Interactions of the Cluster Beams with Solid Surfaces

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The characteristics of a cluster beam interaction with a solid target are reviewed from the viewpoint of computer simulation. The similarity and dissimilarity of irradiation effects between single and cluster ion beams are the main emphasis of the review. The speed-range of a projectile studied is below the Bethe range \( v < v_B Z \) but not so low, where electronic energy loss is significant. Because of the multiple collisions (in time and space) a classical molecular dynamic simulation is useful, whereas the multiplicity in energy is more significant for a molecular projectile. Here the collision stage of energy transfer from a projectile to target during the collision stage is separated from the following relaxation stage. The multiplicity in the collision stage can cause molecular effects, however they are not always so significant. In the relaxation stage a somewhat enhanced effect can occur when the locally deposited energy exceeds a certain level.

1. History of the cluster beam science

1.1 The characteristics of clusters

In 1956, Becker et al.\(^*\) first used the diatomic molecule \( \text{H}_2 \text{O} \) or \( \text{N}_2 \) as a source beam in an experiment and showed a significantly different result from that obtained using a single ion beam, which ushered people into the cluster science. The next year, Kubo\(^*\) theoretically predicted the presence of a "quantum size effect" in a microscopic realm below 10 nm. With increases in the size of a cluster, the nature of bulk emerges almost abruptly\(^3,4\). This means that the quantum effect would be essential for cluster science. In fact, the ab-initio molecular orbital method (QMO)\(^5,6\) is indispensable to predict and to identify the geometry and stability of a cluster through comparison with experimental results.

The scope of the cluster science has developed through static and dynamic approaches. The geometry of a cluster governs the electronic property and determines its functions. Among many candidate structures of clusters with the same components but different geometry, the most stable cluster should have the largest binding energy and no molecular vibration mode with imaginary frequency; otherwise the cluster will collapse due to thermal vibration. The static approach pursues a new function or excellent performance by looking at the sophisticated structure of a cluster. For example, such a functional design has produced a core-shell cluster\(^7\), included clusters with new elements, and liquid-phase clusters attached by protective colloids\(^8\).

On the other hand, the dynamic approach pursues modification in materials making use of the energy introduced by cluster ion beams. A molecular dynamic simulation (MD)\(^9\) is often used to examine the collision events in a material, after defining the most stable cluster using QMO. If a cluster is disassociated or associated due to bombardment, QMO and ab-initio molecular dynamic simulation (QMD)\(^10\) is indispensable for a theoretical prediction.

1.2 The onset of the cluster beam science

After Becker's experiment, in 1962 Ewing\(^10\) used "multi-atomic ion" \( \text{H}^+, \text{H}_2^+, \text{H}_2^+ \) beams and observed significant differences from the results using a single ion \( \text{H}^+ \) beam in the pulse spectra. Since then, the so-called molecular effect has been evaluated, for a certain event in terms of a ratio \( R_n = (\text{one kind of yield due to an } X^+_{\text{a}})/n/\text{(same kind of yield due to } X^+) \). Usually one compares a result due to a single ion \( (X^+) \) and that due to a monatomic cluster \( (X^+) \) with a single charge, presuming the same velocity for every atom. In other words, one scales the events by the "partial energy (energy/atom)". The complicated processes like charge-changes in deexcitation\(^1\) cannot be calculated using a classical MD calculation.

First of all, it should be noted that the molecular effect \( R_n \) caused by molecular ion bombardment are not only larger than unity but also less or non-significant\(^12\). For the case of sputtering\(^3\), the heavier the mass of a target atom or a projectile, the larger the value of \( R_2 \) is, which is larger than unity. For the case of stopping force of thin films\(^4\), \( R_n \) due to hydrogen molecules is larger than unity, but not due to other molecules. Brandt et al.\(^4\) and Arista\(^5\) theoretically explained the molecular effect as being due to the contribution of distant collision. For the case of secondary electron emission\(^16\), the molecular effect is weak. The value \( R_n \) is close to unity but decreases when increasing the bombarding energy.

In order to study the interaction between a cluster beam and a solid target, the MD technique is an indispensable technique\(^7\). In 1990, Shapiro and Tombrello\(^9\) used the MD for the first time to study the cluster bombardment on a solid surface and found a compressed region with higher atomic density in collision cascades. Soon afterwards, Hsieh and Averback used a MD and reproduced the crater formation\(^19\) by a cluster beam. Following these pioneers' work, the resear-
2. A single ion bombardment:

Before reviewing cluster bombardment in comparison with single ion bombardment, we will discuss the interaction between a single ion beam and a solid, because it might help to scale the collision events caused by a cluster beam. The beam irradiation initiates a collision stage that transfers the energy to the target, then the target in turn redistributes the deposited energy to its surroundings in the relaxation stage. Thus a target is at first excited and later deexcited. Here we separate the collision stage from the relaxation one, because for the collision stage caused by a single ion beam, there are scaling rules for the stopping forces as a function of the projectile's speed or its energy\(^{21}\).

### 2.1 Speed-ranges

Table 1 shows the speed-ranges of a projectile, which is useful to arrange the energy or speed dependence of the stopping forces. Unless otherwise indicated, we use a conventional unit of "eV" for energy instead of \(1.602 \times 10^{-19}\) J, and also use the atomic unit of "\(v_0\) (Bohr velocity) = \(e/\hbar\), \(\hbar\) is the Plank constant divided by \(\pi\)" for velocity instead of \(2.18 \times 10^{16}\) m/sec. The symbol, \(m_\text{e}\), means the electron's rest mass. Other conventional symbols are; for a projectile, impinging energy \(E_0\), current energy \(E\), the speed \(v_1\), the atomic number \(Z_1\), mass \(m_1\), the radius of close collision area \(r_{\text{close}} = h/(2m_1v_1)\), and the Thomas-Fermi velocity \(v_{\text{TF}} = (v_0 Z_1^{2/3})\). For a target, the atomic number \(Z_2\), mass \(m_2\), mean ionization potential \(I\), and the plasma frequency \(\omega_\text{p}\) which defines the radius of distant collision area \(r_{\text{dist}} = v_1/\omega_\text{p}\). Note that these values are not thermal parameters characteristic to the target material, but kinetic parameters to depict atomic collision partners. This is an implicit reason why we propose to separate the collision stage from relaxation one that reflects the somewhat thermal nature of a solid target.

Each speed-range has different \(v_1\)-dependence of stopping force \((-\text{d}E/\text{d}x)\) that compiles the energy loss due to elemental processes with different cross sections (\(\sigma\)). The suffixes of \((-\text{d}E/\text{d}x)_\text{r}\) and \((-\text{d}E/\text{d}x)_\text{n}\) indicate which (lattice or electronic) system will be excited. The border between (i) and (ii) is the speed that a projectile reaches the largest amount of nuclear stopping force. The borders between (ii) \(- (iii)\) and between (iii) \(- (iv)\) are \(v_{\text{TF}}\) and \(Z_1 v_0\), respectively. In the speed-range (i) and (ii), the \((-\text{d}E/\text{d}x)_\text{n}\) is well described by a universal function of \((-\text{d}E/\text{d}x)_\text{n}(\epsilon)\) in the LSS theory\(^{23}\) using the LSS reduced energy \(\epsilon\) and scaled length. Beyond its maximum at \(\epsilon = 0.3\), electronic collisions become significant. In the range (i), \((-\text{d}E/\text{d}x)_\text{n}\) is proportional to \(v_1\) according to the LSS theory. In the speed-range (iii) and (iv), the Bohr and Bethe-Bloch theory fully describe the collision events, respectively. These descriptions are common, hereafter we will explain a new approach to study collisions.

### 2.2 The collision stage described by the \((-\text{d}E/\text{d}x)\)

Impinged projectiles will lose energy either by means of nuclear or electronic collisions during the slowing down process\(^{21}\) within a period of \(10^{-12} - 10^{-14}\) sec. Some of them can leave target after suffering the "mean energy loss \(\langle\Delta E\rangle\)". Forward ejected projectiles directly determine the stopping force \((-\text{d}E/\text{d}x)\) of a thin film after passing through the film with thickness of \(\Delta x\). Backward ejected projectiles extract the imperfection information of a crystalline target in the Rutherford Backscattering Spectroscopy, which indirectly confirms the reliability of \((-\text{d}E/\text{d}x)\) model for the material. On the other hand, when a projectile is finally embedded in a target, the value of \((-\text{d}E/\text{d}x)\) cannot be directly measured. It is only possible to confirm the accuracy of theorized model of \((-\text{d}E/\text{d}x)_\text{r}\) and \((-\text{d}E/\text{d}x)_\text{n}\) adopted in a simulation, by comparing with measured values. The mean projected range is such a quantity.

The \((-\text{d}E/\text{d}x)_\text{r}\) and \((-\text{d}E/\text{d}x)_\text{n}\) are supposed to be independent in a classical MD based on the LSS theory\(^{23}\). The "break-down of the adiabatic assumption", which denies the independence between them, can occur. Depending on the complexity of an issue concerned, \((-\text{d}E/\text{d}x)\) can be calculated using the coupled-channel method (CC)\(^{20}\), QMD, the density functional theory (DFT), or time-dependent DFT (TDDFT)\(^{23}\), if the transferred energy is integrated with respect to the impact parameter for a single target atom.

The \((-\text{d}E/\text{d}x)\) has brought a good perspective to investigate the collision stage in material, thus both quantities \((-\text{d}E/\text{d}x)_\text{r}\) and \((-\text{d}E/\text{d}x)_\text{n}\) are helpful for a simulation of a single ion bombardment.

### 2.3 The relaxation stage after excitation

The relaxation stage starts from the excited electronic system, if \(E_0\) is high enough to break the bindings of the inner shell electrons in the target, i.e., \((-\text{d}E/\text{d}x)_\text{r}\). An excited electron would see energy levels forming energy bands, each of which is usually coupled with local-phonons (e-p) as is described in the configuration coordinate model\(^{20}\). Because of the finite lifetime of an excited state, which is \(10^{-15} - 10^{-6}\) sec depending on the environment, the excited electron will decay sooner or later. According to the Condon-Shortley model, an electron decays from the bottom of the excited level and emits either (radiative) photons or (non-radiative) Auger electrons. Moreover, if an excited electron could

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<th>Table 1</th>
<th>The speed-ranges for a single ion bombardment. The LSS reduced energy(^{23}) (\epsilon = 0.3) corresponds to (v_1 = (0.6 \times Z_1 Z_2^2/\alpha^2/\mu)^{1/2}), where (\alpha) is the screening length and (\mu) the reduced mass.</th>
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cross over a transition state or level-crossing point in the energy band, the (non-radiative) electron migrates on the potential surface, which plays an important role in a quenching system (e–p interaction).

On the other hand, if the $E_0$ is low, the predominant energy loss is nuclear one. The impinging energy will be distributed to individual atoms (cascade formation) or to the lattice system (phonon ($p$) excitation). The latter reaction is to cause local phonons in around $10^{-13}$ to $10^{-12}$ sec and to let the medium temperature rise and finally quench. For the quenching, collisions between target atoms ($p$–$p$ interaction) usually work in a non-metallic target later than $10^{-11}$ sec, whereas free electrons ($e$–$e$ interaction) play the same role in metals in $10^{-13}$ sec. Finally, we see irradiation effects as sputtering, defect formation, temperature rise, and others. Therefore, the time development of the relaxation stage strongly depends on materials.

Computer simulation for the relaxation stage is not as simple for the collision stage. There are two reasons:

- More individual events: Strong material dependence on the chemical or thermo-dynamic properties prevents scaling the relaxation stage. One example is that a swift ion beam can penetrate a polymer film leaving a hole, whereas the same beam causes amorphization (ion track) in an alloy film along ion's trajectory, as is often used for the negative and positive resists, respectively.

- Slower procedures: For the long elapsed time until the redistribution of deposited energy and material's modification are almost settled before observation, it is impossible to describe entire procedures based on a single simulation model. For example, if a few keV ions enter a solid target, the scale of the relaxation stage changes from $10^{-15}$ to $10^{-6}$ m in length, from $10^{-14}$ to $10^{-3}$ sec in time, and from $10^1$ to $10^{-1}$ eV in energy, before observation. These scale changes over several orders can proceed along a logarithmic scale, as is seen in the case of radioactive decay. Nevertheless we usually adopt a linear scale in numerical solutions in a confined realm of "space, time, and energy". (Some snapshots taken in experiments are also in a confined realm.) Thus, although it is common sense in simulation, no simulation with a single algorithm or one physical model is available for all the stages.

From a viewpoint of modeling, these two reasons relate with the controversial subjects of the "e–p interaction". The e–p interaction was first theorized by Fröhlich and the Kaganov. However, those models are not practically useful for MD, because they assumed non-localized phonons. Caro and Victoria introduced ($-dE/dx$) as an e–p interaction term in the MD equation for a metallic medium, but not for non-metallic one. Whichever (lattice or electron) system is excited, the phonon can take initiative in the relaxation stage, which is not relevant to whether the projectile is a cluster or not. The key to a breakthrough of this issue is to present a reasonable model for the e–p interaction between "excited electrons and localized phonons".

2.4 The settled scaling-rule for the collision stage caused by single ion beam

Figure 1 implicitly shows the issue of different scaling rules for stopping forces ($-dE/dx$) and ($-dE/dx$)\(_e\). An empirical simulator SRIM\(^{30}\) was used for a gold target irradiated by a light (N) and a heavy (Au) ion. The SRIM assumes the binary collision approximation (BCA), and uses a magic formula for scattering angles, and adopts adjustable parameters. For a rough estimate of radiation effects of the collision stage, this can be helpful. Broken lines in Fig. 1 indicate those borders between speed-ranges in Table 1, although the 3\(^{rd}\) border (between (iii) and (iv)) is out of scale in Fig. 1b.

The speed ranges we are concerned with are defined by the availability of a classical MD calculation that is suitable to describe atomic collisions following a cluster bombardment. At the low-speed extreme, chemical reactions\(^{31}\) can be slightly detected experimentally in a...
case of O₂→c-Si[32], whereas they cannot be usually counted in a classical MD. On the other hand, at the high-speed extreme, the computational size is practically too large to execute an MD because of the limit of the number of atoms involved. The record of the largest number is around 2×10⁵ atoms/MD box[33]. If assuming a typical value of atomic density of 2×10²⁸ m⁻³, the maximum volume for a MD will be 10⁻¹⁹ m³ = 0.1 μm³. This sub-micron volume limits the speed-range of a projectile up to (iii) at highest, if evaluated the number of atoms enclosed in collision cascades formed by the projectile, judging roughly from the range parameters (depth, longitudinal and lateral straggling) determined by SRIM[30]. Hereafter, we use speed-classification in Table 1 for a cluster beam, looking at the partial energy.

3. A cluster ion bombardment:
With respect to the characteristics of a cluster bombardment, one general concern can be in the molecular effect during the collision stage. Another concern can be the somehow different irradiation effects in the relaxation stage, e.g., in sputtering and crater formation. It should be noted that most of the phenomena caused by cluster bombardment are reproduced by the MD using single ion. There are, however, some effects which newly emerge when the deposited energy exceeds a certain threshold.

3.1 Collision stage characterized by the multiplicity
Cluster ion bombardment causes multiple-collisions not only of the nuclear but also of the electronic[34,35] type, where various kinds of excitation are concentrated closely in the realm of space, time, and energy. The multiplicity in (−dE/dx) means the multi-step excitation of electrons as was discussed by Kabachnik et al.[35] or an “overlapping distant collision due to molecular ion” as was discussed by Brandt[14] and Arista[35]. A molecular projectile in the speed-range of (ii) or (iv) takes place the distant collision within a region made of overlapped cylindrical region, each of which is defined by a radius of \( r_{\text{dist}} \) centered at each constituent atom of the incident cluster. The molecular effect on (−dE/dx) for high-energy projectiles can be directly observed in experiments as ion transmission through a thin film, because the contribution of (−dE/dx) can be usually ignored in such a case. The molecular effect on (−dE/dx) for molecular beams (H+, H₂⁺, H₃⁺) passing through carbon or gold foils in the speed-range (iv) was measured by Brandt et al. They obtained both enhanced \( R₂ \) and \( R₃ \) beyond 1.5 at (1.55 \( v₀ < 1.25 \) \( v₀ \)). They ascribed the molecular effect to the distant collision caused by a “united point charge” as long as \( r_{\text{close}} < R_{ij} < r_{\text{dist}} \) where \( R_{ij} \) is the intra-atomic distance between \( i \)-th and \( j \)-th atoms within a cluster.

On the other hand, it is not easy to identify the effect of multi-collision in (−dE/dx) due to the cluster, so we need the help of computer simulation. Since sputtering follows the developed collision cascade[31], the molecular effect on sputtering will be mentioned in the next section of the relaxation stage.

Another intrinsic difference of a cluster ion bombardment from that of a single ion is the structure change of the projectile itself. A very low-energy cluster will be deposited on solid surface like a droplet[36]. When increasing the energy of a projectile, the target sets to be seen as a gaseous ensemble of independent atoms rather than a solid material. Accordingly, a very high-energy cluster will enter a target while keeping its original structure for a time and then completely decompose into atoms in bulk[37]. A cluster with intermediate speed will cause a collision-induced dissociation or association depending strongly on the incident orientation[38]. A typical image of a cluster interacting with a solid can be a “liquid drop→buoyball→gaseous nebula” when increasing the impinging energy (\( E_{0} \)) as are often reproduced by simulations. Such a change should depend also on the strength of cohesion among atoms in a cluster, which may be a more essential factor to predict how and where a cluster will be dissociated in the vicinity of solid surface. In 1994, Galli and Mauri[39] first clearly showed a significant influence of the cohesive energy and the energy \( E_{0} \). Their model of (QM+MD) adopted the QMO calculation in a MD based on the Hellmann-Feynman theorem, to calculate the force term in the equation of motion. It was for a case of C₆₀ bombardment onto C (111). Depending on the partial energy (\( E_{0}/60 \)) of incident C₆₀ cluster, the bonging profiles are clearly different. With \( E_{0}/60 = 2 \) eV/atom, below the cohesive energy, clusters leave the surface without forming any bonds between substrate atoms. With \( E_{0}/60 \geq 4 \) eV/atom, the cluster’s cage breaks and those pieces form stable bonds with substrate atoms.

3.2 Relaxation stage after excitation characterized by denser cascade
After the electronic collision, the radiative decay of excited electrons has been often observed. For example, the charge state evolution of the fragment ions inside the target was observed[39] for a C₆₀ cluster with a speed of 3.25 \( v₀ \). The non-radiative decay was partly known from the secondary electron emission after a cluster bombardment with a speed of 0.89 \( v₀ \)–2.83 \( v₀ \)[40] or 0.5 \( v₀ \)–2.5 \( v₀ \)[41]. Even with a low energy cluster bombardment of about 10 eV, exciton luminescence was observed in the neutralization when the A₆⁺ (n=1, 2, 3) clusters were colliding with a metal surface covered by a layer of rare gas[13].

On the other hand, after a nuclear collision, various types of irradiation effects have been observed. Sputtering is one case. In connection with the molecular effect, Andersen wondered whether the concentrated energy deposition due to high-Z ions might be the cause of the high sputtering yield. This was why they tried to measure the sputtering yield caused by molecular beams[34]. In the speed-range (ii) in Table 1, using Cl₂⁺, Se₂⁺, Te₂⁺ beams[35], they obtained the larger \( R₂ \) for the heavier projectile and target. Moreover, in 1997, they added a result of \( R_{₆} \sim 100 \) \( n² \) from a gold target using Au₆⁺ (n = 1–5) clusters in the speed range of \( \{(i)~(ii)\} \) or \{0.064 \( v₀ < 1.0 \) \( v₀ \). They confirmed the sputtering enhancement is due to energy deposition in the localized dense cascades. Note that for Au→Au collision, 800 keV...
Au ion (\(=0.4\) \(v_0\)) receives the maximum loss of \((-dE/dx)_{\text{max}}\). With much lower energy beams, Yao et al.\(^{41}\) found that the lower the partial energy, the stronger the molecular effect was. They obtained \(1 < R_\ell \leq 4\), using \(N_2 (v_1 < 0.038 v_0)\) and \(O_2 (v_1 < 0.035 v_0)\) beams to be implanted into gold target.

Other remarkable effects than sputtering have also be clearly observed, e.g., ion track or crater formation and reduced annealing temperature\(^{44}\). The ion track was produced by a cluster bombardment of 20-MeV \(C_6^2\) in \(\alpha-A_2O_4\), whereas it had been found after exposure of the fission products in mica\(^{46}\). The crater was presented by MD of a cluster bombardment by Hsieh and Averback\(^ {19}\), where a significant enhancement of the crater radius was observed due to a cluster beam. This definition is based on the idea of a "united atom" following a penetrating insight\(^{46}\) which means that the total energy is more essential for scaling than the partial energy. In addition, there are a few calculations or measurements that support the united atom model in the speed-range of (i) or (ii): Andersen et al.\(^{40}\) showed that the total energy of \(Au_1 \sim Au_{15}\) clusters with \(0.020 \sim 5\) (MeV/atom) can be acceptable as a scaling variable for the measured sputtering yield. Zimmermann and Urbassek\(^{47}\) also confirmed that the scaling of a sputtering yield in terms of the total energy of \(Au_1 \sim Au_{20}\) looked reasonable with bombardment energies between \(0.16 \sim 64\) (keV/atom).

In section 2, we said that the scaling is possible in the collision stage but not in the relaxation stage, for the case of a single ion beam. However, there seems no complete single scaling rule for cluster bombardment even in the collision stage because of the geometrical structure of a cluster. This is quite in the natural order of things. From this viewpoint, the discussion of scaling solely using partial energy may be incomplete, however, that using total energy can be still a matter for debate.

4. Computer simulations for the collision and relaxation stages

As was mentioned in § 2.3 especially in (*2), no simulation with a single model can thoroughly cover the entire processes including both collision and relaxation stages. A classical MD has one merit that can follow time-development along trajectory and can examine the (nuclear) multiple collisions between atoms in material\(^ {48}\). Nonetheless, a MD-timestep to solve the equations of motion is usually taken as \(\Delta t \sim 10^{-15} \sim 10^{-17}\) sec, while the champion record of a classical MD has spanned up to microsecond at the longest\(^ {59}\). That is, a MD can cover the collision stage and only the infancy of relaxation stage.

Therefore, in order to cover the huge span of the relaxation stage, some missing scales should be supplemented by hybridizing with other approaches. For example, a Monte-Carlo simulation based on a BCA expands the length\(^ {50}\) up to \(10^{-5}\) \(\mu m\) at the longest, the kinetic Monte-Carlo (KMC)\(^ {51}\) expands the time up to \(10^6\) sec\(^{52}\) at the longest, and QMO\(^ {31}\) or QMD includes excited states and increases the accuracy up to \(10^{-3}\) eV at the highest accuracy. Such a hybridization approach is generally called a "class-simulation", and is an urgent issue in computer simulation.

Classical MD simulations used for cluster bombardment on solid surfaces have successfully reproduced the measured quantities or phenomena\(^ {48}\). One can assume the details of the intermediate situation from snapshots...
taken at any moment in the simulation, because if a phase change occurs, it might accompany changes in atomic and energy distribution.

The stopping forces are calculated in a classical MD as follows: The nuclear stopping ($-\frac{dE}{dx}$), is determined by integrating the reduced kinetic-energy of a projectile, along its trajectory. A trajectory of each projectile is determined by solving the set of equations of motion. Gibson et al. started MD in 1960, where external forces exerted on each atom are determined by the derivative of the interaction potential with the surrounding atoms (assuming the elastic collisions between atoms). Those potentials are given by an empirical function\(^5,^{33,50}\) in a classical MD, or by the total energy determined by the QMD\(^36\). For the electronic stopping ($-\frac{dE}{dx}$), in 1989, Caro and Victoria\(^{29}\) first introduced a term friction force into MD equations for a moving atom as a function of the current energy ($E$). Usually the energy loss $\langle AE\rangle$ is subtracted being proportional to the distance, i.e., $\langle AE\rangle = \langle -\frac{dE}{dx} \rangle \cdot \Delta x$ for atoms moving with an energy larger than 10 eV\(^{55}\) or 5 eV\(^{37}\). This model signifies that electron distribution is uniform in target material. Nevertheless, even for high-speed projectiles, the local electron distribution "p" in a crystal is actually significant for channeling ions. In such a case, another model of ($-\frac{dE}{dx}$), based on DFT is useful\(^{56}\).

As one of the unresolved phenomena of radiation physics, we must consider the ion track or the so-called electronic sputtering, where the atomic displacement occurs after receiving much larger ($dE/dx$) than ($dE/dx$). At present, a semi-empirical model has been proposed by Toulemonde named the thermal spike model\(^{57}\). The following three points are, however, not clear in this model: What are the conditions needed to form a thermal spike? How will the excited electrons transfer their potential energy to the surrounding atoms to be displaced with some kinetic energy? How far can it explain the material dependence? A breakthrough to make a great step forward may be probable by looking at the correlation between a phase change and the changes in the time-gradient and space-gradient of states both in atomic and energy distribution. This new viewpoint is also indispensable when we connect a MD with other scheme in the class simulation.

5. Conclusions

The characteristics of a cluster bombardment of a solid target have been reviewed in comparison with the case of a single atom bombardment. The molecular effect is evident for sputtering and the electronic stopping force for hydrogen molecules. The irradiation effects caused by cluster beams were almost reproduced by classical MD simulations unless the electronic excitation was evident. Most events caused by cluster beam can be essentially reproduced by a simulation of a single ion beam. If one were to point out a difference, it may be that there may be critical conditions leading a phase change when energy is highly deposited in a confined realm in space and time.

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Before this work, only repulsive potentials were used in a classical MD. This work first introduced cohesive term that was literally indispensable to consider the many-body interactions.