A Molecular Dynamics Study on Properties of Poly Dimethyl Siloxane with Silica Nanoparticles for Polymer Nanocomposites: Part I, Modeling and Preliminary Simulations

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Abstract

Abstract: Polymer Nanocomposites (PNCs) have exhibited unique and tunable properties. Particularly, a Poly Dimethyl Siloxane (PDMS) matrix embedded with Silica nanoparticles (NPs) have been shown to produce large charge absement upon uniform electric field and thermal loading conditions. These properties along with several others make PNCs a prime contender for advanced soft robotic touch sensors, specialty dielectrics, signal attenuators, transducers, and more. To better understand these effects and how to manipulate them, a Molecular Dynamics (MD) study of the PDMS-Silica PNC is proposed. This study involves the use of Newtonian physics and Force Field based atomic and molecular interactions to assess the behavior of these PNCs. To perform a simulation, silica NPs are modeled, functionalized, and then packed into a simulation box containing molecules made from predetermined chain lengths of PDMS monomers using various python [1] scripts and open source softwares. The simulation box is then loaded into LAMMPS [2], an open-source MD software, where conditions such as, temperature, pressure, and forces, can be defined. Results consist of atomic trajectory files containing the initial, intermediate, and final positions of the atoms in the system. These trajectory files along with their respective energy, temperature, and pressure curves are to be compared with previous results to verify their accuracy. Future work will include the study of the effects of uniform and non-uniform electric fields on the atomic trajectories of PNC systems by varying parameters such as nanoparticle size and shape. Applications of this research include fine-tuning of properties and improved design of PNCs for use in soft robotic applications in biomedical, construction, military, and environmental industries.

Introduction

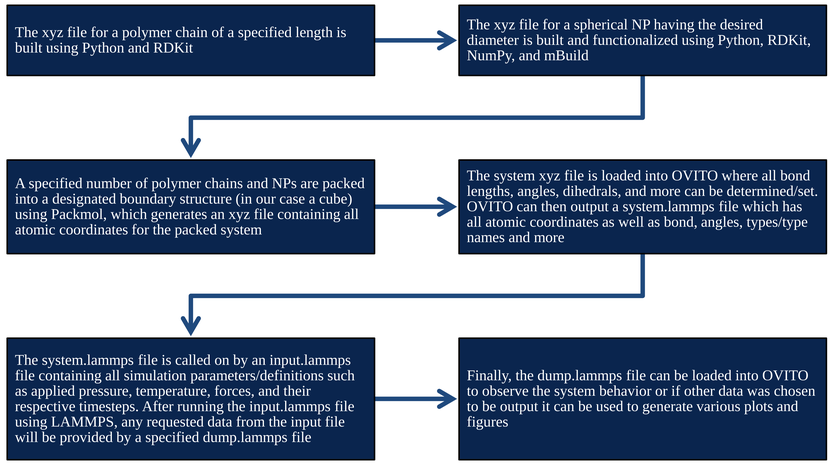
PNCs have varying properties based on variables such as the polymer matrix and NP composition, NP size, shape, functionalization and distribution. Understanding how each of these variables affects material characteristics like charge absement and transition temperatures at the atomic scale will aid in the creation of a tool for computationally developing special materials based on a list of required properties. In other words, how can a user input how they want their PNC to behave into a program and have it tell them its composition and how to manufacture it? Such a program requires being able to start from a list of suitor materials and intelligently manipulate the aforementioned variables to arrive at the optimal PNC solution.

For this intelligent manipulation to happen, the program must have a well of information on how each single variable can affect the overall material. To generate this information, three scales of experimentation/simulation are used, these are subatomic/atomic, atomic/molecular, and physical materials. In this research, we focus on the atomic/molecular scale. At this scale, computational tools for MD such as LAMMPS can be used to answer questions as to how the previously mentioned variables can affect the overall material by outputting data in the form of curves and/or tables which describe the PNCs behavior over time when faced with varying temperatures, pressures and forces.

Currently, we are performing work towards the affirmation of results for the change in glass transition temperature with alteration in NP size [3]. This work will assist in the setup of PNC matrix models and the creation of a baseline for efficiently and effectively setting up and running MD simulations for PNCs. In short, the primary goal of this research is to develop means of creating PNC simulation models and to perform basic preliminary simulations of said models in LAMMPS.

Methods

For Part I of this research, we are focusing most strictly on replicating previous models from MD papers, specifically *A simulation study on the effect of nanoparticle size on the glass transition temperature of polymer nanocomposites* by Raja Azhar Ashraaf Khan and Mengbo Luo [3]. We start by taking a polymer monomer of interest, such as PDMS, and building a polymer chain of a specified length (**Figure 2**). We used n=64 to follow reference [3]. We then used a Python script with an RDKit [4] import to build the 64-monomer polymer chain. This script uses a monomer SMILES and a force tolerance along with some other inputs to generate an .xyz file for the polymer chain at the lowest possible energy state within the provided force tolerance. Next, we built the NPs using another Python script, RDKit, NumPy [5], and mBuild [6] (**Figure 3**). This script takes a .cif file for the NP material under investigation, in this case Silicon Dioxide, as well as the desired NP diameter and generates an .xyz file for the NP. To start, we use a NP diameter of 1nm [3]. We then functionalize the NP by adding Hydrogen atoms to the surface of the NP (**Figure 4**). Next, we used Packmol [7] to define and create the system shown in **Figure 5** [3]. As seen in **Figure 1**, we used a 130nm*130nm*130nm cubic bounding box containing 44 PDMS polymer chains and 88 NPs [3]. Packmol produces the final .xyz file for the entire system as seen in **Figure 6**. This system, however, does not have any bond definitions, so we used OVITO [8] and the bond distances and energies for Class 2 bonds from **Table 1** [9] to assign and create the bonds, bond types, and type names. We then used the export function in OVITO to generate a .lammps file containing all information from the .xyz file as well as all atom bond interactions and bond types. With the system ready to be used in a simulation, we wrote a simple LAMMPS script which observed the system at ambient pressure (1Bar) and room temperature (293°K) for 1μs at a 1fs timestep size with a periodic boundary. For the initial simulations, we only had LAMMPS output dump.lammps files with atomic positions, velocities, and trajectories rather than more quantitative data like system energy or temperature. Finally, we loaded the dump.lammps file into OVITO to observe how the system behaved.



Flowchart 1: Summary of the PNC modelling process.

```
# minimum interatomic distance
tolerance 2.0

# output file name and type
output PDMS_SiO2_Cube.xyz
filetype xyz

# structure shape and composition definitions
structure pdms_n=64.xyz
   number 44
   inside cube 0. 0. 0. 130.
end structure

structure opt_np.xyz
   number 88
   inside cube 0. 0. 0. 130.
end structure
```

Figure 1: SiO2 NP with a 1nm diameter (Tan = Silicon, Red = Oxygen).

$$U^{\mathrm{BOND}}(r_{ij}) = \sum_{n=2}^{4} k_{\alpha\beta}^{\mathrm{BOND}}(n)(r_{ij} - r_{\alpha\beta}^{0})^{n}$$

bonds	$k^{\mathrm{BOND}}(2)$ (kcal/mol/Å^2)	$k^{\mathrm{BOND}}(3)$ (kcal/mol/Å^3)	$k^{\mathrm{BOND}}(4)$ (kcal/mol/Å^4)	$r_{\alpha\beta}{}^0$ (Å)	$r_{\alpha\beta}{}^0$ (Å) (constrained)
Si−O^b	350	−517	674	1.651	1.65
Si−C^b	190	−279	308	1.878	1.88
C−H^c	328			1.092	1.09

Table 1: Khan, R. A. A., Qi, H. K., Huang, J. H., & Luo, M. B. (2021). Parameters for the Nonbonded and Bonded PDMS Potential. https://pubs.acs.org/doi/10.1021/jp047434r

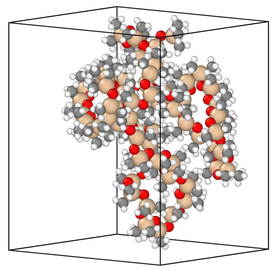


Figure 2: 64 monomer long PDMS polymer chain (White = Hydrogens, Gray = Carbon, Tan = Silicon, Red = Oxigen) [8].

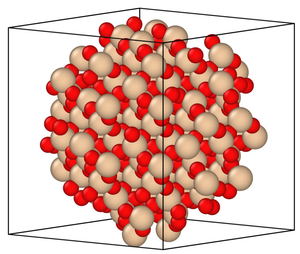


Figure 3: SiO2 NP with a 1nm diameter (Tan = Silicon, Red = Oxygen) [8].

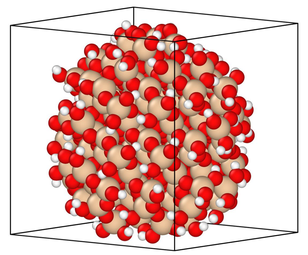


Figure 4: Functionalized SiO2 NP with a 1nm diameter (White = Hydrogen, Tan = Silicon, Red = Oxygen) [8].

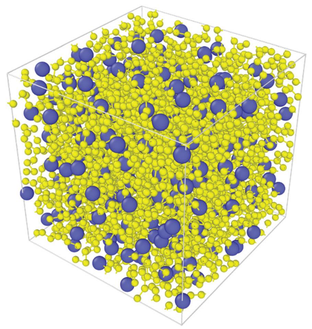


Figure 5: Khan, R. A. A., Qi, H. K., Huang, J. H., & Luo, M. B. (2021). A snapshot of the PNC system at a volume fraction of NPs f_{NP} = 40% and at temperature T = 1. Here the size of NPs is σ_{NP} = 2. Yellow and blue beads represent monomers of polymer chains and NPs, respectively. https://www.researchgate.net/publication/353561284_Simulation_study_on_the_effect_of_nanoparticle_size_on_the_glass_transition_temperature_of_polymer_nanocomposites

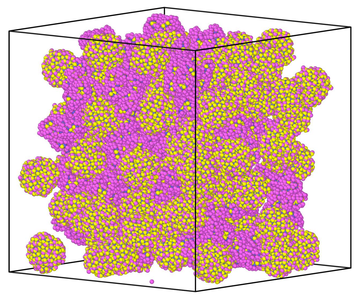


Figure 6: PNC system at timestep 0 (0ns). This is the initial system state after being packed (Pink = Hydrogen, Yellow = Oxygen, Blue = Silicon, Orange =Carbon) [8].

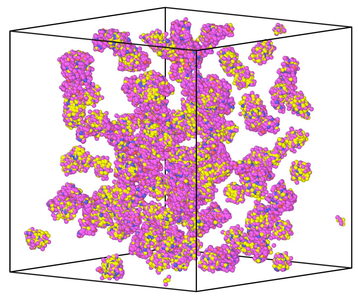


Figure 7: PNC system at timestep 50 (500ns). This is the final system state showing atom clustering and spacing (Pink = Hydrogen, Yellow = Oxygen, Blue = Silicon, Orange =Carbon) [8].

Results

We have successfully developed and used a system for creating PNC material matrix models for MD simulations. The models are similar in appearance and structure to that of the paper we are attempting to replicate [3]. We have also begun preliminary simulations of the system and have already resolved several of the issues which had presented themselves. Using commands to increase the communication distance between atoms and the atom neighbor bin-size the various errors present during the first simulations including dangerous (volatile or potential very unrealistic) builds, lost atoms, exceeded bonds per atom and more have been reduced to only a few issues present in the bond definitions. While current results have revealed that atoms seem to be clustering together without holding proper bond distances and angles (**Figure 7**), we are still confident that with continued development a functioning system for simulating new PNCs is at hand. Throughout the modelling process, we have learned and documented ways work with polymers and NPs which apply to more than just PDMS and SiO2. The most important outcome is that we have created a process to start from basic inquiries about PNC compositions/conditions and go to nearly functioning MD simulations within a few well-defined steps (**Flowchart 1**).

Conclusion

The advent of advanced composites was revolutionary for the scientific and engineering communities. As new ideas and technologies are being realized, even more innovative composites will be needed. Advanced PNCs are the next step towards making the most challenging designs real. The creation of a system to assist in the design and manufacturing of these PNCs will accelerate their usage and allow for even more novel ideas requiring special materials. We believe the first steps towards creating this systems have been made. We now must move on to simulating the models generated by our process. These models and simulations will intern provide valuable information on the behavior of novel PNCs.

Future Work

- Research and use the “Fix Shake” [2] command in LAMMPS to prevent atoms from moving in an unrealistic manor based on bonding energies.
- Develop means of creating and fixing system wide interatomic bond angles and dihedrals.
- Begin outputting numerical data from LAMMPS including system temperature per step, NP displacement per step, and more.
- Continue running simulations to replicated results from [3] in order to develop and affirm simulation techniques.
- Study the effects of uniform and non-uniform electric fields on the atomic trajectories of the PNCs by altering nanoparticle size and shape.

References

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