

Diffusion in Solutions of Lennard-Jones Polymers and Solvent

Abstract

Polymer solutions are presently used in many important industrial applications, including coatings, commodity materials, microelectronics, pharmaceuticals and medical devices, in addition to a plethora of research applications. In these applications the transport properties of the polymer and solvent are of great importance. The goal of this work was to use constant-NVE molecular dynamics simulation to investigate the diffusion properties of a simplified polymer-solvent system composed of linear Lennard-Jones polymer molecules and solvent molecules over a range of molecular sizes and polymer concentrations. The results suggest that in this system polymer diffusivity decreases linearly with increasing polymer concentration for a range of polymer lengths. Additionally, polymer diffusivity obeys a power law relationship with polymer length however the strength of the power law relationship increases with increasing polymer concentration. Solvent diffusivity appears to decrease linearly with increasing polymer concentration and displays a weak power law relationship with polymer length, although this power law relationship becomes more apparent at high polymer concentrations.

Movie Caption

This video shows a molecular dynamics simulation of a solution of Lennard-Jones polymers and solvent particles. The polymer length is 16 particles and the polymer fraction is 0.4. The translucent blue particles represent the polymer, the solid red particles identify a single tracer polymer chain, and the translucent grey particles are solvent.

Introduction

Liquid solutions of polymers and solvent are widely used in industry and research in diverse applications ranging from coatings to biotechnology and pharmaceuticals. An understanding of the transport and diffusion properties of polymer solutions is essential to many of these applications. For example, knowledge of diffusion coefficients is important in the coatings industry because solvent diffusivity influences how quickly coatings dry or cure, whereas the rheological properties of the coating are linked to the diffusivity of the polymer. Moreover, the diffusion properties of each component in solution are not the same as that of the pure component. The interactions between polymer and solvent are diverse and complex, including but not limited to: hydrophobic/hydrophilic interactions, hydrogen bonding, ionic charges and dipole moments, as well as more general enthalpic and entropic contributions to the free energy of mixing. Many of these interactions vary with solvent and polymer chemical identity, and in addition there may be effects from isomers and co-polymerization. In short, generating a physically accurate interaction model for a given polymer-solvent system is a grand undertaking and therefore it may be beneficial to simulate these systems using a very simple model consisting of Lennard-Jones polymers and Lennard-Jones monomers/solvent.

Methodology

As previously stated, a constant-NVE molecular dynamics (MD) simulation was used to explore the dynamics of solutions of Lennard-Jones (LJ) polymer chains and solvent. The interaction potential U_{ij} between two unbonded Lennard-Jones particles i and j (any two polymer particles not directly bonded to each other, one polymer particle and one solvent particle, or two solvent particles) was the standard 12-6 Lennard-Jones potential:

$$U_{ij} = 4(r_{ij}^{-12} - r_{ij}^{-6}) \quad F_{ij} = \frac{\partial}{\partial r_{ij}} U_{ij}$$

Here, r_{ij} is the interparticle distance, the equilibrium Lennard-Jones particle spacing is 1.0, and the potential has been cut and shifted with a cutoff radius r_c of 2.5. The force between these two particles is given by the derivative of the potential with respect to the interparticle distance. A simple Hookean spring model was used to describe the potential and force between any two polymer particles directly bonded to each other (i.e. adjacent particles within the same polymer chain):

$$U_{ij} = \frac{k}{2}(r_{ij} - r_o)^2 \quad F_{ij} = \frac{\partial}{\partial r_{ij}} U_{ij}$$

Here, $k=3000$ and $r_o=1.0$ which are standard literature values.

Other simulation parameters included: $N=240$ particles, reduced density $\rho=0.8$, time step $\Delta t=0.001$, and temperature $T=1.0$. The polymer lengths investigated were $M=2, 4, 8, 16, 24$ particles and the polymer concentrations investigated were $f_{poly}=0.2, 0.4, 0.6, 0.8, 1.0$ with the balance of the system composed of solvent, i.e. unbonded LJ particles, yielding a total of 25 unique sets of simulation parameters. Each unique set was run 9 times with a different random starting configuration to improve measurement statistics. A minimum image distance convention was used to enforce periodic boundary conditions when computing interparticle distances. The number of polymer particles was defined by $N_{poly} = N * f_{poly}$. The first N_{poly} particles were designated as polymer particles with the remainder designated as solvent.

The simulation procedure began with assigning each of the N particles a lattice site sequentially within the simulation box, but perturbing the position by a small random amount in the $x, y,$ and z directions to facilitate the initial energy minimization. The positions of the particles were then randomly shuffled to mix the polymer and solvent components, and then a conjugate gradient energy minimization was performed with fractional energy tolerances for the line search and conjugate gradient of 10^{-8} and 10^{-10} , respectively. The particles were assigned random initial velocities which were then rescaled such that the total kinetic energy matched that expected from a system at the target temperature T . Initial accelerations were computed from the forces on the particles, assuming unit particle masses, such that $F = A$. The Velocity Verlet integrator was used to perform the MD steps. The system was equilibrated to the target temperature using a Berendsen thermostat with $\tau = 200 * dt$ and velocities were rescaled at each equilibration MD step according to the following:

$$v_{scale} = \sqrt{1 + \left(\frac{dt}{\tau}\right) \left(\frac{T_{target}}{T_{instantaneous}} - 1\right)}$$

25,000 equilibration steps were performed with the Berendsen thermostat. A final velocity rescaling was performed such that the instantaneous total energy after rescaling was set equal to the average total energy during the last 10,000 steps of equilibration. Following this velocity rescaling, the system was allowed to equilibrate for another 5,000 with the thermostat off, i.e. under constant-NVE conditions. At the end of this second equilibration the positions of all particles was logged and used to compute mean square displacements (MSD's) during production. 100,000 MD production steps were performed with the same Velocity Verlet integrator under constant-NVE conditions and the positions of all particles was logged every 100 steps. The potential and kinetic energy of the system was logged at the same interval to verify that the total energy and system temperature remained constant.

The MSD for each particle at each log point was computed using the following:

$$\vec{D} = \vec{r} - \vec{r}_0$$

$$MSD = \vec{D} \cdot \vec{D}$$

where \vec{D} , \vec{r} , and \vec{r}_0 are the displacement, current position, and initial position of the particle in question and $\vec{D} \cdot \vec{D}$ is the vector dot product. Separate MSD averages were computed for the polymer and solvent particle populations at each log point. The diffusion coefficient was found using the Einstein relation:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |\vec{r} - \vec{r}_0|^2 \rangle$$

The MSD vs. time data was plotted and a line was fit using the least-squares method. Representative MSD vs. time data showing the 9 trials for both polymer and solvent populations from one particular set of conditions are shown in **Figure 1**.

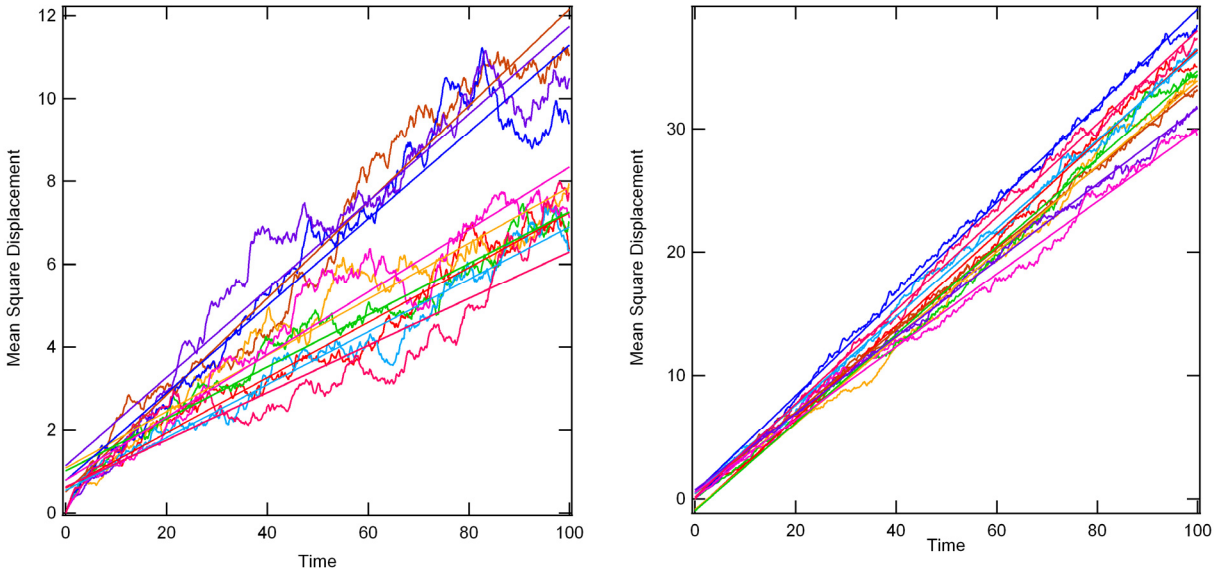


Figure 1: Representative MSD vs. time plots for the polymer (left) and solvent (right) populations, including least-squares line fits. Data shown for 9 trials of the same parameter set.

The diffusion coefficients from each of the 9 trials at each parameter set were averaged to produce mean and standard deviation values, which are shown in **Figure 2** for both polymer and solvent populations as a function of both polymer length and polymer concentration. These results indicate that, for this system, polymer diffusivity scales linearly with polymer concentration over the range of polymer lengths investigated ($D \sim c * f_{poly}$). Additionally, polymer diffusivity obeys a power law relationship ($D \sim M^v$) with polymer length in solution as well as for pure liquid polymer. These trend coefficients are tabulated below. Solvent diffusivity also appears to obey a power law relationship with polymer length at high polymer concentrations, although at low concentrations this relationship is very weak. The current data suggest that solvent diffusivity appears to scale linearly with polymer concentration.

f_{poly}	v	M	c
0.2	-0.90	2	-0.0025
0.4	-1.59	4	-0.0068
0.6	-1.15	8	-0.0056
0.8	-1.14	16	-0.0034
1.0	-1.59	24	-0.0052

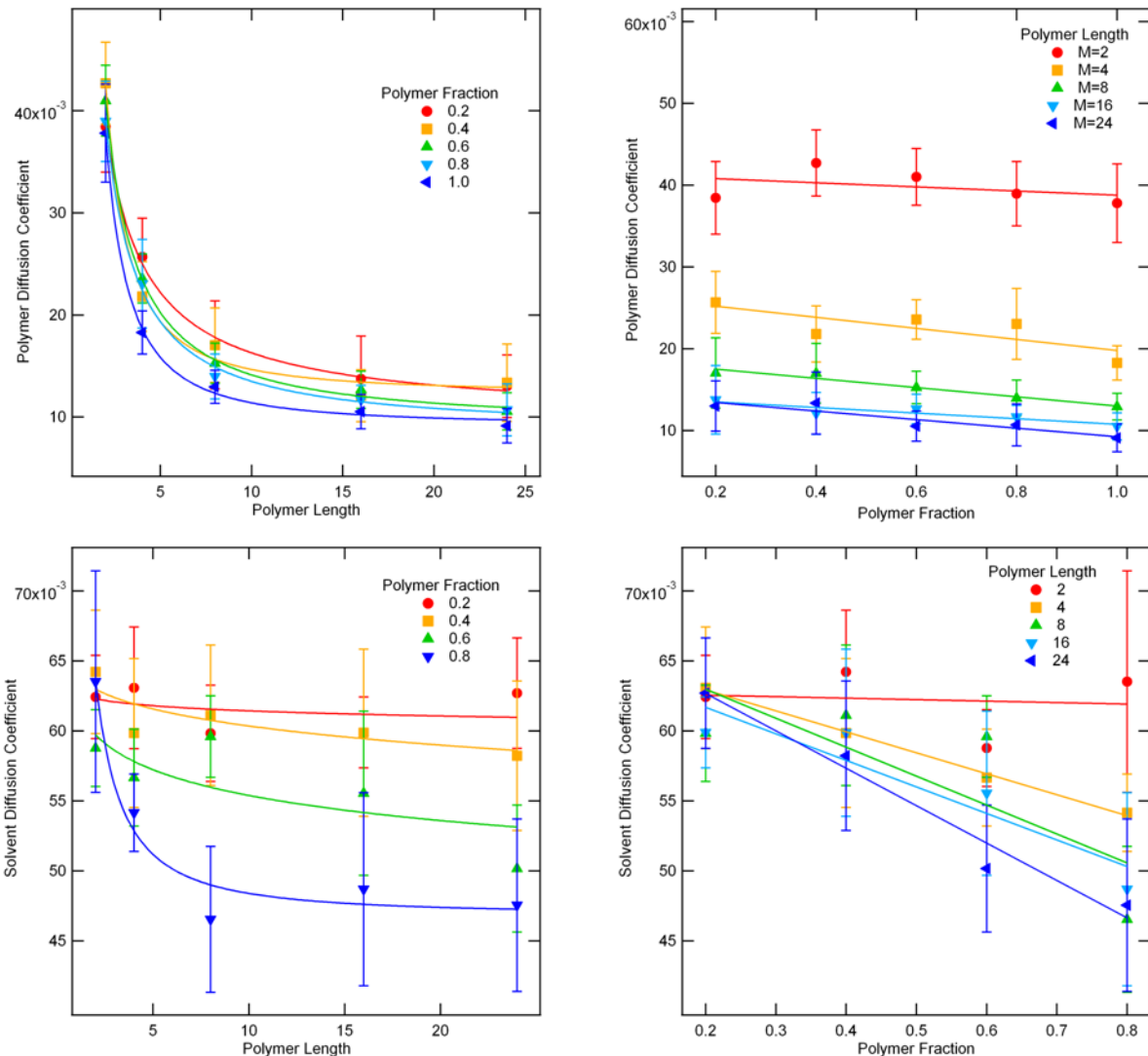


Figure 2: Diffusivity plots for both polymer and solvent populations as a function of both polymer length and polymer concentration. Error bars represent ± 1 standard deviation.

There are several ways in which this simulation could be improved. Beyond the obvious improvements (larger system size, longer simulations, more trials), it would be useful to use a Nosé-Hoover thermostat during the production period in order to introduce a stochastic element to the process as constant-NVE MD is completely deterministic. The statistics could also be improved by using multiple time origins within each trial to improve the statistics of the MSD measurements, however in order to ensure that the measurements are statistically independent the correlation time should be measured and time origins should be spaced several correlation times apart. A wider range of polymer lengths and concentrations could be simulated to fill in gaps in the data and perhaps reinforce trends which may not appear very strong with the current data. It would also be interesting to examine the behavior of the system at very dilute polymer concentrations, i.e. around the overlap concentration, or perhaps simulating a single polymer chain surrounded by only solvent. Multiple temperatures and reduced densities could also be investigated.