Threshold Ion Energies for Creating Defects in 2D Materials from First-Principles Calculations: Chemical Interactions Are Important
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ABSTRACT: The characteristics of two-dimensional (2D) materials can be tuned by low-energy ion irradiation provided that the ion energy is correctly chosen. The optimum ion energy is related to $E_{\text{th}}$, the minimum kinetic energy the ion should have to displace an atom from the material. $E_{\text{th}}$ can be assessed using the binary collision approximation (BCA) when the displacement threshold of the atom is known. However, for some ions the experimental data contradict the BCA results. Using density functional theory molecular dynamics (DFT-MD), we study the collisions of low-energy ions with graphene and hexagonal boron nitride and demonstrate that the BCA can strongly overestimate $E_{\text{th}}$ because energy transfer takes a finite time, and therefore, chemical interactions of the ion with the target are important. Finally, for all projectiles from H up to Ar, we calculate the values of $E_{\text{th}}^{\text{BCA}}$ required to displace an atom from graphene and h-BN, the archetypal 2D materials.

Because of their planar geometry, two-dimensional (2D) materials are ideal systems for the controlled modification of their structure and properties by the introduction of defects and impurities.1–5 Specifically, exposure to low-energy ion beams can give rise to doping of 2D materials by direct ion implantation,6–9 the development of defect-based single-photon emitters,10 the addition of magnetic properties,11,12 or the creation of catalytically active centers.1 Thus, choosing the optimum ion energies for these applications is of pivotal importance. It can be determined empirically by measuring the characteristics of the material after the treatment, but a good "educated guess" can speed up the experiments. The "reference" energy is naturally $E_{\text{th}}^{\text{BCA}}$, the minimum kinetic energy the impinging ion should have to displace an atom from the target. For example, for direct ion implantation, the optimum energy should be close to $E_{\text{th}}$: at lower ion energies implantation is obviously impossible, while at too high ions will simply go through the 2D system and may also create a large number of unwanted defects.

$E_{\text{th}}$ can be estimated using the binary collision approximation (BCA) if the displacement energy $T_d$ (i.e., the minimal kinetic energy the recoil atom must have to leave its position permanently) is known. We note that the BCA, which represents energy transfer from the energetic projectile to the atoms in the target as consecutive elastic collisions involving only two particles, has been extremely successful in describing irradiation effects in various materials.13–17 For 2D systems, $T_d$ can be accurately derived from the results of transmission electron microscopy experiments.18–21 For example, $T_d \approx 21 \text{ eV}$ in graphene,21 19 and 23 eV for N and B, respectively, in hexagonal boron nitride (h-BN),18 and 7 eV for S in MoS$_2$.19

In a head-on collision of two atoms or ions, the kinetic energy $T$ transferred to the recoil atom is

$$T = \frac{4m_i m_r}{m_i + m_r} E_{\text{ion}}$$

(1)

where $E_{\text{ion}}$ is the kinetic energy of the ion (or in general a projectile, which can be a neutral particle) and $m_i$ and $m_r$ are the masses of the ion and the recoil atom, respectively. Ballistic displacement of the recoil atom occurs if $T > T_d$.

One would expect that the actual value of $E_{\text{th}}$ must be higher than the BCA value because of partial transfer of the ion kinetic energy to the atoms neighboring the recoil atom during the collision and, additionally, conversion of a part of the energy into electronic excitations. However, experiments on low-energy ion irradiation22 and plasma treatment23 of 2D materials indicate that this is not the case and that $E_{\text{th}}^{\text{BCA}}$ can actually be lower than $E_{\text{th}}^{\text{BCA}}$. The formation of defects was explained by beam-induced chemical etching or energy release during the de-excitation processes of the ions, but no convincing argument for that was provided.

Here, using density functional theory molecular dynamics (DFT-MD), we demonstrate that $E_{\text{th}}^{\text{BCA}}$ can be substantially lower than the value derived from the binary collision formula. To carry out such simulations in practice, we use a scheme...
aimed at removing some of the intrinsic problems of DFT-MD, which limit the applications of the method in modeling of irradiation effects. Finally, using this scheme we calculate the ion energies required to displace an atom from graphene and h-BN for all elements from H to Ar.

To gain insights into energetic collisions, we employed Born–Oppenheimer (BO) DFT-MD and modeled the impacts of various ions onto graphene and h-BN using the VASP code. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was used. A supercell containing 96 atoms of the free-standing target was fully optimized, and then an ion with a certain kinetic energy and an initial velocity vector pointing toward the target was created exactly on top of one of the atoms to warrant a head-on collision, which gives the maximum energy transfer. The evolution of the system was modeled using the microcanonical ensemble. As for the plane-wave basis set, the cutoff value was chosen to be 300 eV, and sampling over the Brillouin zone was done using a $3 \times 3 \times 1$ k-point mesh, which provided a reasonable compromise between accuracy and computational efficiency. Test simulations with a cutoff of 400 eV and a $4 \times 4 \times 1$ mesh gave essentially the same results. The time step was varied in the range of $0.1–0.2$ fs depending on the ion mass. It should be noted that by “ion” (or “projectile”) we refer to a neutral atom, as at such low ion energies one can expect that the initially charged projectile will be (at least partially) neutralized when approaching the target, so that the difference between impacts of neutral and (at least) single-charged ions should be minor. We also note that BO MD cannot adequately describe charge transfer during ion collisions in any case, and the Ehrenfest dynamics simulations and closely related methods based on time-dependent DFT ideally should be used, but these methods are computationally too expensive for estimating displacement thresholds. The initial kinetic energy of the ion was varied until displacement of the target atom was achieved (with an accuracy of 0.1 eV or better), which corresponded to the threshold energy $E_{\text{ion}}^{\text{th}}$ for each ion.

Prior to carrying out massive calculations, we carefully addressed several issues related to the applications of DFT-MD to ion impact simulations. First, by considering the collisions of two isolated atoms, we made sure that the core regions of the projected augmented wave (PAW) potentials do not overlap for the range of energies of the projectiles we studied and that the energy–distance curve for the dimer is close to the results of full-electron calculations, which were done using the DMol code.

Having analyzed the interaction between two isolated colliding atoms, we studied the role of spin polarization (SP) in the MD simulations by choosing a nitrogen atom as a projectile, as it has a large SP energy of 3.1 eV. We note that non-SP MD is computationally less expensive than SP MD and also numerically more stable, as detailed below. We first calculated $E_{\text{ion}}^{\text{th}}$ for graphene using non-SP DFT-MD, which proved to be 12 eV. Then we repeated the calculations using SP MD and found that the recoil atom is not displaced but remains bound to the system, as illustrated in Figure 1a. Continuation of the MD run resulted in “healing” of the defect (i.e., restoration of the graphene network with N adatoms on top), which is energetically favorable. In the experiment the adatom will likely migrate over the graphene surface, meet another N adatom, and form a N$_2$ molecule, which will desorb from graphene, leaving the intact system behind.

Figure 1b presents the kinetic energies of the ion and recoil atoms as functions of time as well as the position of the recoil atom as a function of simulation time. The neglect of SP leads to a nonphysical increase in the kinetic energy when the projectile approaches the target.
observed, but at $E_{\text{kin}} = 15$ eV the C atom appeared to be displaced. However, the run crashed at some point when the recoil atom was 3.8 Å away from its initial position, as illustrated in Figure 2a. We repeatedly encountered that problem, even though we decreased the time step and tried different algorithms (the preconditioned conjugate-gradient algorithm, blocked Davidson algorithm, and RMM-DIIS algorithm) to solve the eigenvalue problem.

Analysis of the magnetic and electronic structure evolution of the system indicated that the numerical instabilities are inherently related to the practical implementation of the SP DFT-MD algorithm. At each time step, to speed up the convergence, the initial SP electron density is taken from the previous atom configuration. Thus, when two energy surfaces corresponding to different spin configurations cross, the system may remain on that same surface, which is no longer the lowest-energy configuration, as schematically illustrated in Figure 2d. We call this the “memory” effect. Moreover, the system may instantaneously “jump” between the two configurations, so that the total energy (the sum of kinetic and potential energies) is not conserved. In particular, for the case of the nearly sputtered C atom, which still weakly interacts with the graphene sheet, this corresponds to the changes in the magnetic configuration of the recoil atom and its interaction with the N atom embedded in the graphene sheet, which may also have a magnetic moment. It is hypothetically possible to start calculations of the electronic structure of the material at each time step from a random (or even several random) electron/spin densities, but this would slow down the calculations by 1–2 orders of magnitude and make them virtually impossible even on the most advanced parallel computer systems.

To find a practical solution to the problem of computationally efficient but approximate non-SP and physically more accurate but numerically unstable SP DFT-MD, we carried out the following calculations: we took the non-SP trajectory and at each time step statically calculated the potential energy of the system. The energy profiles for SP, non-SP, and non-SP “corrected” calculations are presented in Figure 2b, and the corresponding magnetization of the system is shown in Figure 2c. As is evident from the energy profiles, the major differences in the energy surfaces occur when either the projectile or the recoil atom are far from the target 2D material—the bound states do not differ much. This finding indicates that energy-corrected non-SP DFT-MD can be used to determine the threshold energy correctly without underestimating the threshold, thereby avoiding the problems present in SP DFT-MD. Furthermore, it is only necessary to correct the initial and final points of the trajectory and thus adjust the calculated $E_{\text{th}}^{\text{ion}}$ by the SP energies of the ion and sputtered atoms:

$$E_{\text{th}}^{\text{ion}} = E_{\text{th}}^{\text{ion}}(\text{non-SP}) + \Delta E_{\text{spin}}^{\text{corr}}$$  \hspace{1cm} (2)$$

where $E_{\text{th}}^{\text{ion}}(\text{non-SP})$ is the displacement energy obtained using non-SP DFT-MD and the correction due to spin polarization can be estimated as follows:

$$\Delta E_{\text{spin}}^{\text{corr}} = \Delta E_{\text{spin}}^{\text{corr}}(\text{recoil}) - \Delta E_{\text{spin}}^{\text{corr}}(\text{projectile})$$  \hspace{1cm} (3)$$

Figure 2. Impact of a nitrogen ion with an initial kinetic energy of 15 eV onto graphene. (a) Kinetic energy and position of the recoil atom with respect to its original site as functions of the simulation time with and without account of SP. The SP MD run crashes (as indicated by the red cross) when the recoil atom is about 3.8 Å away from its initial position. (b) Potential energy vs elapsed time for the same set of simulations. For isolated atoms at large separations from the 2D material, the non-SP potential energy profile (blue) needs to be adjusted (see the dashed orange curve) by static SP calculations to correctly describe the energetics. (c) Evolution of the magnetization with elapsed time. Starting at around 65 fs, sudden jumps in the magnetization occur, which cause the MD run to crash. At the same time, the corrected trajectory yields the expected behavior. (d) Schematic illustration of the origin of the oscillating magnetization in the DFT-MD run due to the “memory” effects close to the intersection of two energy surfaces corresponding to different spin configurations, so that the MD algorithm fails to find the lowest-energy configurations.
in which \( \Delta E_{\text{sp}} = E_{\text{sp}} - E_{\text{sp,spin}} < 0 \) is the SP energy of the isolated atom. The formula can be straightforwardly generalized if several atoms (or none) are sputtered away. In addition to N as the projectile, its validity was checked for P (which has a large magnetic moment) and Mg (which has no magnetic moment). We note, however, that this is not a strict and universal approach that will always work and give the exact results but rather is just an irradiation-simulation-related improvement of a specific technical implementation of DFT-MD in the VASP code.

Making use of this scheme, we carried out DFT-MD simulations for a broad range of chemically different projectiles (all of the chemical elements from hydrogen to argon) for two typical 2D systems, graphene and h-BN. The results are presented in Figure 3. At ion energies close to the displacement threshold, the interaction with the impinging ion takes place on a longer time scale (compared with high-displacement threshold, the interaction with the impinging ion can be understood as follows. Upon impact, three qualitatively different outcomes are possible: (i) the ion is backscattered without sputtering of the target atom; (ii) it is reflected, and the recoil atom is sputtered; and (iii) it substitutes for the recoil atom and binds to its neighbors. It is intuitively clear that the third possibility should be associated with the lowest value of \( E_{\text{sp}} \) and the defect formation process can be called “replacement” instead of “displacement”.

To better understand the trend, we statically calculated the energy penalty for the exchange of the C atom in graphene with the chemical elements. For example, for N the penalty \( \Delta E \) is

\[
\Delta E = [E_{\text{subst}}(N) + E_{\text{isol}}(C)] - [E_{\text{pristine}} + E_{\text{isol}}(N)]
\]

(4)

where \( E_{\text{subst}}(N) \) is the SP energy of the graphene sheet with a substitutional N impurity, \( E_{\text{isol}}(C) \) is the energy of the isolated recoil atom, \( E_{\text{pristine}} \) is the energy of pristine graphene, and \( E_{\text{isol}}(N) \) is the energy of the isolated N atom. It should be noted that for carbon \( \Delta E \) is equal to zero by definition. For graphene, \( \Delta E \) is shown as the purple curve in Figure 3a. It is evident that the interaction of the ion with the system can lower \( E_{\text{isol}}(N) \), as in this case the energetically unfavorable atomic configurations with dangling bonds can be avoided. This is not relevant to the light ions (H, He, Li), which are quickly backscattered, or heavy noble gas ions with closed shells (e.g., Ne, Ar), which do not interact with the target and because of their relatively large sizes and low velocities transfer part of their kinetic energy to the atoms neighboring the recoil atom. It is interesting to note that little energy (about 5 eV) is required to sputter a C atom from graphene by C ion, consistent with the experimental observations that at high temperatures (1300 °C) C atoms penetrate through pristine graphene sheet by the exchange mechanism.

Qualitatively similar results were obtained for h-BN (Figure 3b,c). The displacement or replacement of both B and N atoms was studied. The DFT-MD results show strong deviations from the BCA and emphasize the importance of chemical interactions during the impact. As could be expected, the minima of the displacement energies match B/N and the heavier elements from the same group in the periodic table.

In order to check our predictions experimentally, ion beams with precisely defined energy and narrow distribution (an energy spread of 2–3 eV can be achieved with the existing ion source designs) have to be used. Furthermore, care has to be taken to avoid contaminations that would also affect \( E_{\text{sp}} \). The experimental verification of substitutional doping or defect creation at energies above \( E_{\text{sp}} \) can be done directly by transmission electron/scanning tunneling/atomic force microscopy or indirectly by spectroscopic methods such as Raman or photoemission spectroscopy. For implantation applications, however, the ion energy needs to be chosen at the optimum value for substitutional defect production, which is certainly higher than the threshold energy \( E_{\text{sp,spin}} \) describing the onset of sputtering in a head-on collision. The threshold energies must also be taken into account when sputtering should be avoided (e.g., for intercalation or creation of nanobubbles without defect formation), provided that the ions are small enough to penetrate through the sheets, that is, through the middle of hexagons in graphene or h-BN.
In summary, using a DFT-MD-based approach, which makes it possible in practice to carry out SP ion impact simulations onto materials, we assessed the minimum ion energies (for all projectiles from H up to Ar) required to displace an atom from graphene and h-BN, the archetypal 2D materials. We also showed that even if the displacement threshold of an atom from the target is known, the BCA approach cannot be used for many ions, as displacement of atoms occurs during a finite time and the chemical interaction of the ion with the system is important. We have discussed the experimental verification of our findings, which should be crucial for the controlled creation of single-type defects and the introduction of dopants in h-BN (or other wide-gap 2D materials), which should be beneficial for further development of single-photon emitters and other quantum applications.

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