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Thermal conductivity and chemical order

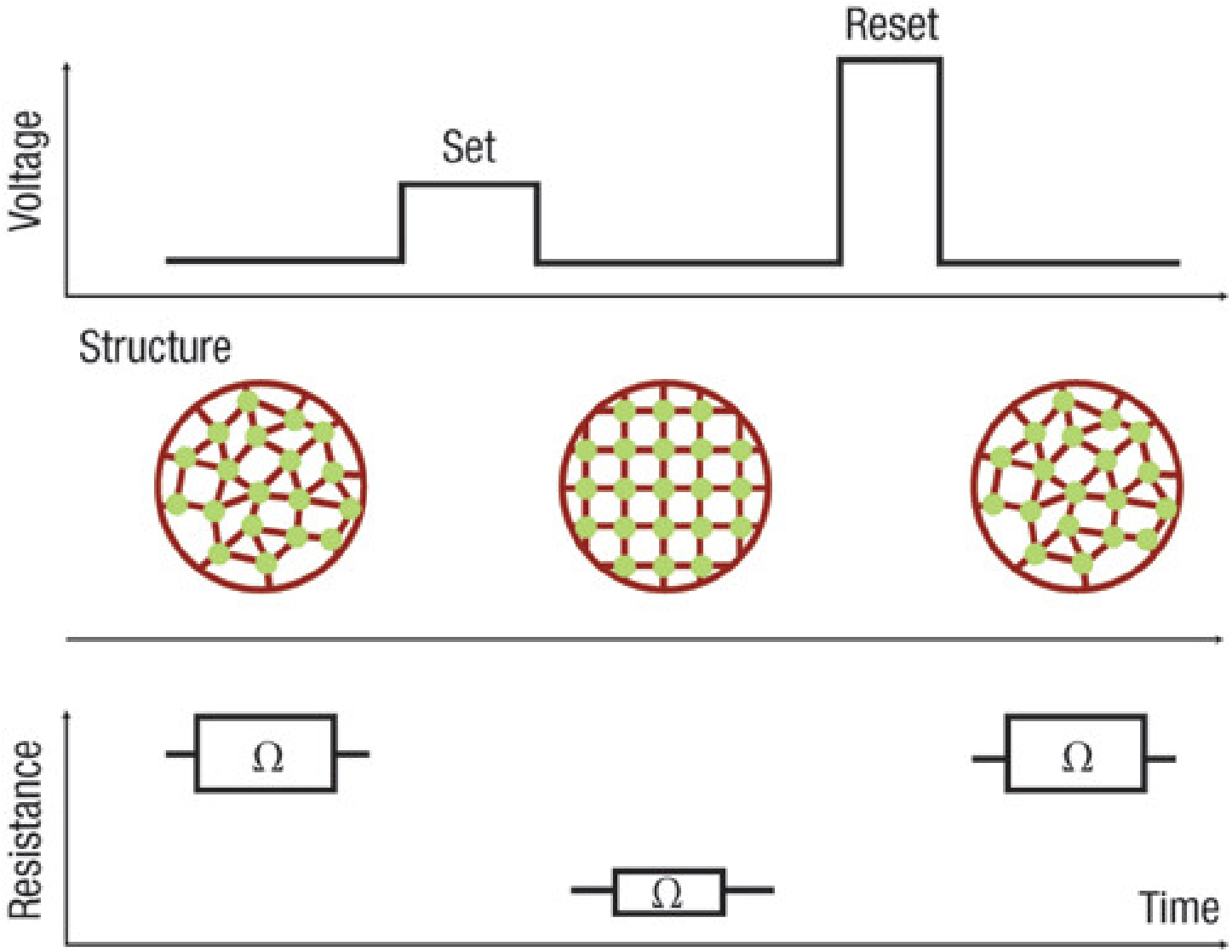
in irradiated models of amorphous $Ge_2Sb_2Te_5$

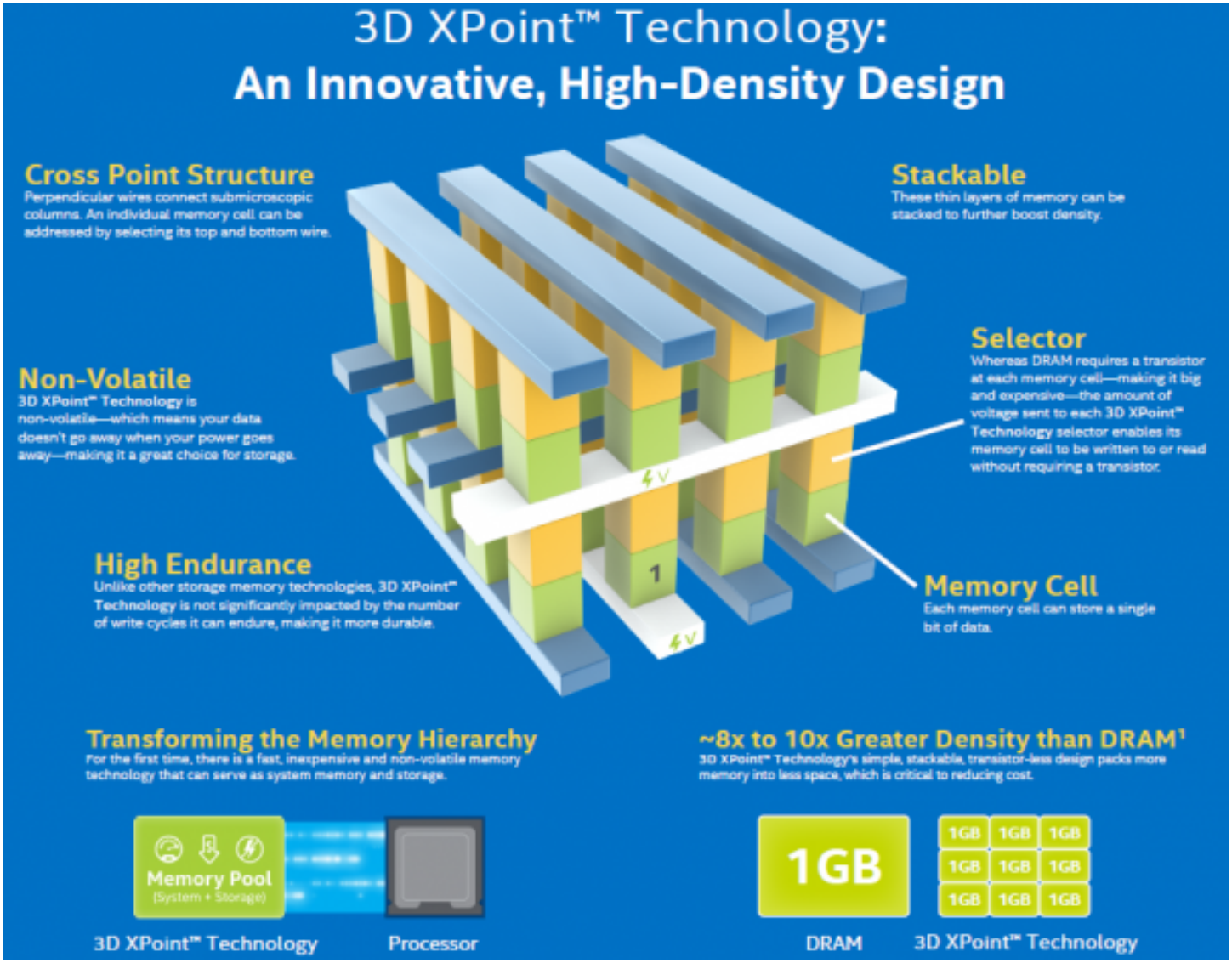
Felix Cosmin Mocanu, Dr. Konstantinos Konstantinou, Prof. Stephen R. Elliott

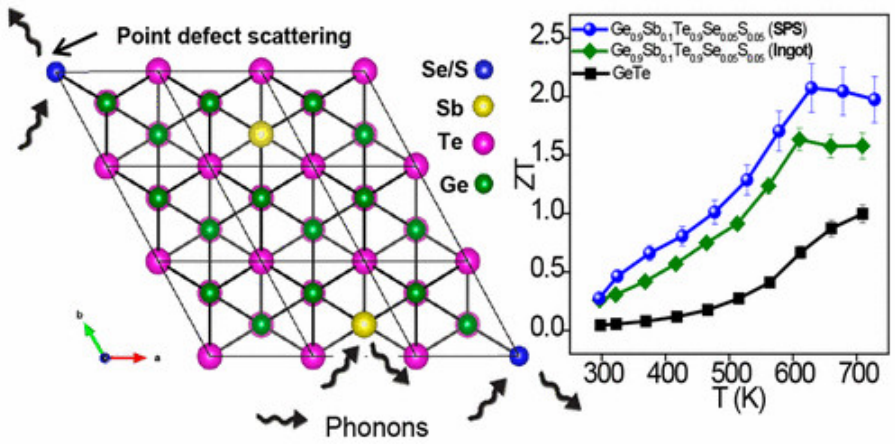
January 4th 2019

INTRODUCTION

Phase-change memory




3D XPoint™ Technology:
An Innovative, High-Density Design
Cross Point Structure
Perpendicular wires connect submicroscopic columns. An individual memory cell can be addressed by selecting its top and bottom wire.
Stackable
These thin layers of memory can be stacked to further boost density.
Selector
Whereas DRAM requires a transistor at each memory cell—making it big and expensive—the amount of voltage sent to each 3D XPoint™ Technology selector enables its memory cell to be written to or read without requiring a transistor.
Non-Volatile
3D XPoint™ Technology is non-volatile—which means your data doesn't go away when your power goes away—making it a great choice for storage.
High Endurance
Unlike other storage memory technologies, 3D XPoint™ Technology is not significantly impacted by the number of write cycles it can endure, making it more durable.
Memory Cell
Each memory cell can store a single bit of data.
Transforming the Memory Hierarchy
For the first time, there is a fast, inexpensive and non-volatile memory technology that can serve as system memory and storage.
~8x to 10x Greater Density than DRAM¹
3D XPoint™ Technology's simple, stackable, transistor-less design packs more memory into less space, which is critical to reducing cost.
Memory Pool
(System + Storage)
3D XPoint™ Technology
Processor
1GB
DRAM
1GB
3D XPoint™ Technology



taken from[1]

Figure of merit

Optimization of thermoelectrics is often discussed in terms of maximising the figure of merit $zT = \frac{\sigma S^2 T}{\kappa}$ where $\kappa = \kappa_e + \kappa_l$

[1] Manisha Samanta and Kanishka Biswas. "Low Thermal Conductivity and High Thermoelectric Performance in (GeTe)1–2x(GeSe)x(GeS)x: Competition between Solid Solution and Phase Separation". In: Journal of the American Chemical Society 139.27 (2017). PMID: 28625055, pp. 9382–9391. doi: 10.1021/jacs.7b05143. eprint: https://doi.org/10.1021/jacs.7b05143.

Non-equilibrium doping

Ion implantation (Ga+) was used to reduce the thermal conductivity in ZnO nanowires,[2] and (He) implantation in Si nanowires[3].

It can also be a tool for tweaking the electrical properties, for example Bi implantation of GeTe and Pb implantation of GaLaS resulted in p to n-type cross-over.[4]

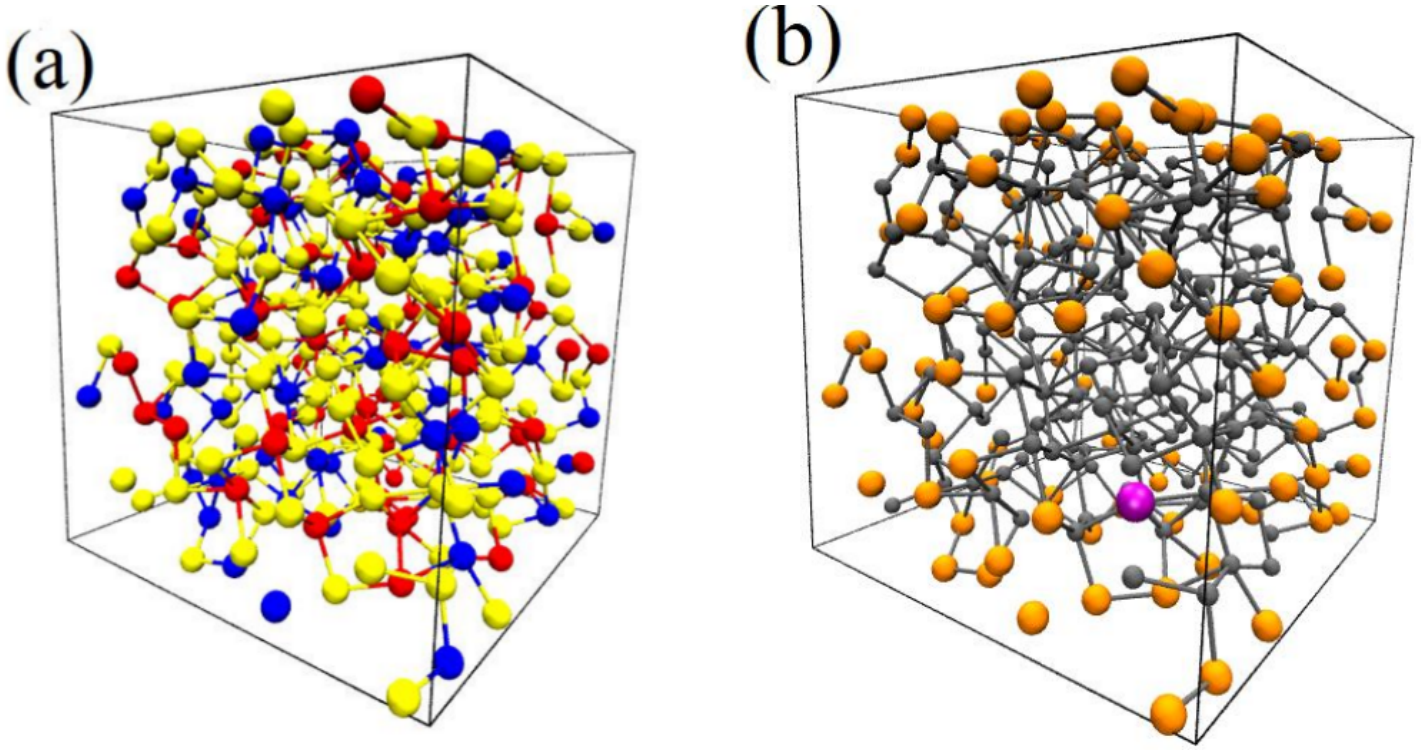
[2] Minggang Xia et al. "Gallium ion implantation greatly reduces thermal conductivity and enhances electronic one of ZnO nanowires". In: AIP Advances 4.5 (May 2014), p. 57128. doi: 10.1063/1.4880240.

[3] Yunshan Zhao et al. "Engineering the thermal conductivity along an individual silicon nanowire by selective helium ion irradiation". In: Nature Communications 8 (June 2017), p. 15919. doi: 10.1038/ncomms15919.

[4] Mark A Hughes et al. "N-type chalcogenides by ion implantation". In: Nature Communications 5.1 (Dec. 2014), p. 5346. doi: 10.1038/ncomms6346. url: http://www.nature.com/articles/ncomms6346.

MODELING ION IMPLANTATION

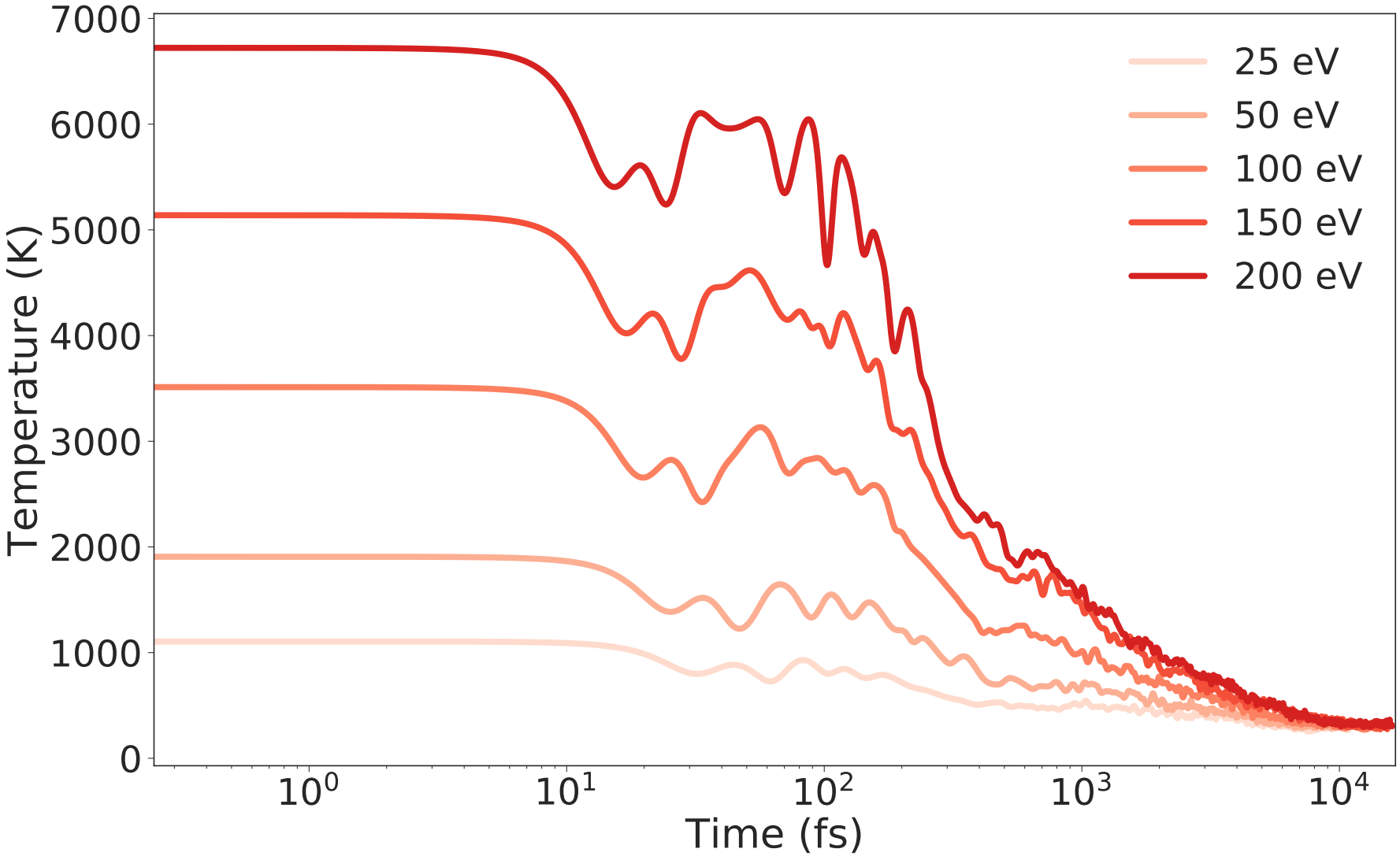
Stochastic Boundary Conditions



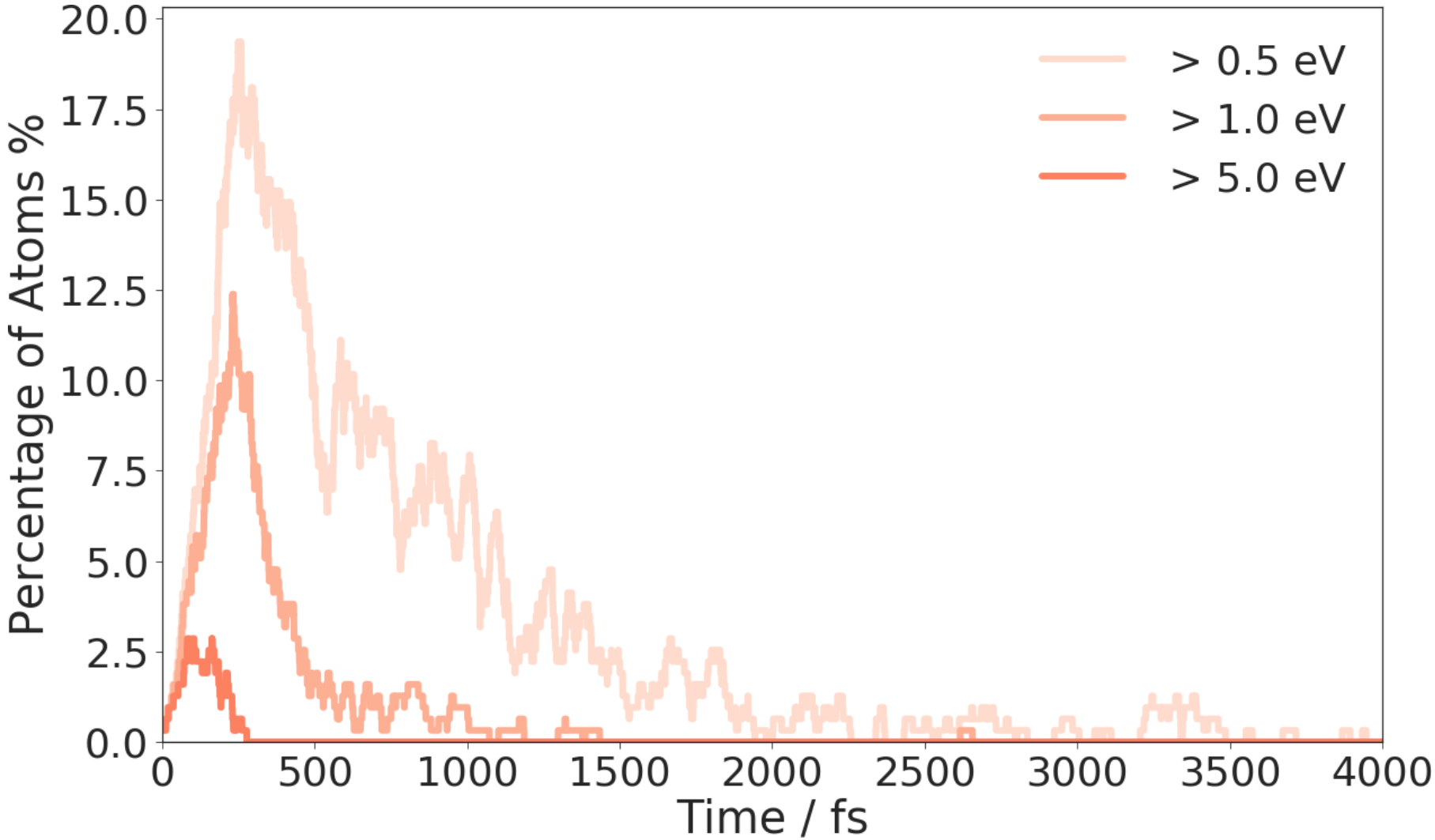
[5]

[5] Konstantinos Konstantinou et al. "Ab initio computer simulations of non-equilibrium radiation-induced cascades in amorphous $Ge_2Sb_2Te_5$". In: Journal of Physics: Condensed Matter (Sept. 2018). issn: 0953-8984. doi: 10.1088/1361-648X/aae340.

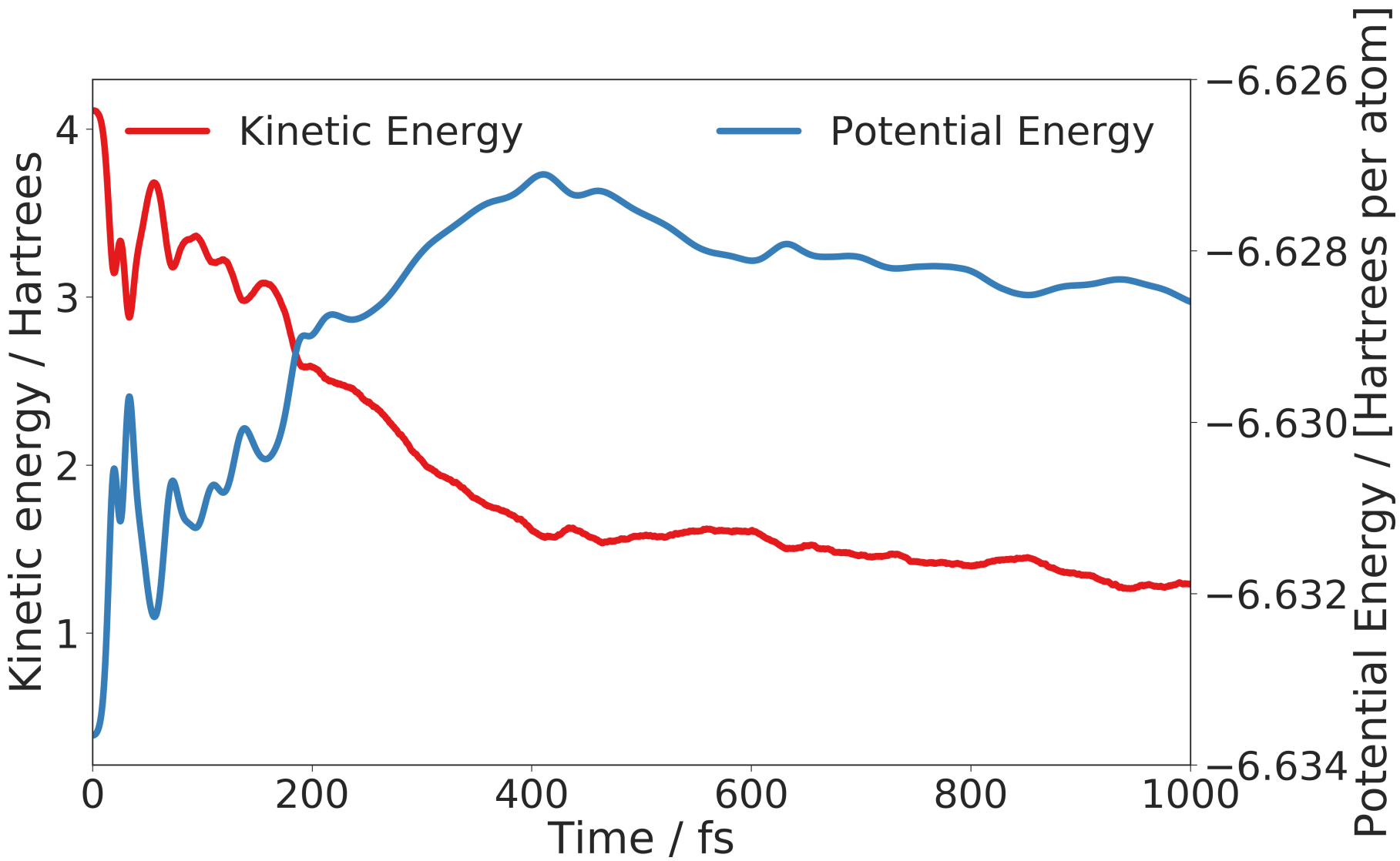
Cascade Kinetics



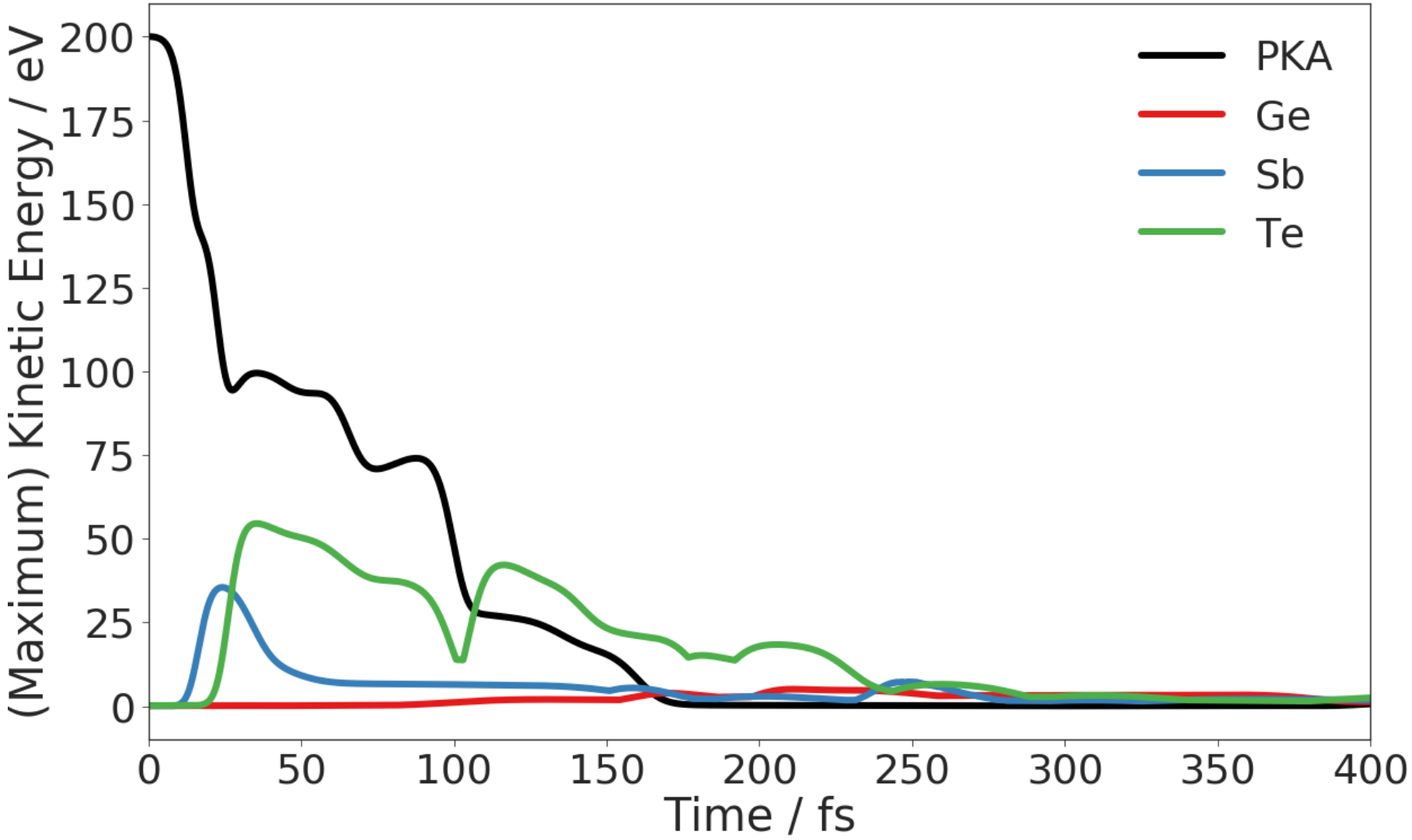
Cascade Kinetics



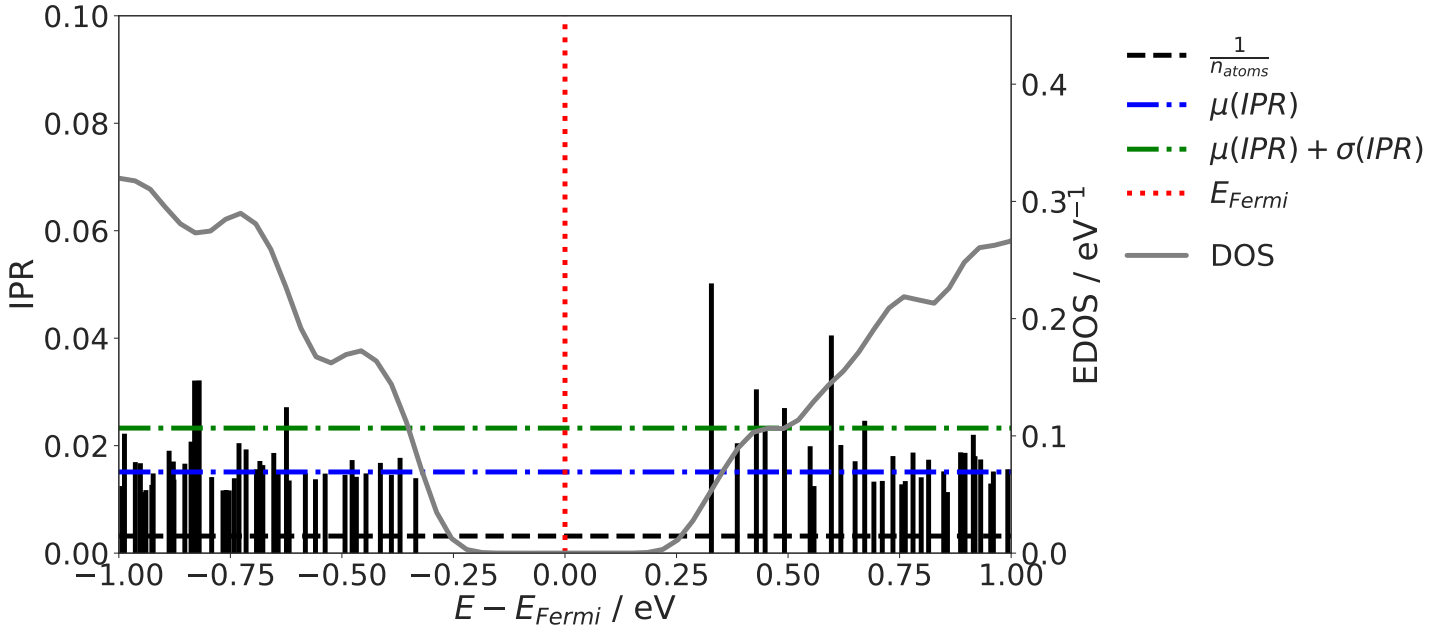
Cascade Kinetics

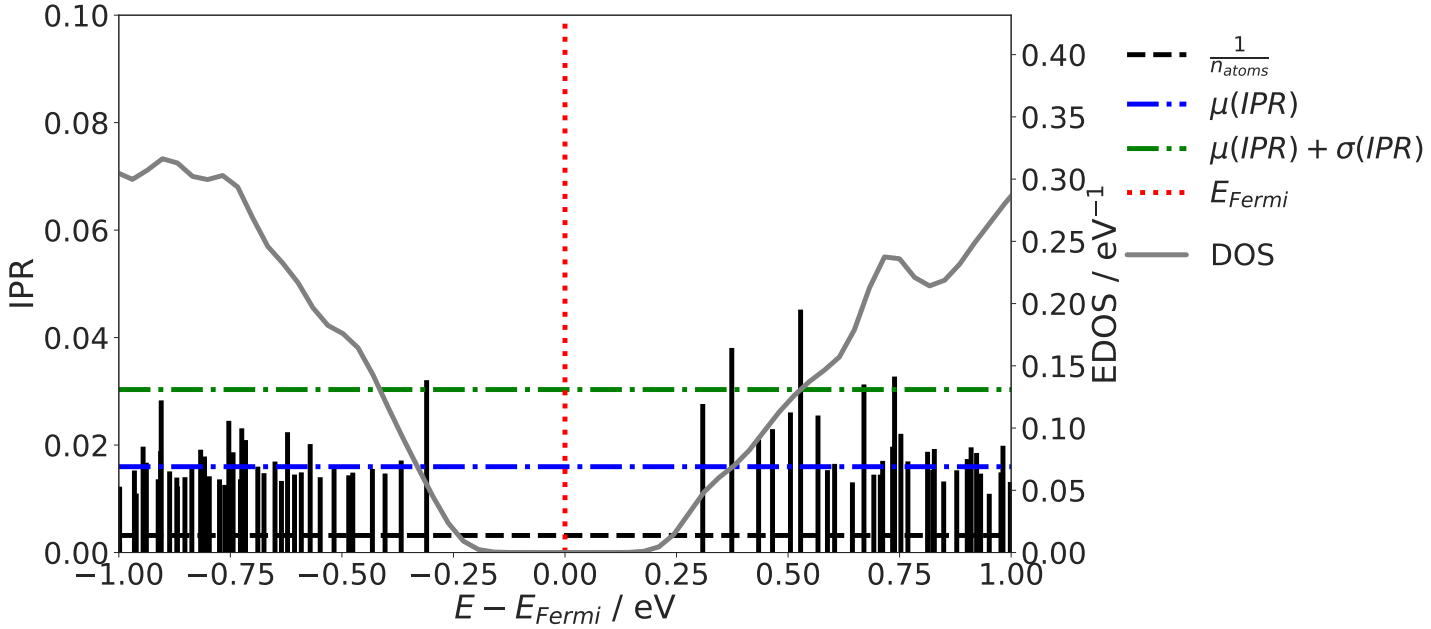


Cascade Kinetics

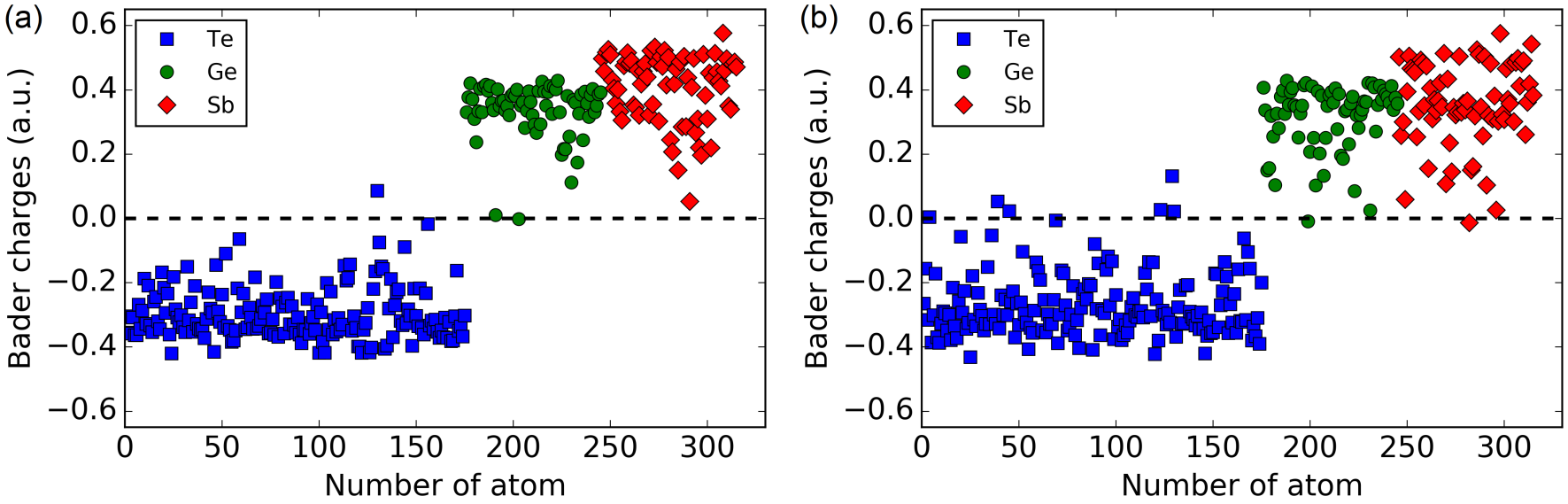


Electronic Structure



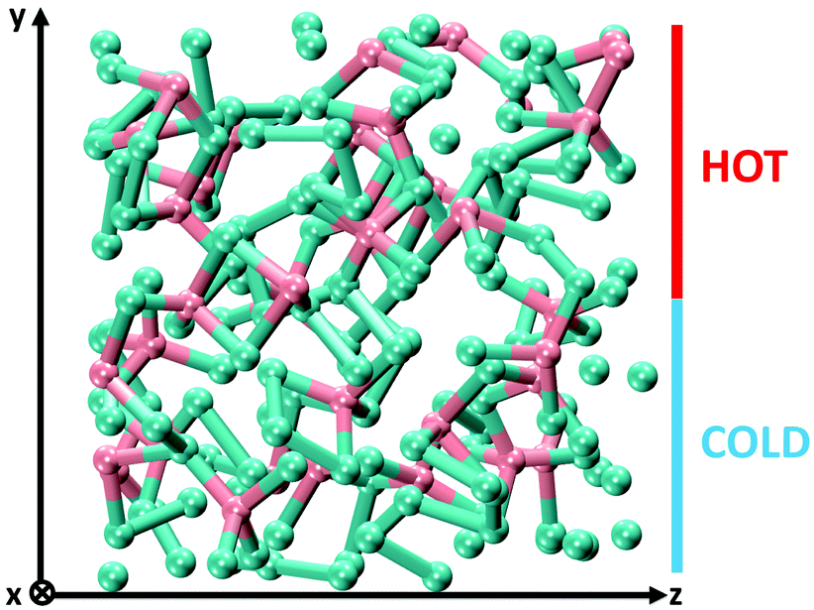


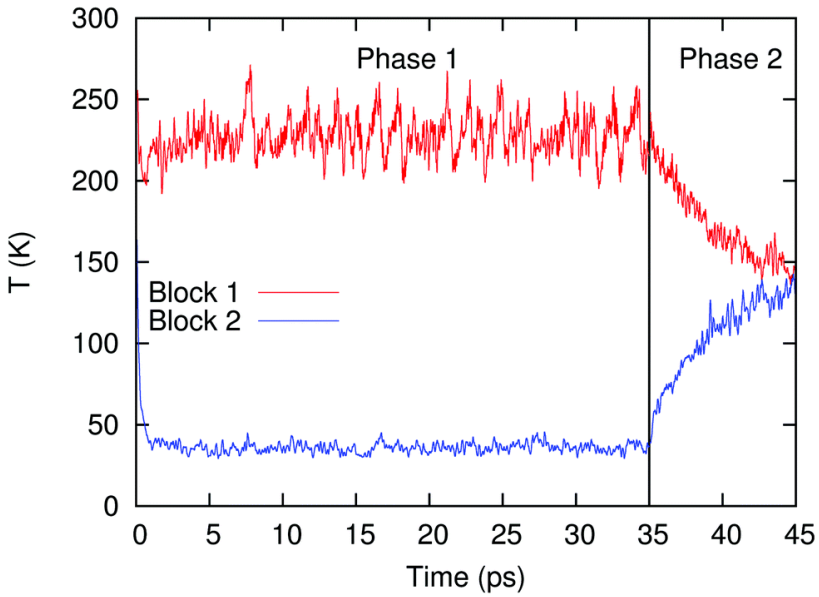
Bader Charges



THERMAL CONDUCTIVITY

Approach to equilibrium

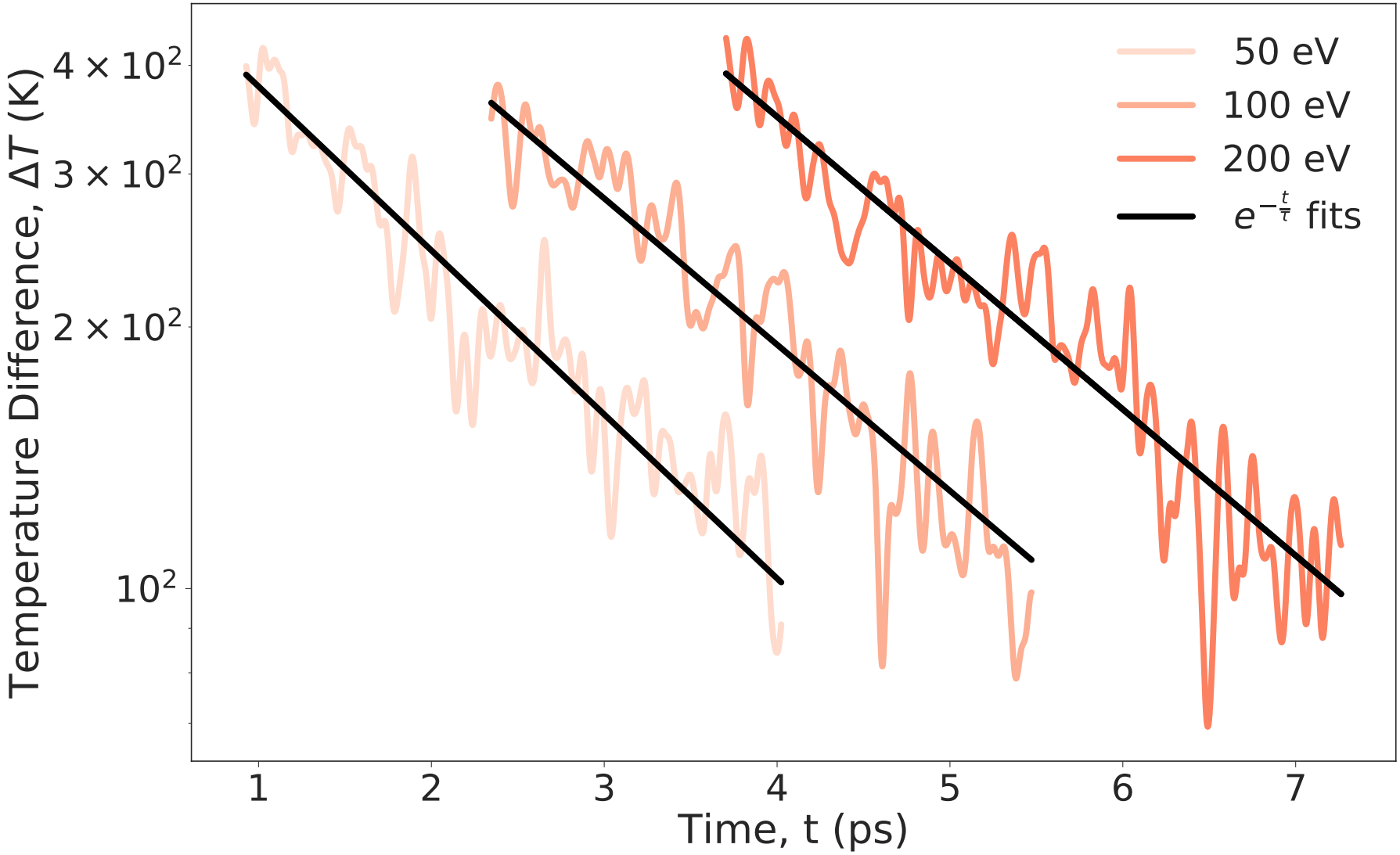




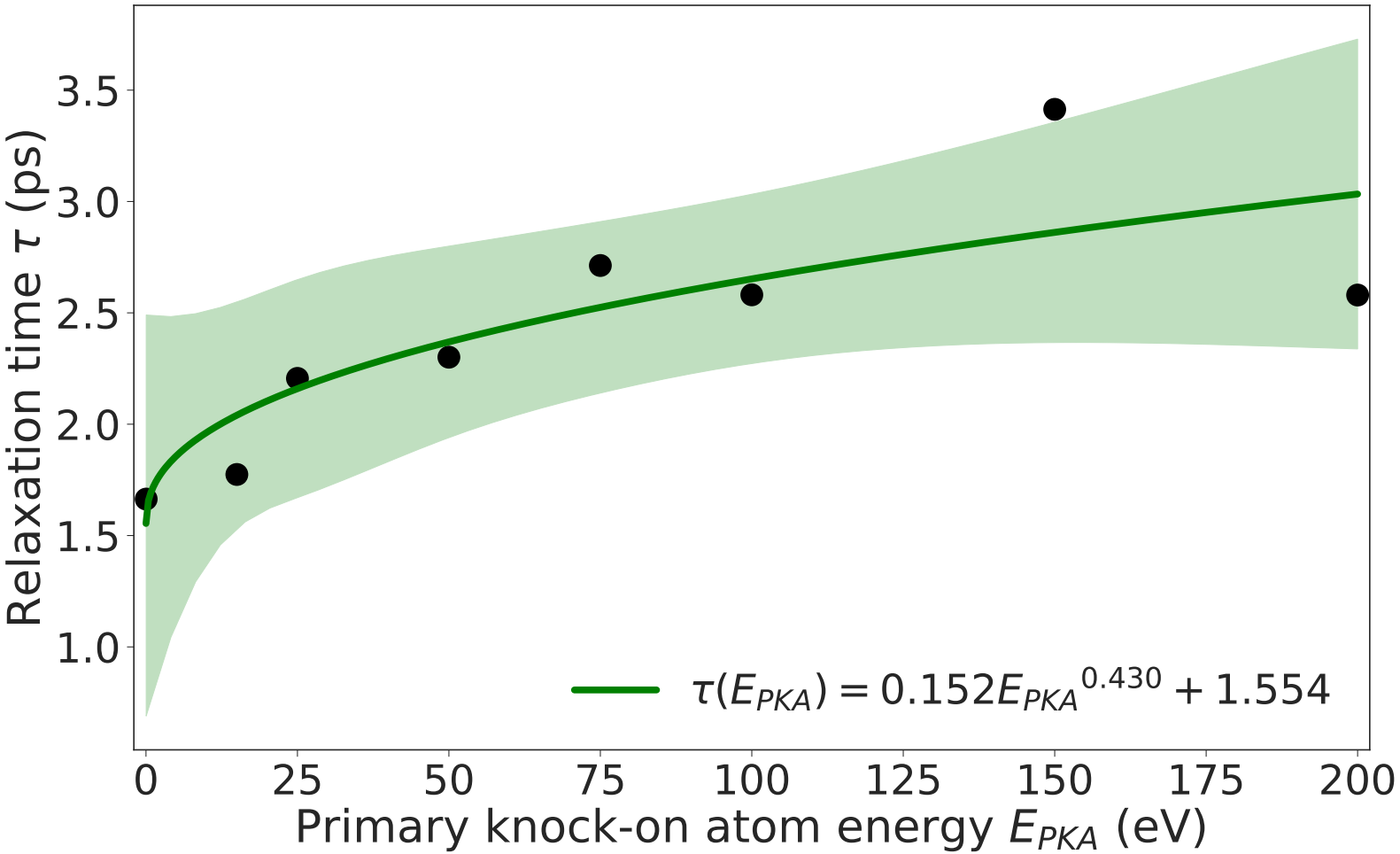
Recent work on the thermal conductivity of $GeTe_4$[6] showed it is possible to estimate the thermal conductivity using approach-to-equilibrium molecular dynamics to within an order of magnitude of experiment. (0.013 compared to $0.1\,\mathrm{W\,m^{-1}\,K^{-1}}$ experimentally)

[6] Assil Bouzid et al. "Thermal conductivity of glassy $GeTe_4$ by first-principles molecular dynamics". In: Phys. Chem. Chem. Phys. 19.15 (2017), pp. 9729–9732. doi: 10.1039/C7CP01063J. url: http://xlink.rsc.org/?DOI=C7CP01063J.

Thermal Transients



Relaxation Times

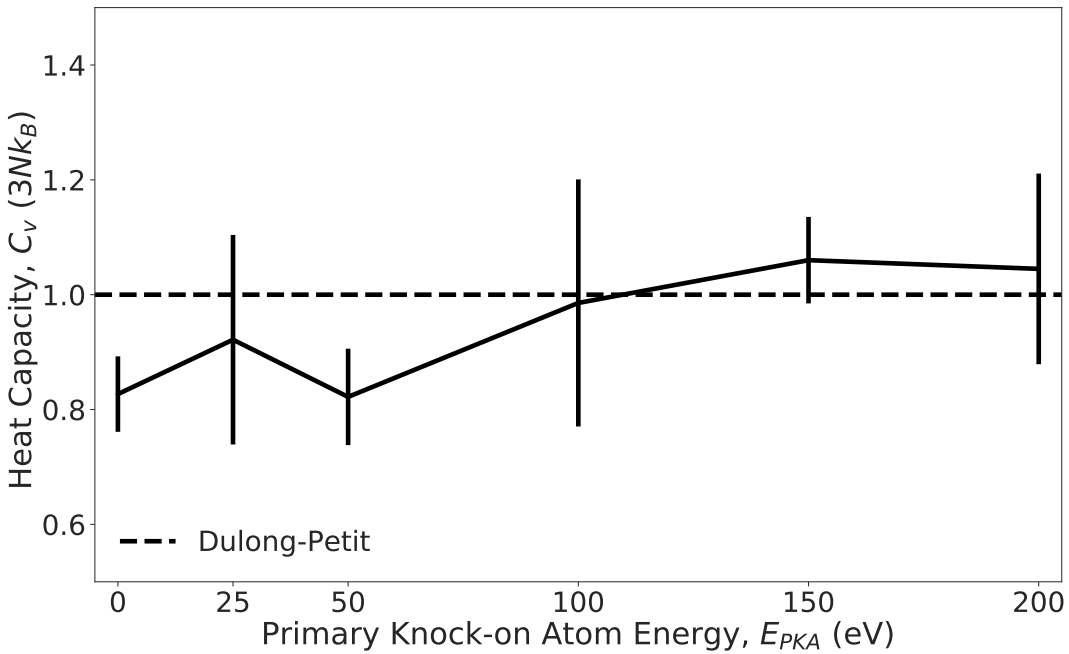


Heat Capacity

Estimated from NVT energy fluctuations $\delta E = E - \langle E \rangle$.

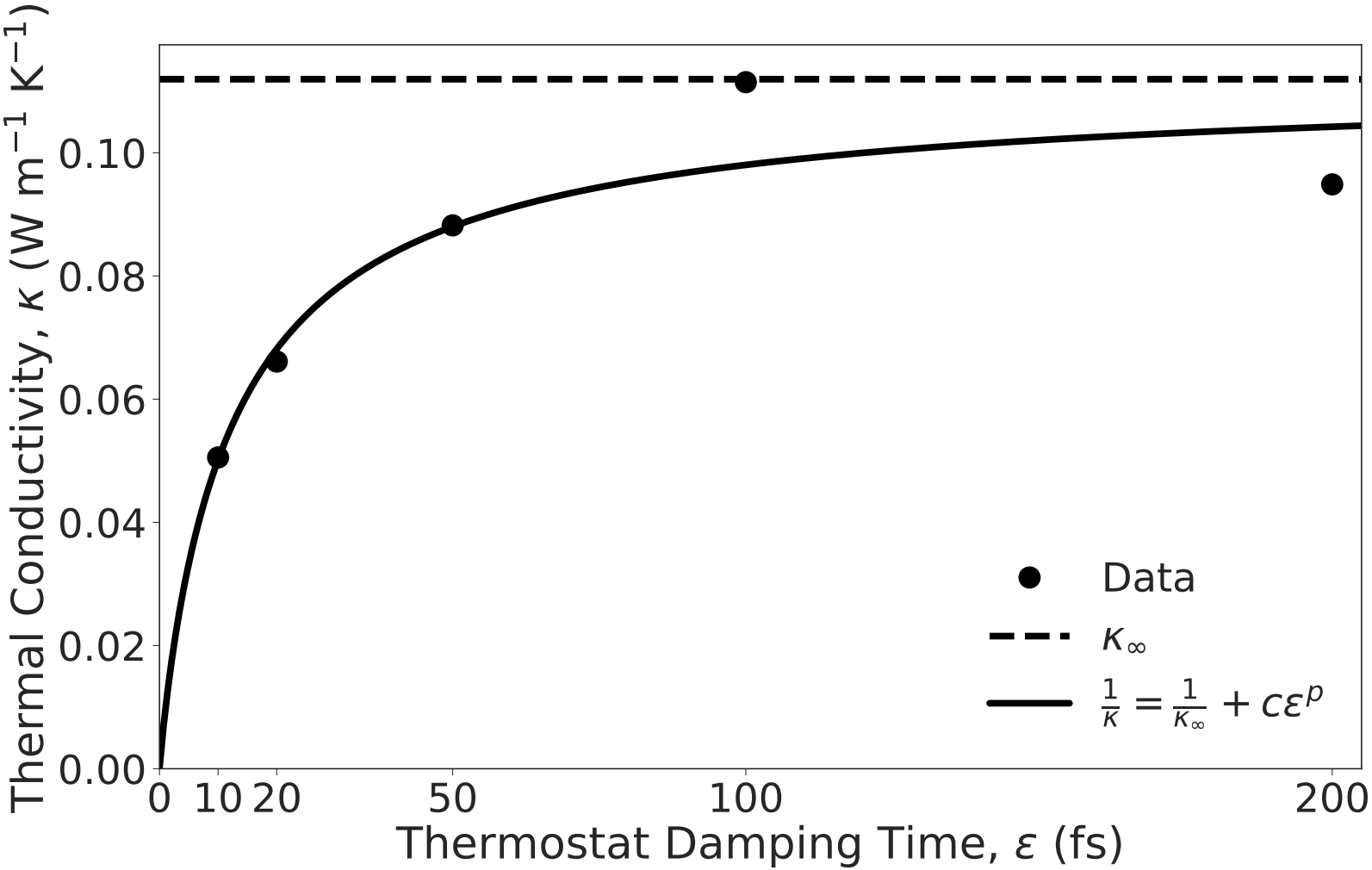
$$C_v = \frac{\langle \delta E \rangle^2}{k_B T^2}$$

Optimal coloured-noise total-energy sampling allowed for a good estimation of C_v from shorter trajectories (10 ps, 10000 steps).[7]



[7] Michele Ceriotti, Giovanni Bussi, and Michele Parrinello. "Colored-noise thermostats àla Carte". In: Journal of Chemical Theory and Computation 6.4 (Apr. 2010), pp. 1170–1180. doi: 10.1021/ct900563s. arXiv: 1204.0822v1.

Thermostat Effects



Experimental values for $Ge_2Sb_2Te_5$ are between $0.19-0.3\,\mathrm{W\,K^{-1}\,m^{-1}}$

E_{PKA} (eV)	C_v ($3Nk_B$)	κ (W/mK)	κ_∞ (W/mK)
-	0.827 ± 0.066	0.111 ± 0.010	0.130 ± 0.011
25	0.922 ± 0.182	0.094 ± 0.019	0.106 ± 0.022
50	0.822 ± 0.084	0.080 ± 0.008	0.089 ± 0.009
100	0.986 ± 0.215	0.086 ± 0.019	0.096 ± 0.021
150	1.060 ± 0.075	0.070 ± 0.005	0.076 ± 0.006
200	1.045 ± 0.166	0.091 ± 0.015	0.102 ± 0.017

CHEMICAL ORDER

The quasi-binary order parameter of Cargill and Spaepen has been calculated,[8] with the formula below:

$$\eta^0_{AB} = \frac{\frac{n_{AB} n}{x_B n_A n_B} - 1}{\eta^{max}_{AB}}$$

$$\eta^{max}_{AB} = \begin{cases} \frac{x_B n_B}{x_A n_A} & x_B n_B \leq x_A n_A \\ \frac{x_A n_A}{x_B n_B} & x_B n_B > x_A n_A \end{cases}$$

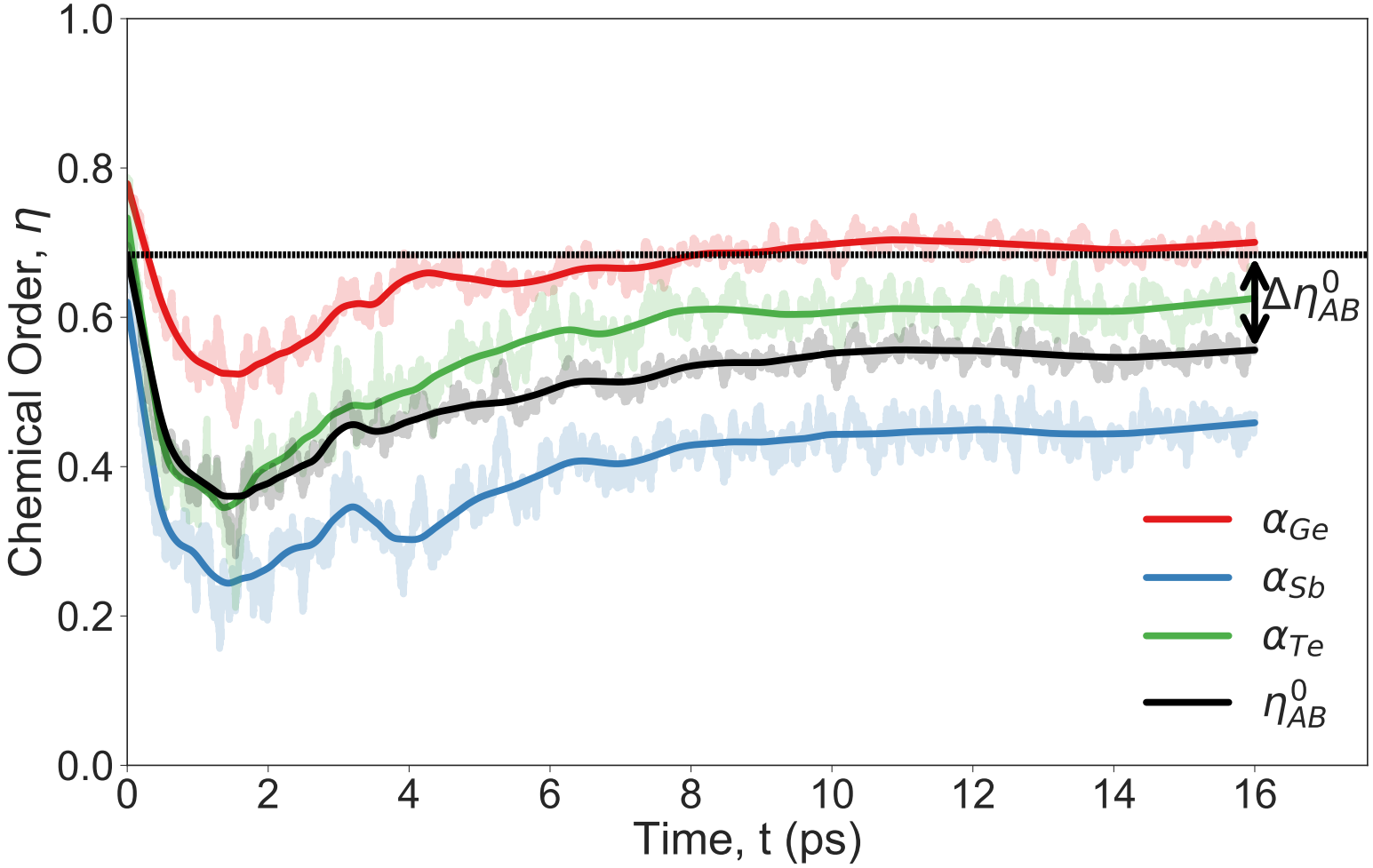
[8] G.S. Cargill and F. Spaepen. "Description of chemical ordering in amorphous alloys". In: Journal of Non-Crystalline Solids 43.1 (Jan. 1981), pp. 91–97. doi: 10.1016/0022-3093(81)90174-5. url: http://linkinghub.elsevier.com/retrieve/pii/0022309381901745.

The quasibinary classification groups Ge and Sb ions together as type "A" and leaves Te as type "B".[9] A related order parameter, denoted by α_x (where x=Ge, Sb, Te) can be obtained for each species.

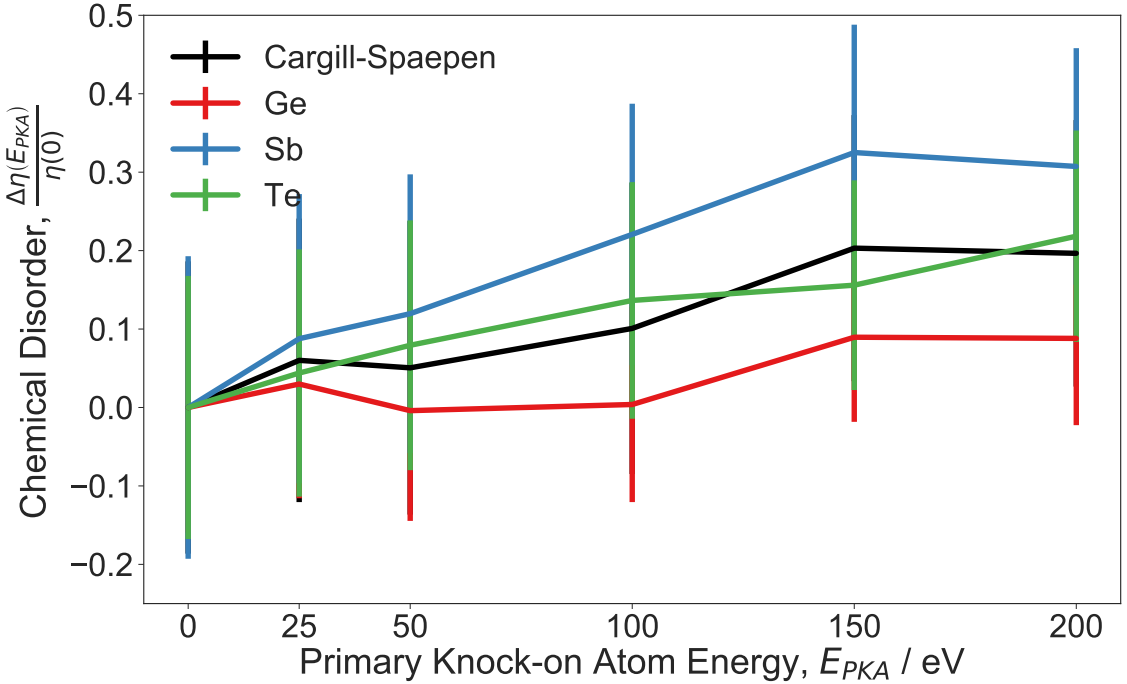
$$\alpha_x = \begin{cases} \dfrac{1 - \dfrac{n_{xB}}{x_A x_B (n_A + n_B)}}{1 - \dfrac{n_x}{x_A x_B (n_A + n_B)}} & x = \mathrm{Ge, Sb} \\[2ex] \dfrac{1 - \dfrac{n_{xA}}{x_A x_B (n_A + n_B)}}{1 - \dfrac{n_x}{x_A x_B (n_A + n_B)}} & x = \mathrm{Te} \end{cases}$$

[9] J. Kalikka, J. Akola, and R. O. Jones. "Crystallization processes in the phase change material $Ge_2Sb_2Te_5$: Unbiased density functional/molecular dynamics simulations". In: Physical Review B 94.13 (Oct. 2016), p. 134105. doi: 10.1103/PhysRevB.94.134105.

Time-Evolution



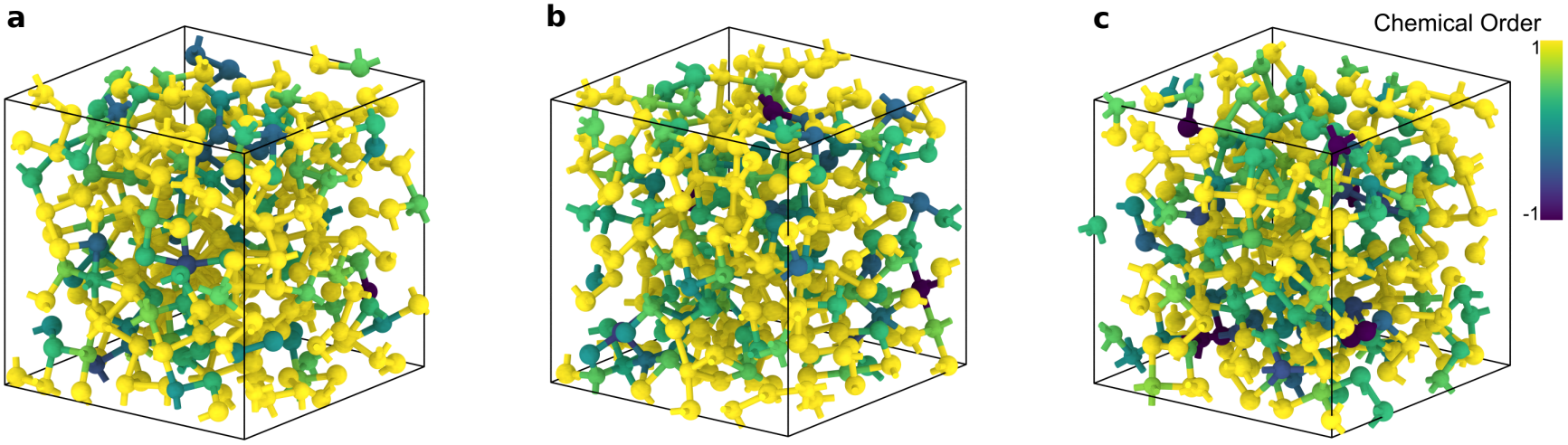
PKA Energy dependance



Despite the modest increase in disorder, there is otherwise an almost perfect recovery of the structure and electronic structure of the material.[10]

[10] Konstantinos Konstantinou et al. "Origin of radiation tolerance in amorphous $Ge_2Sb_2Te_5$ phase-change random-access memory material". In: Proceedings of the National Academy of Sciences 115.21 (May 2018), pp. 5353–5358. issn: 0027-8424. doi: 10.1073/pnas.1800638115.

Local Picture



Local chemical order from -1 to 1 in amorphous $Ge_2Sb_2Te_5$ models corresponding to (a) pristine amorphous phase; (b) 100 eV, and (c) 200 eV trajectories.

Future Work

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- Link the chemical disorder and low thermal conductivity to the vibrational density of states (Allen-Feldman theory).[11]
- Discuss the energy landscape of the thermal spike using atomic descriptors.[12]
- Use a recently developed a GAP model for Ge−Sb−Te to reduce the error-bars and evaluate the finite-size effects.[13]

[11] Gabriele C. Sosso et al. "Understanding the thermal properties of amorphous solids using machine-learning-based interatomic potentials". In: Molecular Simulation 44.11 (July 2018), pp. 866–880. doi: 10.1080/08927022.2018.1447107.

[12] Juraj Mavračić et al. "Similarity between Amorphous and Crystalline Phases: The Case of TiO_2". In: Journal of Physical Chemistry Letters 9.11 (June 2018), pp. 2985–2990. issn: 19487185. doi: 10.1021/acs.jpclett.8b01067.

[13] Felix C. Mocanu et al. "Modeling the Phase-Change Memory Material, $Ge_2Sb_2Te_5$, with a Machine-Learned Interatomic Potential". In: Journal of Physical Chemistry B 122.38 (Sept. 2018), pp. 8998–9006. issn: 1520-6106. doi: 10.1021/acs.jpcb.8b06476.

Acknowledgements

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Dr. Noam Bernstein (Naval Research Laboratory)
Prof. Gábor Csányi (Engineering Laboratory, University of Cambridge)

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Thank you for your attention!

Questions?