that during sliding of interacting surfaces the atomic cluster equilibrium, counteraction balancing of atoms and structural adjustment leads to self-lubrication [24]. This capability is acquired by customizing and varying the architecture of the composite matrix with different solid lubricants. The incorporation of solid lubricants eliminates the need of external lubrication [3]. These are available as inert polymeric agents like PTFE-based metal-polymer, thermoplastic-based metal-polymer, graphite-metal, graphene-metal, carbon nanotubes (CNTs) and MoS2-based nano-structural composites.

2.2.1 Poly tetra-fluoroethylene (PTFE)

This polymer is used in metal-, ceramic- and organic based composites to enhance the thermal, mechanical and tribological performance such as decrease in friction coefficient and wear rate, formation of transfer film and chemical stability [25-28]. PTFE exhibits self-lubricating behavior and nanoscale transfer films are seen in the composite which can be shown by atomistic models using simulation techniques. Onodera et al.,[29, 30] analysed the mechanism of chemical reaction and friction performance of polymeric agent, PTFE on aluminium oxide interface representing aluminium alloy surface using quantum chemical molecular dynamics (QCMD) modeling. The vertical pressure of 500MPa which exerts pressure on the layers of polymer and shear velocity of 100m/s is applied to slide on polymer. The tribochemical reaction of Al-F formation and presence of tribofilm enhances tribological behavior as shown in Figure 1.

![Figure 1. Tribochemical reactions with formation of transfer film][29].
In another classical MD modeling, the tribological behavior enhanced by the chemical reactions occurring at the surface between aluminium alloy and water vapor, further presence of carboxyl group adds to the formation of transfer film which improves self-lubricating properties. The bottom layer was fixed and sliding velocity of 10m/s with pressure 500MPa was applied in the vertical position, temperature of 300K. The three cases of formation of transfer film are shown in Figure 2 where it can be seen clearly carboxyl group terminated surface generates the potential transfer film.

2.2.2 Carbon nanotubes (CNTs)
They are carbon atoms in the form of rolled sheet/s and are classified on the basis of number and diameter of carbon nanotubes as single walled- and double- or multi walled carbon nanotubes with diameter 1-2 nm and 4-20 nm respectively [31]. Ni and Sinnot [32] investigated the responses to the forces and tribological behavior using nanotubes of carbon sliding between diamond walls via classical MD simulations predicting the nanotubes withstand shear forces by changing their shape configuration thereby sliding as per the forces applied. The directions w.r.t the axis and bonding of nanotubes determine the responses produced and the flexibility exhibits low wear rate. Kim et al.,[33] simulated single and numerous carbon nanotubes in different sliding directions to study the impact of orientations on the friction behavior with normal load from 3 nN to 32 nN. The simulation revealed lowering in friction coefficient for single tube with increase in load. The single and multiple nanotubes exhibited the lowest friction coefficient with 0° and 90° alignment respectively.

2.2.3 Graphite and graphene
The structure of graphite consists of strong and weak electronic bonds between carbon atoms with adjacent atoms in the form of layers. The weak electronic π-bonds result in the sliding of the layers which reduces the friction between interacting surfaces [34]. Xu et al.,[35] simulated behavior of few layers(3-8) graphene (FLG) during internal layer sliding by applying constant velocity which represents unique characteristics in transition like layer-stacking which is periodic and different from flake-on-substrate conditions. The interface sliding exhibited by graphene layers is mainly due to stick-slip which occurs in various stages divided from initial stage to final stable stage. Zhang et al.,[36] using MD simulations analyzed the role of graphene layer in the course of intervention of C60 where graphene layer was present on the top of upper and lower Si substrate where included angle ranges from 20° to 90° with lower substrate moving with constant velocity of 3 nm/ps. The nano-wear was controlled by the presence of graphene layers as the behavior depends on the included angle and the position of layers. Zhang et al.,[37] used diamond tip for nanoscratching on layers of graphene to study behavior of friction coefficient via MD simulations. The simulations revealed that up to scratch depth of 5.3 Å the graphene layers exhibited low friction behavior which increases about 10 times with further increase in scratch depth as the changes in phases cause increase in friction coefficient.
3. Conclusion

1. This review enlightens the basic methods of simulations with brief idea of molecular dynamics done by available software models. The molecular dynamics simulation proved to be a very powerful computational method which has developed into a mature technique to study the dynamics of motion and structure-to-function relationships.

2. The structural, orientation and tribological behavior of various interacting contacts has been overviewed with self-lubrication of materials as the main focus. The property of self-alignment and lubrication of solid lubricants is easily understood by the computational methods using molecular dynamics simulation via LAMMPS software model.

3. There are still only a few researches on molecular dynamics of self-lubricating materials keeping in view the complexity of the properties, availability and cost of computational methods and models. More research and investigations must be done on the molecular dynamics to understand various latent characteristic phenomena of materials to control friction and wear at molecular level.

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