Coarse-Grained Molecular Dynamics Simulations to Probe the Structure and Dynamics of Polystyrene grafted Silica Nanoparticles

Charles Pennington [1] Sachin Shanbhag[1]

[1]Florida State University, Department of Scientific Computing

Abstract

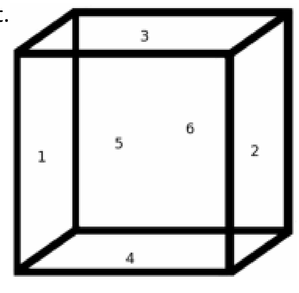
Before attempting to perform a potentially costly experiment, running a simulation to ascertain some of the possible outcomes becomes a sound investment. Our intent with this simulation is to build an assortment of structures using polystyrene grafted silica nanoparticles, and using those structures we seek an understanding of the dynamics involved. We attempt to solve this problem by using Lennard-Jones type interactions on the silica nanoparticles, and using Kremer-Grest-type bead-spring chains as a model for the polystyrene chains. Using these models in a Markov Chain Monte Carlo simulation we are able to gain information on the structures of many different combinations of polystyrene grafted silica nanoparticles. From these simulations also comes the information on the dynamics involved in these structures which can be used for reference in laboratory experiments in an attempt to pinpoint the possible resulting structure.

Experimental Setting

- Simulation Space: Cube
- Boundary Conditions: Periodic
  - Using the cube from below; if you left the cube from side 1, you would reenter the cube from side 2. This is the same for 3 to 4 and 5 to 6. The size of the cube is dependent upon the number of objects we plan to put inside of it.

Experimental Prerequisites

- Number of
  - Silica Nanoparticles
  - Strands on each Silica
  - Polystyrene Beads on each Strand
- Size of Cube found from Number of Objects in cube



Initialization

- Place Silica Nanoparticle
  - Choose a random location
  - Check for Overlap
    - Retry if Overlap
  - Repeat till all Silica in cube
- Place Polystyrene
  - Choose a non-filled strand
  - Pick a random position a set distance away from last object on the strand
  - Check for Overlap
    - Retry if Overlap
  - Repeat till all Polystyrene in cube
- With all Silica and Polystyrene in cube
  - Simulation can begin

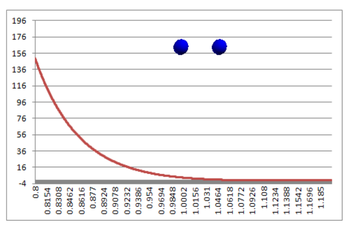
Method

Our simulation will be using a Markov Chain Monte Carlo (MCMC) method to find a shape of the system. This MCMC method takes one object at a time and moves it a little bit. It then checks to see if that movement fits a criteria. In our case, the criteria is dependent upon Potential Energy calculations obtained by using coarse-grained force-fields. If it fits that criteria then the move is accepted and recorded, otherwise the move is rejected and another move is attempted. In doing this our simulation will be able to find a natural state in which the system will at one point exist.

Force-Fields

Using Weeks-Chandler-Anderson potential for the polystyrene to polystyrene interactions, were the exclude distance is $r < 2^{(1/6)}\sigma_{pp}$
The potential energy is

$$U_{pp}(r) = 4\varepsilon_p\left[\left(\frac{\sigma_p}{r}\right)^{12} - \left(\frac{\sigma_p}{r}\right)^{6} + \frac{1}{4}\right],$$



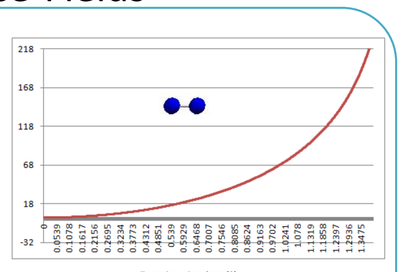
Formulas taken from [1]

Treating the bonds between particles as finitely extensible nonlinear elastic (FENE) springs, where the optimum distances are

$$r < R_0 = 1.5\sigma_{pp}$$

The potential energy is

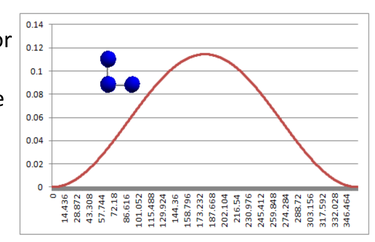
$$U_{FENE}(r) = -\frac{1}{2}k_{FENE}R_0^2\ln\left[1-\left(\frac{r}{R_0}\right)^2\right],$$



Formulas taken from [2]

The stiffness of the strands or the bond angles, provides potential energy through the formula

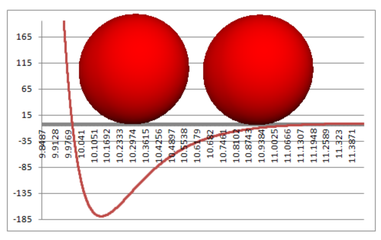
$$U_{bend}(\theta) = k_\theta(1-\cos\theta)$$



Formulas taken from [2]

Lee and Hua [3] parameterized "generalized Lennard-Jones" potentials for spherical silica nanoparticles between 0.6nm – 100nm in diameter using a multiscale simulation methodology. We get the formula

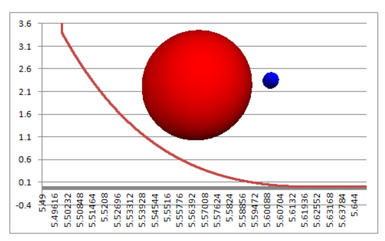
$$U_{nn}(r) = 4\varepsilon_n\left[\left(\frac{\sigma_n}{r}\right)^{2\alpha} - \left(\frac{\sigma_n}{r}\right)^{\alpha}\right]$$



Formulas taken from [3]

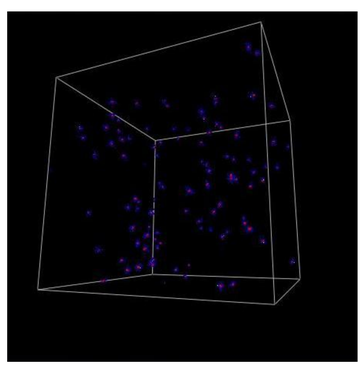
We used a shifted-Weeks-Chandler-Anderson potential for the interactions between the Silica nanoparticles and the Polystyrene. This gave us an exclusion distance of $r < r_{min} = 2^{1/6}\sigma_p + \Delta$
To use in the formula

$$U_{np}(r) = 4\varepsilon_p\left[\left(\frac{\sigma_p}{r-\Delta}\right)^{12} - \left(\frac{\sigma_p}{r-\Delta}\right)^{6} + \frac{1}{4}\right],$$

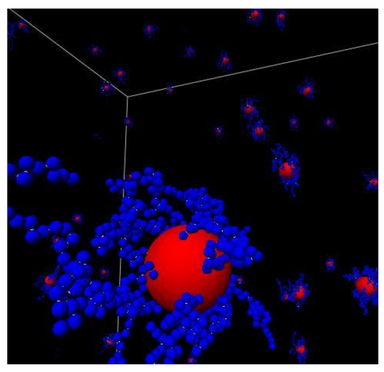


Formulas taken from [4]

Images of the Starting Positions of a System of 100 Silica Nanoparticles with 13 Strands of 40 Polystyrene



Overall View



Up-Close View of One Silica Group

Future Plans

At our current stage of development we have a working prototype created in FORTRAN, and are in the process of speeding it up using Cell Lists. Once this is complete we will find the optimum system configuration and pressure at a much faster rate. From there we will use the positions of the particles and the Molecular Dynamics Simulator LAMMPS to test the system. We will be using LAMMPS to study the dynamic properties of the system for comparison to experimental data.

References

[1] Weeks, J. D., Chandler, D. & Andersen, H. C. Role of Repulsive Forces in Determining the Equilibrium Structure of Simple Liquids. The Journal of Chemical Physics 54, 5237–5247 (1971).

[2] Auhl, R., Everaers, R., Grest, G. S., Kremer, K. & Plimpton, S. J. Equilibration of long chain polymer melts in computer simulations. *The Journal of Chemical Physics* **119**, 12718–12728 (2003).

[3] Lee, C. K. & Hua, C. C. Nanoparticle interaction potentials constructed by multiscale computation. The Journal of Chemical Physics 132, 224904–224904–9 (2010).

[4] Chremos, A., Panagiotopoulos, A. Z., Yu, H.-Y. & Koch, D. L. Structure of solvent-free grafted nanoparticles: molecular dynamics and density-functional theory. J Chem Phys 135, 114901 (2011).