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Author(s)	Vinchon, P.; Spiske, L.; Miyamoto, Y. et al.
Citation	サイバーメディアHPCジャーナル. 2026, 16, p. 44-47
Version Type	VoR
URL	https://doi.org/10.18910/106232
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Contribution of subthreshold energy ions' neutralization on defect formation in monolayer graphene

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1. Introduction

Since its isolation in 2004, monolayer graphene has been the focus of numerous research efforts to harness its properties. In particular, it is necessary to control structural defects in the graphene lattice, as they can be either beneficial or detrimental to the final application. Little attention has been focused on the influence of very-low energy ions (Energy <25 eV) on graphene structure. Indeed, numerous experimental and theoretical studies established a strict energy threshold for defect generation in graphene at 18-22 eV. Still, graphene irradiation by low-pressure Argon plasma containing ions with kinetic energy around 12 eV results in a significant generation of defects [1]. Such a phenomenon is not yet clearly understood. One hypothesis considers that, at such low kinetic energy, ions can neutralize themselves to the surface. Hence, a fraction of the ion's potential energy (15.7 eV) could be transferred to the lattice on a similar timescale to the impact and contribute to defect generation [2].

To test this assumption, accurate first-principle numerical simulations are needed. Real-time Time-Dependent Density Functional Theory (TDDFT) for Ehrenfest dynamics enables the analysis of electrons and ions altogether directly coupled with a Molecular Dynamics scheme. The proposed approach can overcome the conventional theory, which relies on a classical adiabatic picture in which electrons are always sitting in their ground state throughout atomic motions.

2. Numerical Simulation scheme

Real-time TDDFT simulations using the open-source code FPSEID²¹ were performed to investigate ion interactions with suspended graphene. A detailed presentation of the numerical simulation scheme can be found in [3,4]. Calculations were performed using a plane-wave basis set. Norm-conserving pseudopotentials and a cut-off energy of 60 Ry were implemented. The periodic structure is presented in Figure 1, consisting of a graphene model with 50 atoms within a hexagonal simulation box. Ar ion (Ar⁺) and neutral (Ar(N)) are introduced at the beginning of the simulation with an initial velocity in the Z direction corresponding to a kinetic energy of 1eV. Since both ions and electrons are treated, a small time step of 0.726 as (0.726×10⁻¹⁸ s) is required. Simulations are run using the vector-node available on the supercomputer SQUID, at the University of Osaka. Ar⁺ case has been run up to 260 fs, while the Ar(N) case could have been run up to 180 fs.

Output data files were written every 100 timesteps. Two impact location has been chosen, to grasp how it can influence the end results. In total, four simulations run has been carried out, which took over 4

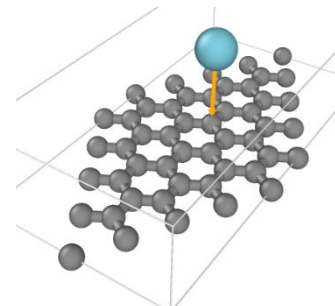


Figure 1: TD-DFT simulation set up with 50 Carbon atoms (black ball) and 1 Ar atom or ion (blue ball). The orange arrow represents Ar velocity.

weeks per run to reach the desired simulation time. A custom MATLAB code was developed to perform data analysis.

3. Results and Discussion

3.1 Atoms behavior

From the simulation output, the kinetic energy evolution of Ar^+ and $\text{Ar}(\text{N})$ with time can be extracted from the velocity values. Figure 2 presents the evolution of both Ar^+ and $\text{Ar}(\text{N})$ as a function of simulation time when a) atoms collide on the top of a carbon atom and b) in the center of the hexagonal lattice

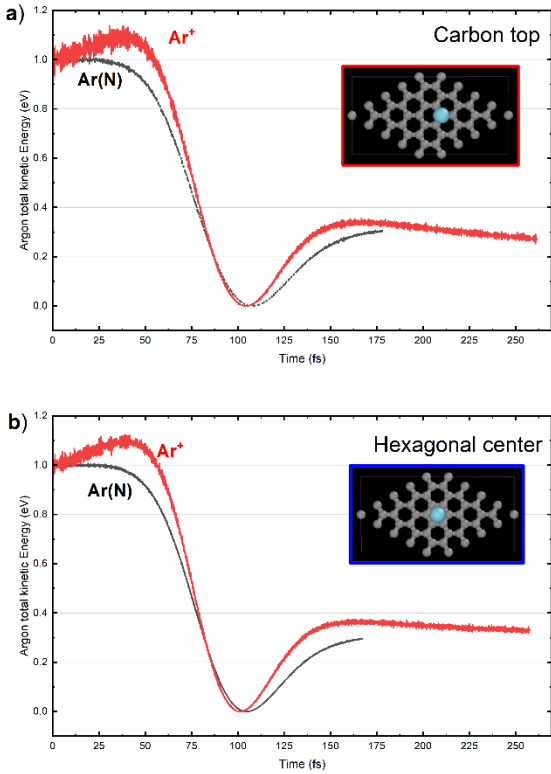


Figure 2: Ar^+ (full red line) and $\text{Ar}(\text{N})$ (dashed black line) kinetic energy evolution as a function of simulation time for a) a head on collision with a Carbon atom and b) when the targeting the center of an hexagonal lattice.

Interestingly, regardless of impact position, no significant change is observed during impact. Figure 2a shows that as time goes on, $\text{Ar}(\text{N})$ and Ar^+ are getting closer to the graphene layer. Consequently, $\text{Ar}(\text{N})$ kinetic energy decreases to become null at 110 fs before increasing again as it is being repelled,

acquiring a final kinetic energy of 0.30 eV. On the other hand, Ar^+ is first affected by an attractive force, which can be related to the image charge effect, as the entire simulation is positively charged. After 50 fs, Ar^+ kinetic energy decreases to reach a null value at 105 fs before rising and reaching a maximum around 15 fs. Then, Ar^+ slowly loses its kinetic energy as it goes further away from graphene's surface, due to the attractive force from the mirror charge image influence. It is interesting to extract the amount of kinetic energy lost by $\text{Ar}(\text{N})$ and Ar^+ by impacting graphene and compare to the classical view of maximum energy transfer as expressed as :

$$E_{\text{transf}} = \frac{4M_{\text{C}}M_{\text{Ar}}}{(M_{\text{C}}+M_{\text{Ar}})^2} E \quad (1)$$

With M_{C} and M_{Ar} being the mass of Carbon and Argon respectively, and E being the initial kinetic energy of $\text{Ar}(\text{N})$ or Ar^+ . From equation 1, 71% would be the maximum portion of energy transferred to graphene. From the TDDFT calculations, $\text{Ar}(\text{N})$ and Ar^+ lost 70% and 68%, respectively, of their initial kinetic energy. While the agreement between the TDDFT and classical estimation of energy transfer is excellent for the $\text{Ar}(\text{N})$ case, the Ar^+ case is slightly worse. This minor discrepancy might hint that Ar^+ interaction with graphene varies compared to its neutral counterparts. To investigate it, it is pertinent to focus on the Force applied to Ar, normal to the graphene plane, as a function of simulation time. Furthermore, to better take into account the charge image influence, the force applied on Ar^+ can be estimated as [5] :

$$F_z = -\frac{e^2}{4\pi\epsilon_0(2d)^2} \quad (2)$$

With e , the elementary charge, ϵ_0 the vacuum permittivity, and d the distance between the ion and the substrate. Figure 3 compares the force exerted on Ar normal to graphene extracted from TDDFT simulation for both Ar^+ and $\text{Ar}(\text{N})$ with the analytical form presented in equation 2 as a function of Ar position relative to the position of the closest carbon in

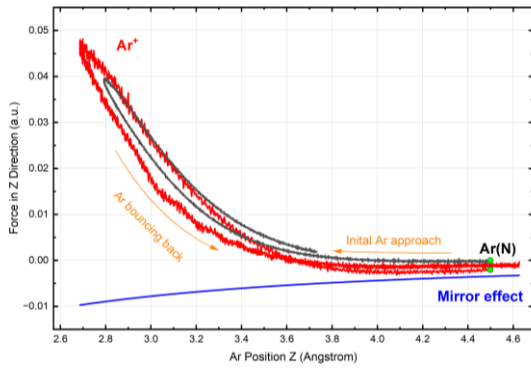


Figure 3: Force evolution exerted on Ar^+ (red line) and $\text{Ar}(\text{N})$ (black line) as a function of the distance between Ar and the targeted Carbon atom. Force estimation for the charge graphene.

At the initial position (4.5 Å), $\text{Ar}(\text{N})$ is not subjected to any force, confirming it is introduced sufficiently far from graphene. As the distance decreases below 3.8 Å, a repulsive force appears, which will attain its maximum at 2.8 Å. Interestingly, as it is being repelled, the force evolution with position differs depending on $\text{Ar}(\text{N})$ direction. On the other hand, Ar^+ is attracted to graphene as expected from the charge image effect. The force deduced from equation (2) is higher by an order of magnitude than calculated by TD-DFT. Still, as Ar^+ reaches 3.6 Å, the force becomes null before reaching a maximum at 2.7 Å. Then, the force decreases to reach a final negative value, but lower than at the beginning of the simulation. Such disparity suggests that Ar^+ is partially neutralized. In the TD-DFT scheme, it could be interpreted as a probability for Ar^+ neutralization.

3.2 Electrons behavior

From the FPSEID21, it was possible to output charge density files for every time step. It resulted in many large files, totaling 120 Gbs for only one case. Hence, more effort is needed to fully grasp the physics hidden in those data. Still, it was possible to map charge density for various times. Figure 4 presents a cross-section view of the charge density map of graphene and Ar^+ atoms a) initially and b) after 100 fs, as Ar^+ reaches the graphene surface.

Comparing Figures 4a and 4b, it can be clearly seen that the Ar's electron cloud is significantly merging with graphene's electrons. However, the overall distribution of Ar's electrons seems relatively unperturbed. However, the carbon atom that is impacted has shifted down, and its electron cloud did so as well. Nevertheless, little change can be observed.

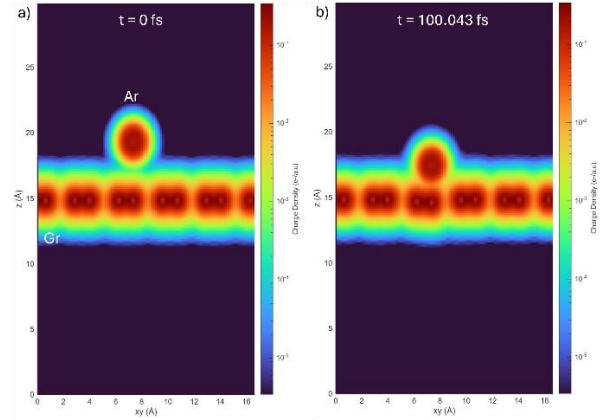


Figure 4: Charge density distribution at a) initial time and b) at 100.043 fs. Note that the color bar is in log scale.

To better investigate graphene's electron behavior, it was interesting to investigate sigma bonds evolution in graphene's plane. To do so, charge density was integrated over the maximum values close to atoms' central positions. Figure 5 presents the absolute value of charge density a) initially, b) after 100.043 fs, and c) the difference between the two is shown.

Figure 5a and 5b show no obvious differences in charge density of sigma bonds during Ar^+ irradiation. Both figures show very clearly sigma bond maxima, while electron density is minimum at the center of each hexagonal lattice. However, Figure 4c shows some variations. Electron density at the sigma bonds close to the impacted carbon are weaker as it seems the charge accumulates on the closest neighboring atoms. Overall, it seems only the closest carbon atoms are affected by Ar^+ impact. Such behavior is also observed in the $\text{Ar}(\text{N})$ case and does not appear to be unique to the ion. Nevertheless, more work is necessary to investigate electron dynamics.

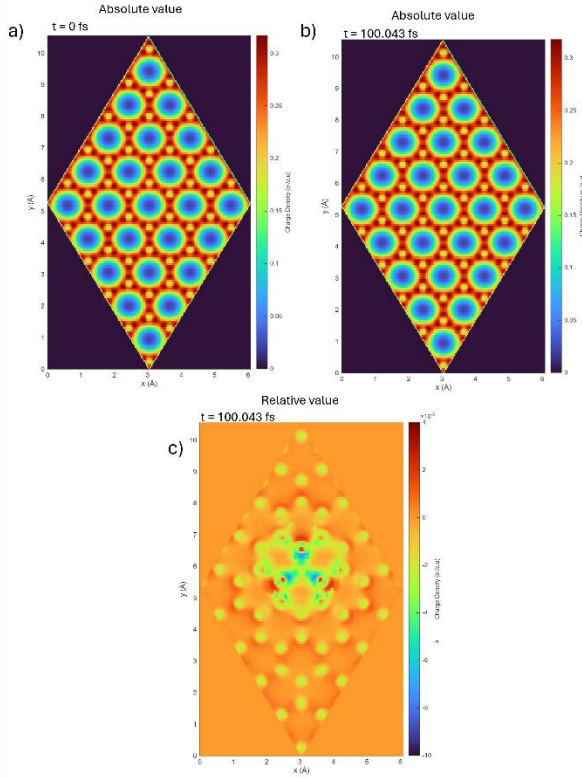


Figure 5: charge density distribution in graphene plane a) initially, b) after 100.043fs. Relative change between a) and b) is shown in c)

4. Conclusion

First-principle simulations such as RT-TDDFT have been used to investigate Ar⁺ and Ar(N) interaction with suspended graphene. Kinetic energy loss due to impact is close to what is expected classically. However, forces exerted on the ion and neutral differ, partially due to the charge image effect. Furthermore, from Ar ion behavior, partial neutralization of the ion seems to occur. Such phenomena cannot be seen in current charge-density-state analysis. Further data analysis is required to grasp its influence on graphene. Especially, it is planned to extract the density of states of electrons to determine if any excited electrons are generated during the Ar⁺ impact.

Acknowledgements

This work was partly supported by the use of Supercomputer System SQUID at the D3 Center, the

University of Osaka (2025-Exp-04) and by the Japan Science and Technology Agency (JST)'s "Adopting Sustainable Partnerships for Innovative Research Ecosystem (ASPIRE)" Project JPMJAP2321.

References

- [1] P. Vinchon, X. Glad, G. Robert Bigras, R. Martel, L. Stafford, Preferential self-healing at grain boundaries in plasma-treated graphene, *Nat. Mater.* 20 (2021) 49–54. <https://doi.org/10.1038/s41563-020-0738-0>.
- [2] P. Vinchon, L. Stafford, N. Mauchamp, S. Hamaguchi, On the role of positive ion neutralization in defect generation in monolayer graphene exposed to sub-threshold energy ions, *Journal of Physics D: Applied Physics* 59 (2025) 025202. <https://doi.org/10.1088/1361-6463/ae2877>.
- [3] Y. Miyamoto, A. Rubio, Application of the Real-Time Time-Dependent Density Functional Theory to Excited-State Dynamics of Molecules and 2D Materials, *J. Phys. Soc. Jpn.* 87 (2018) 041016. <https://doi.org/10.7566/JPSJ.87.041016>.
- [4] O. Sugino, Y. Miyamoto, Density-functional approach to electron dynamics: Stable simulation under a self-consistent field, *Physical Review B* (1999). <https://doi.org/10.1103/physrevb.59.2579>.
- [5] M.A. Lieberman, A.J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing: Second Edition*, 2005. <https://doi.org/10.1002/0471724254>.