

Some Essentials of Simulating Nano-Surfacing Processes Using the Molecular Dynamics Method

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ABSTRACT

This paper outlines some essentials in the simulation of nano-surfacing operations using the molecular dynamics analysis. Issues addressed include (a) the generation of an initial molecular model and its initial relaxation process, (b) the control of simulation temperature, (c) the selection of size of a control volume, (d) the application of the technique of moving control volume, (e) the setting of integration time steps, (f) the principle of conversion of temperature rise, (g) the method of stress analysis, and (h) the selection of potential functions. The proper understanding and use of the above will be of help to minimise the misuse of molecular dynamics and improve the accuracy of analysis.

1. INTRODUCTION

With the rapidly growing interest in nano/micro-surface processing, such as nano-sliding (nano-tribology), nano-cutting, nano-grinding and nano-polishing, molecular dynamics simulation is fast becoming a widely used technique in understanding the deformation mechanisms of materials [1-4]. However such simulation technique as in many other computer simulations depends a lot on essential modelling factors. Improper modelling and poor treatment of some key factors, such as the generation of the initial model and the treatment of temperature rise, will lead to inaccurate or even wrong results. It is therefore of great importance that a molecular dynamics analysis is carried out reliably and efficiently based on proper simulation settings. Much of the knowledge on these factors and how they can affect the simulation results are derived from the deeper understanding of the principle of molecular dynamics.

Fig.1 provides an outline of the procedure of molecular dynamics simulation and analysis. The very first step involved in molecular dynamics modelling is to choose the appropriate molecular interaction potential and the means of calculating the equations of motion. Next, the model has to be initialized. This is followed by relaxation or equilibration, where the model is allowed to relax from its initial state to its dynamically equilibrium condition. Finally, the simulation can be made to run and the results obtained can be analyzed.

This paper tends to lay down some guidelines to facilitate the understanding and direct programming in conducting a molecular dynamics simulation by highlighting the key issues involved in each stage of the modelling process as depicted in Fig.1. This will be particularly useful for new users of the method.

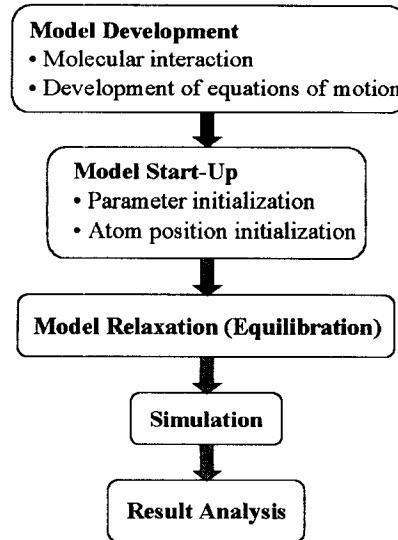


Fig.1 Outline of the procedure of molecular dynamics simulation and analysis

2. BASICS

2.1. Numerical Integration

The atoms in a molecular dynamics model interact simultaneously with many other molecules. Such interactions are not instantaneous. Rather, they are strong attractive and repulsive forces that occur over a finite duration. The classic tools for solving differential equations derived from such models are finite-difference methods and the simplest one widely used in molecular dynamics simulation is the Verlet's method.

The Verlet's algorithm is obtained from two Taylor's expansions, combined together. To obtain Verlet's algorithm, first write the Taylor series for position from time t forward to $t + \Delta t$:

$$\mathbf{x}(t + \Delta t) = \mathbf{x}(t) + \frac{d\mathbf{x}(t)}{dt} \Delta t + \frac{1}{2} \frac{d^2\mathbf{x}(t)}{dt^2} \Delta t^2 + \frac{1}{3!} \frac{d^3\mathbf{x}(t)}{dt^3} \Delta t^3 + O(\Delta t^4) \quad (1)$$

Then write the Taylor series from t backward to $t - \Delta t$:

$$\mathbf{x}(t - \Delta t) = \mathbf{x}(t) - \frac{d\mathbf{x}(t)}{dt} \Delta t + \frac{1}{2} \frac{d^2\mathbf{x}(t)}{dt^2} \Delta t^2 - \frac{1}{3!} \frac{d^3\mathbf{x}(t)}{dt^3} \Delta t^3 + O(\Delta t^4) \quad (2)$$

Adding the two expansions leaves:

$$\mathbf{x}(t + \Delta t) = 2\mathbf{x}(t) - \mathbf{x}(t - \Delta t) + \frac{d^2\mathbf{x}(t)}{dt^2} \Delta t^2 + O(\Delta t^4) \quad (3)$$

The acceleration term in Eq. (3) can be obtained from the intermolecular forces and Newton's second Law. A first-order central difference estimator can estimate velocities:

$$v(t) \approx \frac{x(t + \Delta t) - x(t - \Delta t)}{2\Delta t} \quad (4)$$

The Verlet's algorithm estimates $x(t+\Delta t)$ from the current position $x(t)$ and the previous position $x(t-\Delta t)$. It offers the virtues of simplicity and good stability for moderately large time steps.

2.2. Potential Function of atoms

Given the adequacy of the simulation techniques and the appropriate selection of the control volume and time step size, the reliability of the results of the simulation depends on the quality of the atomic interaction potential used in the study. If the potential function does not model the behavior of the atoms correctly, the results produced by the simulation will be unable to simulate the actual deformation correctly.

It would be desirable to take the interactions directly from first principle calculations. However, this would take up far too much computational time. Thus in order to obtain useful atomic interactions, empirical potentials have been developed.

In general the potential energy of a system of N atoms is a function of the atomic co-ordinates. Thus the potential energy may be expressed in a series of N-body inter-atomic potentials

$$V = \phi_0 + \sum \phi_1(i) + \sum \phi_2(ij) + \sum \phi_3(ijk) + \dots + \phi_N(ijk, \dots) \quad (5)$$

where ϕ_N is the N-body interaction potential which is a function of the positions of N atoms $ijk\dots$. The sums in Eq. (5) are over all combinations (excluding redundant contributions) of N atoms in the system. The potential ϕ_N , and the number of terms, which are retained in a practical application, depends on the nature of the system under investigation.

In s-p bonded metals, *i.e.* metals with free electrons outside the ion cores, the structure-dependent part of the system energy can be accurately expressed in terms of the second-order (pair potential) terms of Eq. (5). Hence pair potentials (such as Lennard-Jones, Morse, etc.) have a firm theoretical basis in simple metals [5]. Examples of such metals are copper, sodium, magnesium and aluminium. The authors have employed the use of Morse pair potential in the modelling of copper atoms and find the results of the simulation satisfactory [2]. A detailed explanation and expression for the Morse potential used in the modelling of copper can be found in Ref. [2].

When using the pair potential function, the omission of angle dependent forces and many-body effects results in a severe restriction on its application to more covalent systems such as silicon where the directionality of the localization of charge in the bonding region is important. In such cases, it will require an empirical potential incorporating two and three-body interactions. The parameters used in this potential function are determined by least-square fits to a database of calculated energies of real and hypothetical atomic structures. However, due to the exclusion of some atomic structures outside the database, it is difficult to evaluate the generality of the potential. Also, this method of simulation requires much computational time.

To address these shortcomings of the above-mentioned potential function, the Tersoff potential is developed. This replaces the traditional two and three-body expansion of the interaction energy with a simple pair-like potential where the bond order of the atoms is affected by its local environment [6]. In this way, structural chemistry is included in a classical empirical potential. It has been found that energies and geometries for silicon are very well described using the Tersoff potential. The authors have made use of Tersoff potential in the modelling of silicon atoms in a

nano-indentation process with satisfactory results [7]. A detailed explanation and expression for the Tersoff potential used in the modelling of silicon can be found in Ref. [7].

2.3. Integral Time Step

The prediction of the phase-space trajectories of atoms in molecular dynamics simulation is based on the second law of motion of Newton. To solve the differential equation, the finite difference method is often necessary because collisions between atoms are not instantaneous; rather, they are strong repulsive and attractive interactions that occur over a finite duration. However, the use of the finite difference method implies that the size of the integration time step Δt , must be determined very carefully, because both the global truncation error and global round-off error depend on Δt . Moreover, these two types of errors are affected differently by changes in Δt , as shown in Fig. 2. The global truncation error decreases with decreasing Δt , while the other depends on the number of calculations. This means that the smaller the size of the time steps, the more calculations to be done and the greater will be the global round-off error.

A way to reduce the round-off error is to have an efficient code and use high precision arithmetic. To reduce the truncation error, however, it is necessary to reduce the size of Δt . It must also be noted that a smaller time step is usually associated with a greater computational cost.

In addition to the above problems, it is essential to note that the finite difference algorithm commonly used in molecular dynamics, the Verlet's method, is conditionally stable. That is to say, it will become unstable when Δt reaches a critical value, though the threshold can be determined through a series of experiments. Generally, a suitable time step should be less than ten percent of the vibration period of an atom. Hence the optimum time step is dependent on both the specific material and the potential function used. For instance, with the Tersoff potential [7], an individual atom of silicon or diamond can be forced to move in a direction to show the corresponding stiffness k , as shown in Fig. 3, so that the period of vibration of the atom in the direction T , can be determined by $T = 2\pi (m/k)^{1/2}$, where m is the mass of an atom.

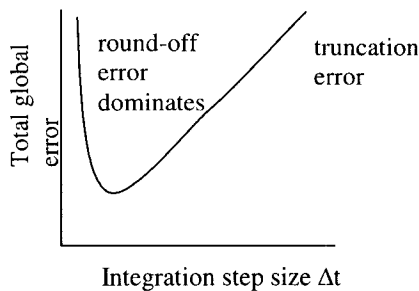


Fig. 2 Different types of errors against size of time steps.

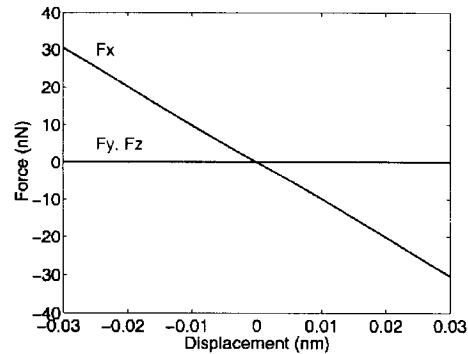


Fig. 3 Force-displacement relationship when moving a silicon atom in the [100] direction under Tersoff potential. The material stiffness k can be obtained from the gradient of the plot.

3. MODELLING

3.1. Initial Position

The very first step involved in molecular dynamics modeling is to generate an initial molecular model of the material for the simulation of a nano-processing operation. One way is to take the initial positions of atoms from the end of an earlier simulation [8]. However this may not be viable as one may often change the size and shape of a model. A rational alternative is to initially locate atoms on a perfect crystal lattice structure that represents the real atomic structure of the material subjected to study. For example, atoms in a model to simulate copper will be positioned in accordance to a Face Centred Cubic (FCC) lattice structure with its lattice constant, while a model to simulate diamond will be positioned in accordance to a diamond cubic structure.

3.2. Initial Velocity

Initial velocities of the atoms can be randomly assigned or may be taken from a previous simulation. The model having atoms positioned and assigned velocities in such a way implies that additional potential energy between atoms has been artificially applied to the system because in a real solid, atoms are actually vibrating around their equilibrium positions.

3.3. Initial Relaxation

Before simulation can go on, it is necessary to 'relax' this constructed initial model from its artificially assigned initial conditions to its natural, dynamically equilibrium status consistent with the environmental temperature. This involves the execution of the constant temperature molecular dynamics program for a specified number of time steps under the chosen potential function, say for example, 50 time steps for initial relaxation. During the relaxation process, the velocities of Newtonian and thermostat atoms that are initially assigned based on a normal distribution will gradually reach equilibrium at the specified environmental temperature of the simulation by a velocity scaling (this will be discussed in the next section). The number of time steps required to run for such a relaxation is determined by the time needed for the model to arrive at this equilibrium temperature specified.

3.4. Temperature

3.4.1. Thermostat Atoms

The portion of the material simulated by the molecular dynamics model, or the control volume to be discussed later, is usually a small part of the material in the neighborhood of the deformation zone of interest. This portion in reality is continuous with the rest of the material. As such, any heat generated during a nano-processing within the control volume will be conducted away by the surrounding material. If this heat conduction process cannot be simulated in a molecular dynamics analysis, the simulation results can be incorrect. To achieve reasonable heat conduction outward the control volume, special layers of atoms, called thermostat atoms, must normally be arranged to surround the model (See Fig. 4). Then based on the temperature conversion rule to be discussed in section 2.4.2 in this paper, temperature regulation is made by scaling the velocities of the thermostat atoms so that the temperature due to the kinetic energy of these atoms will always be consistent with the environmental temperature. When the dimension of the control volume is sufficiently large, the arrangement of the thermostat atoms provides an efficient and reliable way for the natural heat conduction in the solid.

The scaling of velocities [2] can be done by

$$V_{new} = V_{original} \sqrt{\frac{\text{Kinetic energy corresponding to the environmental temperature}}{\text{Kinetic energy of a thermostat atom before scaling}}} \quad (6)$$

where V_{new} is the scaled velocity of a thermostat atom and $V_{original}$ is its original velocity.

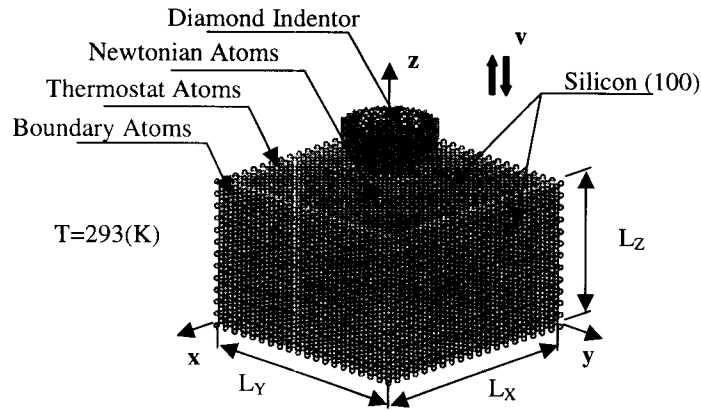


Fig.4 Molecular dynamics model of silicon specimen with a hemispherical indenter.

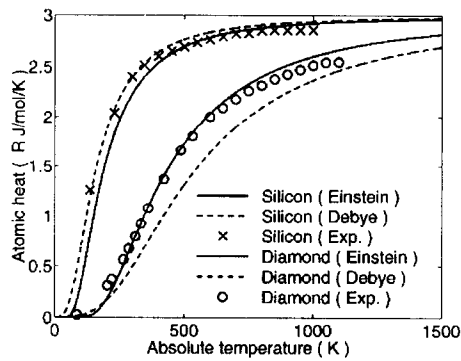


Fig. 5 A comparison of theoretical calculation of atomic heat with experimental measurement provides by Sinott.

3.4.2. Temperature Conversion

Another important factor in a successful molecular dynamics analysis is the reliable conversion between the kinetic energy and temperature of an atom. An inappropriate conversion between kinetic energy and temperature of an atom will result in an error in the velocities of the atoms and hence render the simulation incorrect. It is always essential that for any given material, a temperature conversion model is identified carefully before carrying out a molecular dynamics simulation. In studying the deformation mechanisms of monocrystalline silicon under the nano-interaction with diamond tools [1,3,7], for instance, there are three models available [9] for the

conversion. They are the Dulong-Petit model, which takes into account the independent lattice vibration, the Einstein model, which is based on the consideration of the single characteristic frequency, and the Debye model, which involves a range of frequencies. A comparison with the experimental measurement given by Sinnott [10] shows, as demonstrated in Fig. 5, that in the temperature regime encountered in nano-surfacing, the Debye model is the best for silicon and the Einstein model is the most suitable for diamond. Clearly, if these models are incorrectly used, the result of molecular dynamics simulation cannot be correct.

4. TECHNIQUE

4.1. Computational Time

Though it is ideal to create a molecular dynamics model that exactly replicates the mechanics model, too large a model results in impractical computational time. Hence, different techniques are used to keep the molecular models small and yet produce results that are accurate.

4.1.1 Size of Control Volume

There are three major issues that must be considered in the dimension selection of the control volume of interest. To reduce computational time, the volume should be as small as possible. However, a too small volume will bring about significant boundary effects that make the results unreliable. These include the boundary temperature effect and the boundary displacement effect. To eliminate these effects, the dimension of the control volume must be sufficiently large so that at its boundary, the temperature is close to the environmental temperature. Then the application of thermostat atoms can make the natural heat conduction happen in simulation. Similarly, the volume should also be sufficiently large so that the motion of the boundary atoms does not affect the atoms in the deformation zone of interest. By following this, the boundary atoms can be treated as fixed in space or moving in a specific direction to facilitate simulation without influencing the accuracy of analysis. Normally, an error analysis is necessary to generate a suitable dimension. The selection process of the control volume for nano-indentation [1], which has fixed boundary atoms, and that for nano-cutting/polishing/grinding/sliding [3], which uses moving boundary atoms, are good examples.

4.1.2 Moving Control Volume

In cutting, grinding or sliding, the distance of relative motion of a tool to a workpiece is significant. An apparent way of simulating the steady-state behaviour of the workpiece material is to take a large portion of the work material as the control volume for simulation. However, this is infeasible because the cost and capacity of computation limit the number of atoms in a model. The moving control volume technique [2,3] is then necessary and advantageous, in which the dimension of control volume is similar to that of a non-moving one but with special atom removal and addition techniques. Shown in Fig. 6 is an example of nano-cutting, where zone 1, the zone affected by cutting deformation, is equivalent to the normal control volume discussed in the last section. Zones 2 to 5 are those unaffected by the cutting deformation. When the cutting proceeds, atoms in zone 5 can be removed because the removal will not affect the behaviour of the atoms in zone 1. However, zone 4 becomes a transition one because the boundary between zones 4 and 5, which is originally inside the workpiece, becomes a free surface. The dimensions of both δ_4 and δ_5 must be determined by an error analysis such that the removal of zone 5 and the creation of the new free surface do not influence the behaviour of atoms in zone 1. Similarly, because atoms are added in zone 2 after the removal of atoms from zone 5, zone 3 becomes a transition zone. Due to the same reason, the dimensions of both δ_2 and δ_3 must also be determined by an error analysis. Zone 6 consists of the boundary and thermostat atoms.

4.1.3. Periodic Boundary Condition

A simple way to reduce the effects of the boundary on atoms in a control volume is to increase the size of the control volume. When the size of the control volume needs to be kept small, periodic boundary conditions can be used to reduce the boundary effects.

To use Periodic Boundary Condition in a simulation that consists of N atoms in a control volume of size V , imagine the volume V to be only a portion of the bulk material. The volume V is known as the primary cell. The primary cell is surrounded by exact replicas of itself. These replicas are known as image cells. Thus the primary cell is replicated in all directions to form the material of interest. The atoms in the image cells replicate the atoms in the primary cells both in terms of the positions and the momenta. Image atoms in image cells follow trajectories that are exact duplicates of those followed by the atoms in the primary cell (See Fig.7).

All the cells are separated by open boundaries, so atoms and images can freely enter or leave any cell. The number of atoms in each cell remains constant at N because when an atom leaves the primary cell, an image of the atom will simultaneously enter the primary cell through an opposite face.

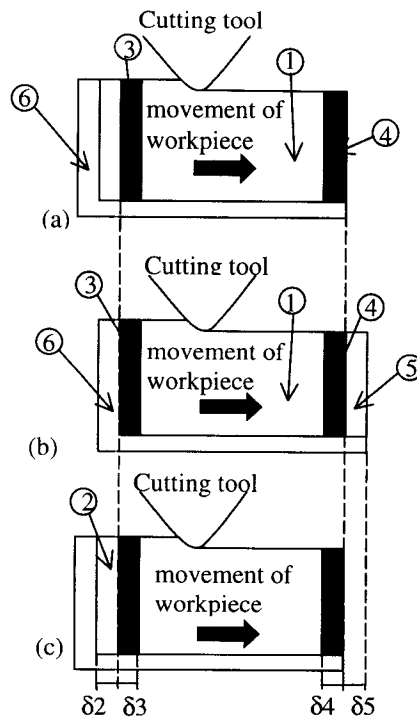


Fig.6 The concept of moving control volume of a workpiece subject to nano-cutting. (a) Initial control volume, (b) The control volume before the operation of removal and addition, (c) the control volume after the operation of removal and addition.

Each atom in the primary cell will interact with all $N-1$ other atoms and all their images. The number of image cells required will depend on the range of intermolecular forces.

4.2. Analysis

4.2.1. Stress

The analysis of stress in a material is an important part in our understanding of characteristics such as deformation or transformation of the material under various machining processes. Stress analysis also allows useful criteria to be set for the prediction of phase transformation or plastic deformation of the material under processing.

However, on a fine scale, materials cannot be treated as a continuum and the conventional definition of stress is no longer valid [7]. This section will take the deformation of monocrystalline silicon as an example to discuss the stress analysis on the atomic scale.

Fig. 8 shows a conceptual atomistic model for calculating stresses. Assume that a solid is divided into an upper part Ω_1 and a lower part Ω_2 by a plane A. Consider a small element Γ in Ω_1 with a base area S in plane A. The stress vector on S is defined by

$$\sigma = \frac{\mathbf{F}}{S} \quad (7)$$

where \mathbf{F} is the resultant force on S induced by the interaction between the atoms in Ω_2 and those in Γ and should be calculated by

$$\mathbf{F} = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \mathbf{f}_{ij} - \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} \mathbf{f}_{0ij} \quad (8)$$

in which N_A is the number of atoms in Γ , N_B is the number of atoms in Ω_2 , \mathbf{f}_{ij} is the inter-atomic force vector during indentation between atom i in Γ and atom j in Ω_2 and \mathbf{f}_{0ij} is the inter-atomic force vector before indentation between atom i in Γ and atom j in Ω_2 . The contribution of interatomic forces before indentation, \mathbf{f}_{0ij} , must be eliminated as the stress analysis considers only the effect of deformation due to indentation (external forces). This consideration ensures consistency with the definition of stress in continuum mechanics.

It is important to note that in continuum mechanics a stress vector is defined at a mathematical point but in the definition here on the atomic scale, area S should always be finite. Moreover, to obtain a representative stress vector on S , the height of the element must be selected in a way that the interaction force between atom j in Ω_2 and atom i in Ω_1 but beyond the top surface of Γ is negligible. In the stress analysis of silicon specimen subjected to nano-indentation, it is found that the optimum size for element Γ is $2L_c \times 2L_c \times L_c$ as shown in Fig. 8 where $L_c = 0.543 \text{ nm}$ is the side length of a unit cell of silicon.

There are two questions that arose from the above stress definition on a molecular scale. The first pertains to the momentum flux of atoms within the material. That is if it is necessary to consider the contribution of this element in the calculation of stresses. In fact, each element of the stress tensor will compose of a kinetic part and a potential part [8], ie,

$$J_{\alpha\beta} = m \sum_i^N v_{i\alpha} v_{i\beta} + \frac{1}{2} \sum_{i \neq j}^N r_{ij\beta} F_{ij\alpha} \quad (9)$$

where m is the atomic mass, $v_{i\alpha}$ is the α -component of the velocity of atom i , $r_{ij\beta}$ is the β -component of the vector \mathbf{r}_{ij} separating atoms i and j , and $F_{ij\alpha}$ is the α -component of the force exerted on atom i by atom j . However, simulation results have shown that for a solid, the contribution due to the momentum flux of atoms within the body is very small compared to the

effects of inter atomic forces between the atoms. Hence, if the simulation is done for a solid, this term may be neglected.

The second question is if it is necessary to include the interaction forces between workpiece atoms and tool atoms in the stress analysis of the workpiece. It has been shown that the effect of this interaction is very small when the work-tool interactive potential is low and hence negligible if the region of interest for the stress analysis is not in close proximity with the tool. Stress calculation of the workpiece in such cases can therefore be achieved by considering the atoms of the workpiece alone.

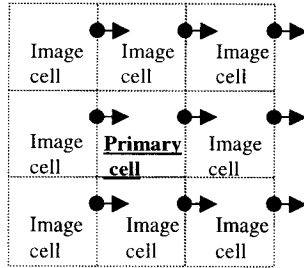


Fig.7 Periodic boundary conditions in two dimensions

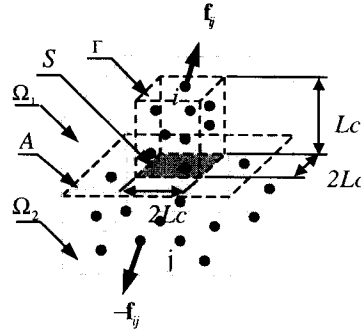


Fig. 8 Concept of stress vector on an atomic scale.

5. CONCLUSION

The paper has discussed various important issues in setting up a molecular dynamics model for simulating a nano-surfacing process. It is hoped that with the guidelines provided in this paper, new users will be able to attain a satisfactory level of realism in their simulations using molecular dynamics simulation.

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Precision Machining of Advanced Materials

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