

Lithium Diffusion in Graphene System through Molecular Dynamics

Leon Gonzalez¹, Dr. Jose L. Mendoza-Cortes^{1, 2}

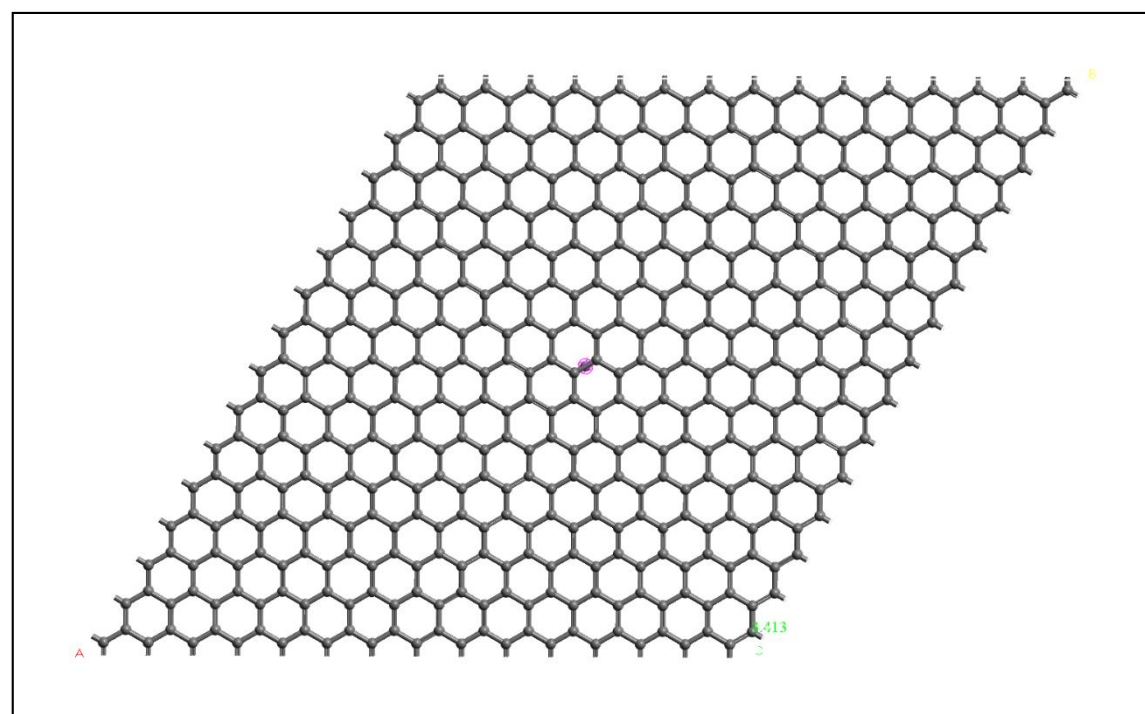
¹Department of Chemical & Biomedical Engineering, FAMU-FSU College of Engineering, Florida State University, Tallahassee FL, 32304, USA

²Scientific Computing Department, Materials Science and Engineering, High Performance Materials Institute, Condensed Matter Science, National High Magnetic Field Laboratory.



INTRODUCTION

Current state-of-the-art lithium-ion battery technologies utilize graphitic carbon as their primary means of ion storage in the negative electrode. While these systems possess high theoretical reversible capacities, their charge and discharge rates have proven to be rather poor. Structural electrode surface damage is typically a direct result of prolonged exposure to these low transport rates. If higher rates of ion diffusion are possible, determining and understanding how we may achieve them will unquestionably lead to longer battery lifespans.



Further study of lithium's behavior in graphite, or similarly, graphene systems can potentially help us understand how we may improve current standards for ion storage in energy devices. One such method of analyzing the transport properties of lithium in a graphitic environment is through the use of molecular dynamics. This presentation briefly outlines how the transport self-diffusion coefficient may be derived through usage of force field molecular dynamics.

In order to simplify the system, two uniform, defect-free graphene layers are arranged parallel to each other with varying amounts of lithium ions present in the middle. By solving Newton's second law (Eq. 1) at discrete time steps, the energy of the system may be found and subsequently, the velocity and displacement of each particle in question.

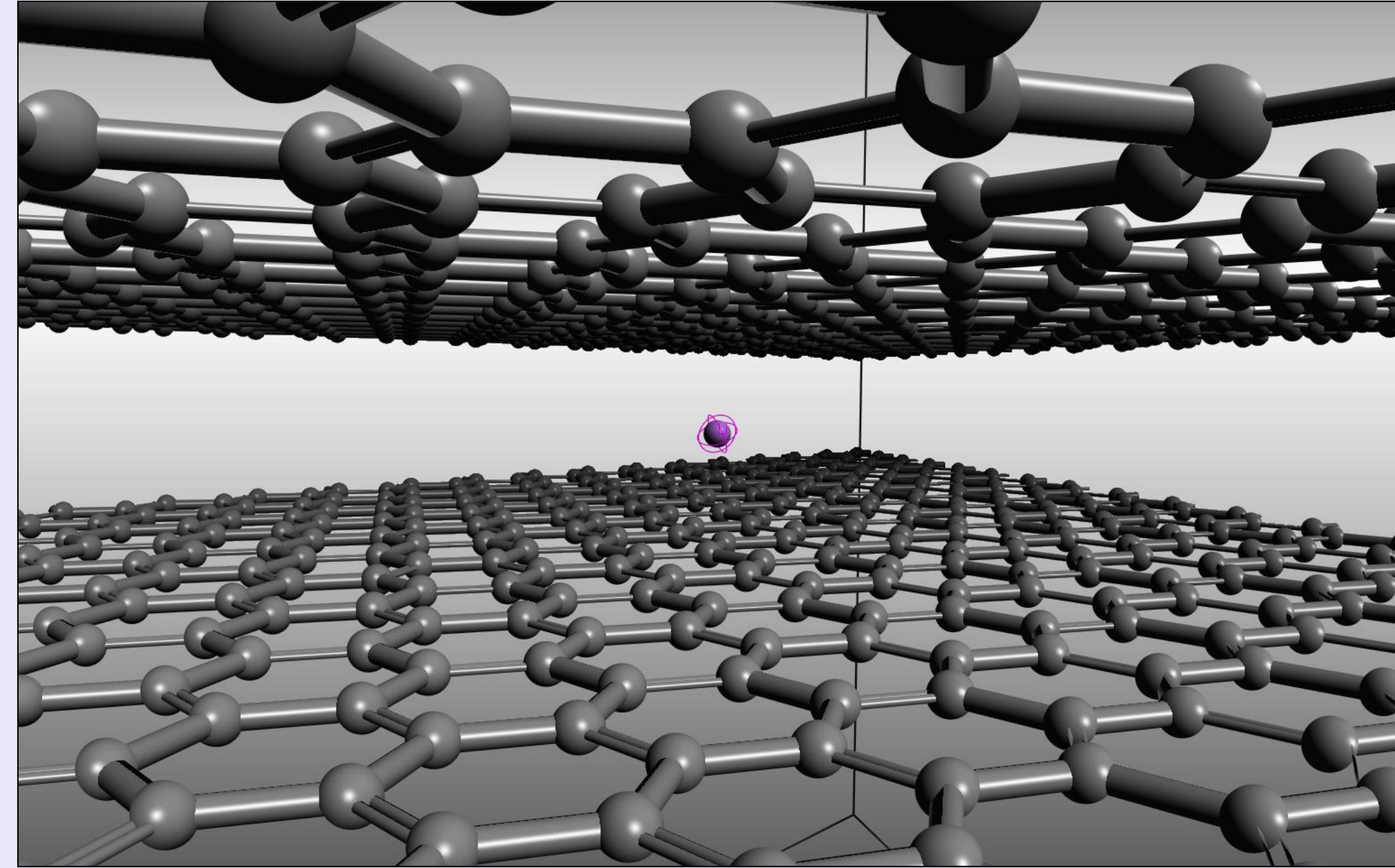
With known velocities, the Green-Kubo relation (Eq. 2) for transport parameters may be used in order to extract a diffusion coefficient.

GOALS

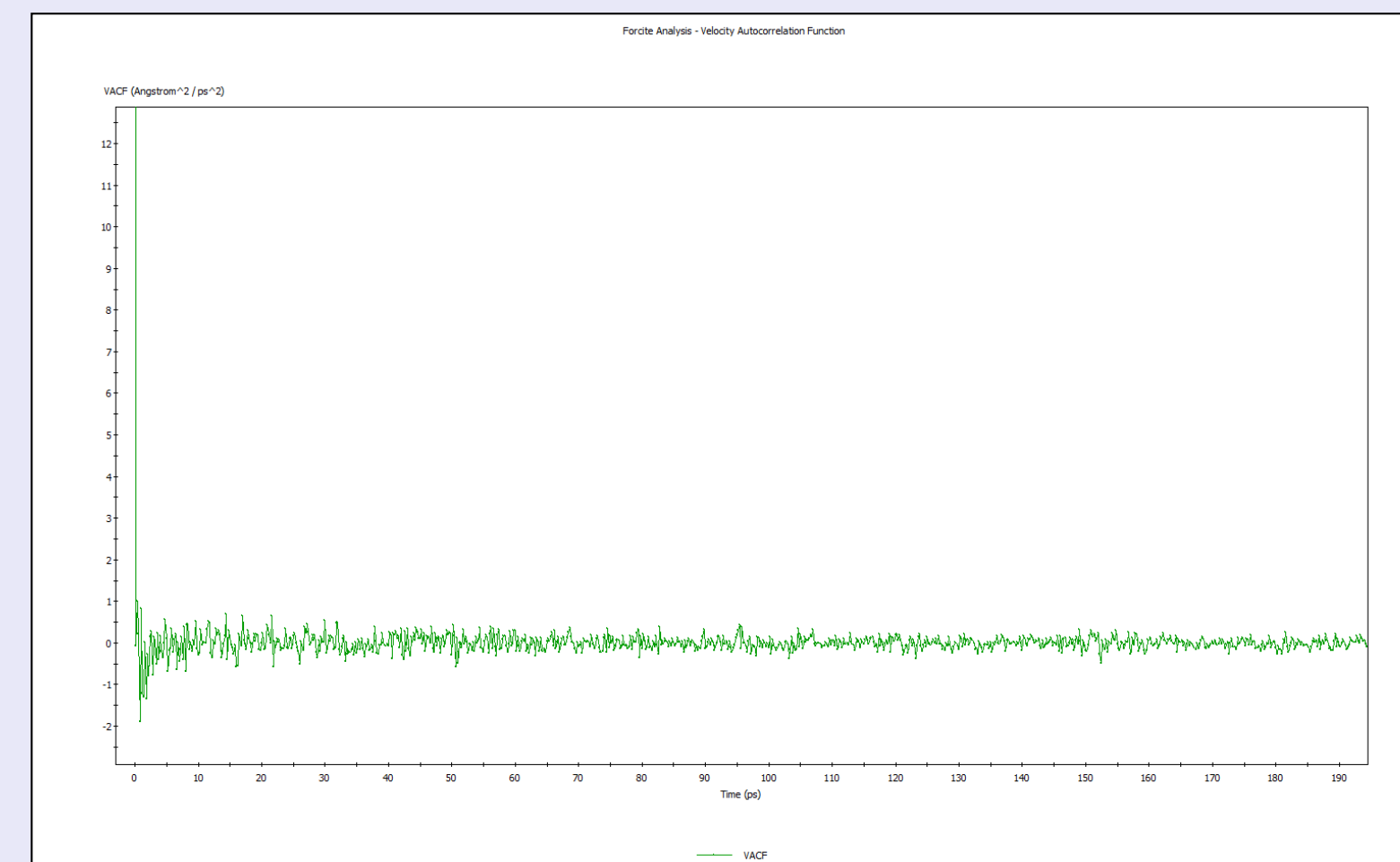
- Calculate self-diffusion coefficients for lithium ions in graphene system.
- Determine diffusion coefficients of lithium in different system configurations.
- Automate process of diffusion coefficient analysis in similar systems.

RESULTS

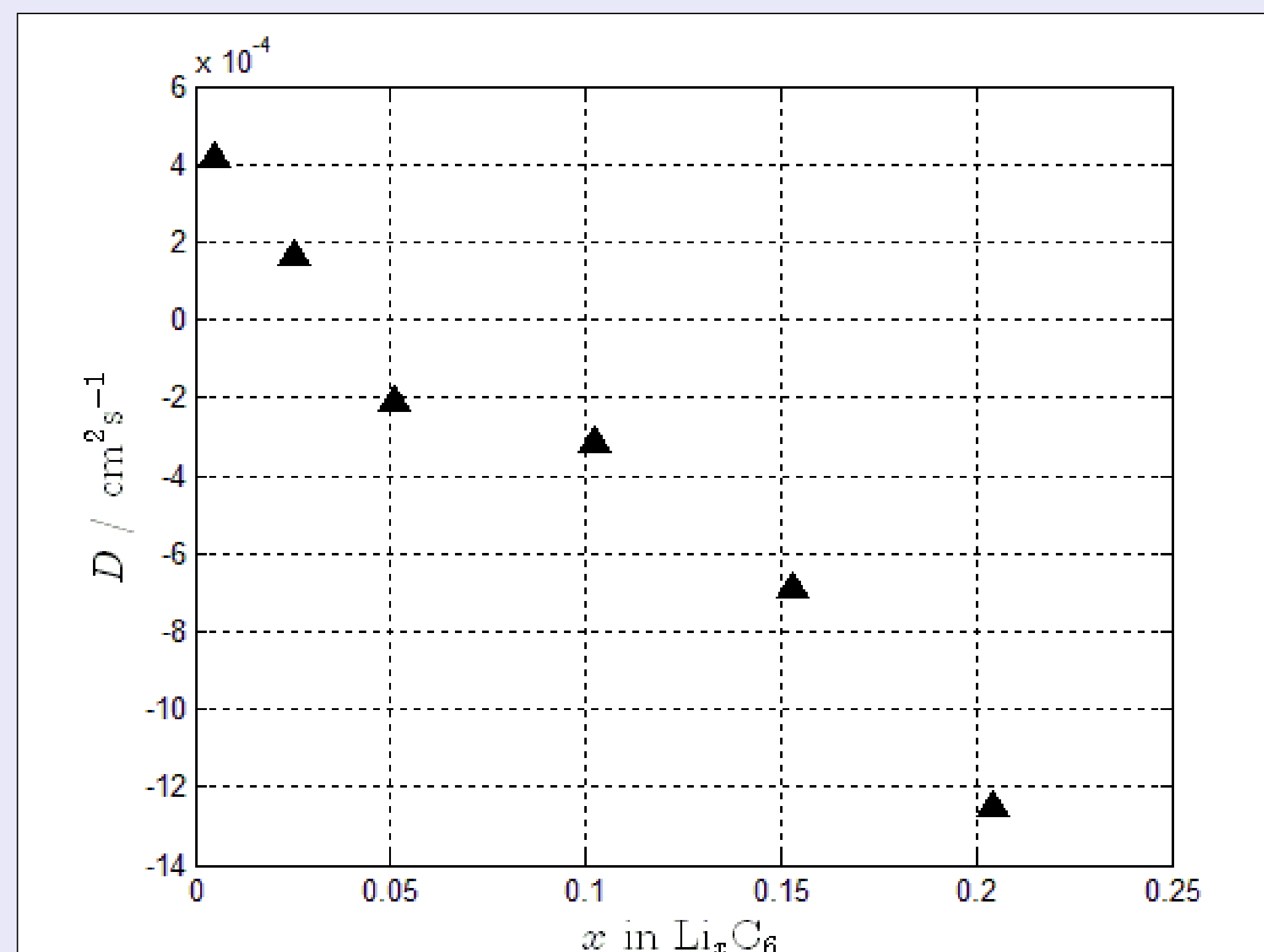
Velocity autocorrelation function



Velocity autocorrelation function



Self diffusion coefficient



Li:C ₆	0.0051	0.0255	0.051	0.102	0.153	0.204
D (cm ² s ⁻¹)	4.19E-04	1.63E-04	-2.08E-04	-3.18E-04	-6.92E-04	-1.25E-03

CONCLUSIONS

While results found from calculations produced unexpected results, both the order of magnitude as well as the general trend observed as lithium ion concentrations were increased proved to be relatively agreeable with those found in literature [1]. As lithium concentrations are increased in the system, ease of diffusion is seen to decrease as the diffusion coefficients become increasingly smaller. This is expected since having more ions present in a system means that unbound energies between particles more frequently restrict the number of directions in which the ions are free to move in.

The diffusion coefficients shown as negative numbers are most likely a result of analysis on a short time domain. Increasing the time over which the simulation is allowed to run might produce more accurate and physical results. Furthermore, seeing as the robust universal force field (UFF) parameters were used in the simulation, a certain degree of error was expected considering that more refined force field parameters do exist for such a system.

$$(1) -\frac{\partial V}{\partial r} = m \frac{\partial^2 r}{\partial t^2} \quad (2) \gamma = \int_0^{\infty} \langle \dot{A}(t) \dot{A}(0) \rangle dt$$

FUTURE WORK

- Calculate self-diffusion coefficients using Einstein's mean square displacement relation:
 $\langle r^2 \rangle = \lim_{t \rightarrow \infty} 6Dt$
- Utilize more system-specific force field parameters as well as expand simulation to millisecond time domain.
- Investigate different stages of graphene (number of stacked sheets between lithium-occupied layers).
- Investigate application of this type of analysis to molecular separations processes.

ACKNOWLEDGEMENTS

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REFERENCES

- [1] Persson, Kristin, et al. "Lithium diffusion in graphitic carbon." *The journal of physical chemistry letters* 1.8 (2010): 1176-1180.
- [2] Green, Melville S. "Markoff Random Processes and the Statistical Mechanics of Time-Dependent Phenomena. II. Irreversible Processes in Fluids." *The Journal of Chemical Physics* 22.3 (1954): 398-413.