

Study of molecular dynamics of a solution of polymer using LAMMPS

Table of Contents

Abstract

Abbreviations

1 INTRODUCTION

1.1 Background/Rationale

1.2 Statement of the Problems

1.3 Objectives of the Research

1.4 Scope

2 LITERATURE REVIEW

2.1 Information

2.2 Summary

3 METHODOLOGY

3.1 Concepts

4 RESULTS AND DISCUSSION

4.1 Purpose

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

REFERENCES

ACKNOWLEDGEMENTS

APPENDICES

Study of molecular dynamics of a solution of polymer using LAMMPS

TEJASV JOTWANI

Mechanical third year undergraduate, Indian Institute of Technology Bhubaneswar, Address-A-205, Royal Castle Krishna Nagar, Lucknow 226023

Prof. ALOKE KUMAR

Department of Mechanical Engineering Indian Institute of Science, Bangalore, India, Karnataka, Bangalore - 560012

Abstract

The behavior of polymers in their solution has been the subject of a considerable number of theoretical and experimental investigations for so many years. We try to investigate Brownian dynamics of a viscoelastic solution of polymer containing 25-50 monomer units. We try to probe into the behavior of the system when another particle is introduced into the polymeric melt. By finding the mean square displacement of the foreign particle, we figure out the diffusivity of the particle and therefore the viscoelasticity of the melt. The results are calculated with the help of molecular dynamic simulation software LAMMPS and then are visualized on Ovito. In that we try to create a virtual environment of polymeric melt. In our investigation we are considering FENE (Finitely Extensible Nonlinear Elastic Model) type model to create a better resemblance to the polymer chain, (which is considered to be finite). The insights obtained from our simulation can aid one in understanding is essential for predicting particle transport and dispersion during composite and hydrogel processing and in oil production and exploration. Many researches are going on in the field of non-Newtonian liquids as they can assist to multiple causes related to behavior of polymers in different conditions

Keywords or phrases: Polymer chemistry, Brownian Dynamics, Non-Newtonian liquids, viscoelasticity, FENE model.

Abbreviations

Abbreviations/ Symbols

LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
FENE	Finitely Extensible Nonlinear Elastic
SRD	Stochastic Rotation Dynamics
CT	Coupling Theory
MPCD	Multiparticle Collision Dynamics
MD	Molecular Dynamics
GSE/SE	Generalized Stokes Equation/ Stokes equation
σ	Diameter of a particle
ξ	Correlation Length
MSD	Mean Squared Displacement

1 INTRODUCTION

1.1 Background/Rationale

We try to investigate the Brownian dynamics of a Nano particle/Colloids suspended in a Polymer solution (Viscous liquid). Traditionally, described by the SE equation, which relates the diffusivity D to the ratio of thermal energy of the colloid to the viscous drag over the particle surface. Whereas, for complex fluids, polymer solutions, the colloid dynamics are in addition affected by viscoelastic contributions, which can be incorporated into the GSE expression through a complex viscosity $\tilde{\eta}$. Simulations are an ideal method to probe short-time dynamics and have been extensively used to investigate nanoparticle dynamics in polymer melts. CT proposes that the nanoparticle dynamics directly couple to the segmental relaxations of the surrounding polymer chains. Under this assumption, nanoparticles are locally trapped by the polymer chains, leading to sub diffusive motion on short time scales. As

the polymer chains relax over the particle surface, the nanoparticle can break out of its local cage and begin to freely diffuse through the solution. Extending these methods to investigate dynamics in polymer solutions, however, remains challenging due to the computationally demanding nature of accurately modelling, solvent mediated interactions. These interactions are strongly screened in melts but influence short-time dynamics in polymer solutions. Here, we simulate the dynamics of nanoparticles in semi-dilute solutions of comparably sized polymers using MPCD to account for solvent-mediated hydrodynamic interactions.

1.2 Statement of the Problems

In previous experimental work, it was found that there was excellent agreement between coupling theory and long-time particle diffusivities and for the short-time particle dynamics in the limit of small or large nanoparticles relative to the characteristic length scales of the polymer solution (i.e., $\sigma_{np} < \xi$ and $\sigma_{np} \gtrsim 10\xi$, respectively). Substantial deviations from the predicted behavior, however, were observed at short times for particles of size comparable to the correlation length. Across a broad range of polymer concentrations, the nanoparticle sub-diffusive exponents α_{np} were much larger than predicted and varied with both particle size and polymer concentration.

1.3 Objectives of the Research

1.3.1 Overall objective

We investigate the dynamics of nanoparticles in semi-dilute polymer solutions when the nanoparticles are comparably sized to the polymer coils using solvent simulation methods. The nanoparticle dynamics are sub-diffusive on short time scales before transitioning to diffusive motion on long time scales (LAMMPS).

1.4 Scope

Semi-dilute polymer solutions are non-Newtonian fluids used commonly during polymer composite processing, as sweep fluids in enhanced oil recovery methods, and to produce hydrogels. They serve as ideal models for complex heterogeneous materials because their characteristic length scales, such as the polymer radius of gyration R_g and the correlation length ξ , are well-defined and easily tuned by changing the molecular weight and concentration of the polymer.

2 LITERATURE REVIEW

2.1 Information

Movement of particles through polymer solutions has traditionally been portrayed or explained using **geometric obstruction models** in which the diffusivity decreases with an increase in concentration of the polymers, due to a higher frequency of collisions between the particles and polymer chains, or using **hydrodynamic models**, in which the polymer chains increase the solution viscosity and screen hydrodynamic interactions.

The success of these models, however, is typically limited to a narrow range of particle sizes, polymer molecular weights, or polymer concentrations; furthermore, these models do not specifically address the deviations of nanoparticle dynamics from SE predictions.

Recent theoretical treatments have employed **modified model coupling theory** or self-consistent Langevin equations to relate the nanoparticle dynamics to local fluctuations in the polymer mesh. Such treatments accurately reproduce the longtime dynamics of the nanoparticles but have largely not investigated dynamics on shorter time and length scales due to the sensitivity of the theoretical calculations to the dynamic propagator of the polymer fluctuations. To model nanoparticle dynamics over a wide range of time and length scales, coupling theory proposes that the nanoparticle dynamics directly couple to the segmental relaxations of the surrounding polymer chains. Under this assumption, nanoparticles are locally trapped by the polymer chains, leading to sub diffusive motion on short time scales. As the polymer chains relax over the particle surface, the nanoparticle can break out of its local cage and begin to freely diffuse through the solution with a size-dependent diffusivity, which scales as σ_{np}/ξ , where σ_{np} is the nanoparticle diameter. In the previous experimental work it was found excellent agreement between coupling theory and long-time particle diffusivities and for the short-time particle dynamics in the limit of small or large nanoparticles relative to the characteristic length scales of the polymer solution (i.e., $\sigma_{np} < \xi$ and $\sigma_{np} \gtrsim 10\xi$, respectively). Substantial deviations from the predicted behavior, however, were observed at short times for particles of size comparable to the correlation length. Across a broad range of

polymer concentrations, the nanoparticle sub-diffusive exponents α_{np} were much larger than predicted and varied with both particle size and polymer concentration.

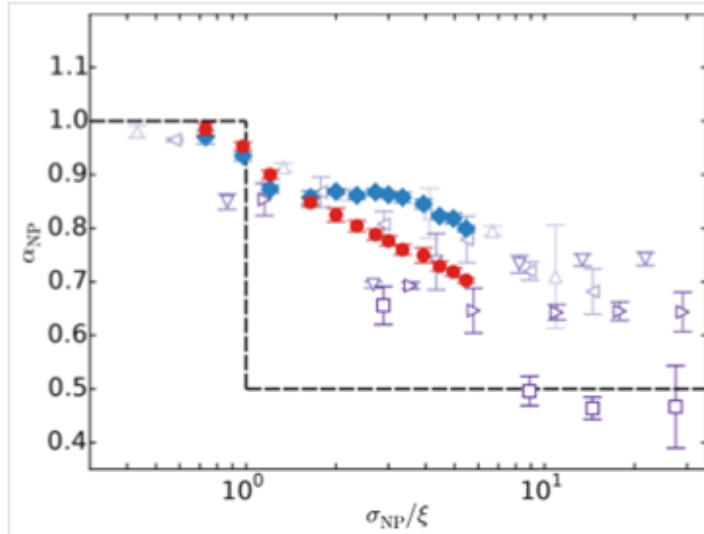


Figure 2. Nanoparticle subdiffusive exponent α_{NP} as a function of the ratio of nanoparticle diameter σ_{NP} to correlation length ξ for MPCD (red circles) and LD (blue diamonds) simulations with $\sigma_{NP}/2R_{g0} = 0.61$. Open symbols are experimental data from ref 23 for particles with $\sigma_{NP}/2R_{g0} = 0.56$ (\triangle), 0.74 (\diamond), 1.1 (∇), 1.5 (\triangleright), and 3.7 (\square). Dashed line is prediction from coupling theory in ref 22. For $c/c^* > 1$, $\xi = R_{g0}(c/c^*)^{-\nu/(3\nu-1)}$ with $\nu \approx 0.62$ (experiment) and 0.61 (simulation). For $c/c^* \leq 1$, we calculate ξ according to the mean geometric separation distance $R_{g0}(c/c^*)^{-1/3}$.

Picture credits: Coupling of Nanoparticle Dynamics to Polymer Center-of-Mass Motion in Semi-dilute Polymer Solutions

2.2 Summary

As we can infer from the above figure that shows a set of experimental and simulated values obtained in the above-mentioned paper, that the main point of discussion or the short coming is that CT is not satisfied for the range $\xi < \sigma_{np} < 10\xi$, in short time scales. And in order to address this problem, we must find out the reason behind this phenomenon. We, here, have tried to carry out our own set of simulated observations using the existing framework provided to us by the paper.

3 METHODOLOGY

3.1 Concepts

FENE MODEL-

FENE model is used to model long-chained polymers. It simplifies the polymers by connecting a sequence of beads with nonlinear springs

The models can be broadly categorized as bead-rod models such as Kramers chain and bead-spring models such as the FENE model. These models use a bead to represent an inflexible segment of monomers in the polymer chain, and use rods or springs to model the interactions between the beads. With these simplifications, the degrees of freedom in the system are greatly reduced. Brownian dynamics (BD) simulations of this class of models are used to describe the extension and refolding of a polymer chain on hydrodynamic time scales.

The FENE model incorporates a nonlinear spring into the basic dumbbell model. In its simplest form the connecting force can be found by the following equation:

$$\mathbf{F}^c = \frac{H\mathbf{Q}}{1 - Q^2/Q_0^2}$$

Where

- \mathbf{F}^c is the connector force
- \mathbf{Q} (bolded) is the connector vector between the beads
- H is the spring constant

- Q is the extension of the connector vector
- Q_0 denotes the maximum possible spring extension.

Fene potential is given as-

$$U_{\text{FENE}}(r) = \begin{cases} -\frac{1}{2} \kappa r_0^2 \ln \left[1 - \frac{r^2}{r_0^2} \right], & r \leq r_0 \\ \infty, & r > r_0 \end{cases}$$

, where r is the scalar separation distance between two bonded beads. Excluded volume interactions are modeled using the purely repulsive, shifted Weeks–Chandler–Andersen (sWCA) potential to simulate good solvent conditions.

$$U_{\text{sWCA}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma_{ij}}{r - \Delta_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r - \Delta_{ij}} \right)^6 \right] & r \leq 2^{1/6} \sigma_{ij} + \Delta_{ij} \\ + \epsilon, & \\ 0, & r > 2^{1/6} \sigma_{ij} + \Delta_{ij} \end{cases}$$

All simulations were performed in a cubic box with a $40\sigma_p$ edge length and periodic boundary conditions in all directions. We used **LAMMPS** to conduct our simulations. A value of $\epsilon = kBT$ was used for all particle interactions, where kB is Boltzmann's constant and T is temperature. The polymers were modeled using $N_m = 50$ beads and the standard Kremer–Grest parameters for the bonded interactions.

We use 5 nanoparticles in each simulation and set $\sigma_{np} = 6\sigma_p$, such that they are similar in size to the polymer coils. The simulations were visualized using LAMMPS visualization software called **OVITO**.

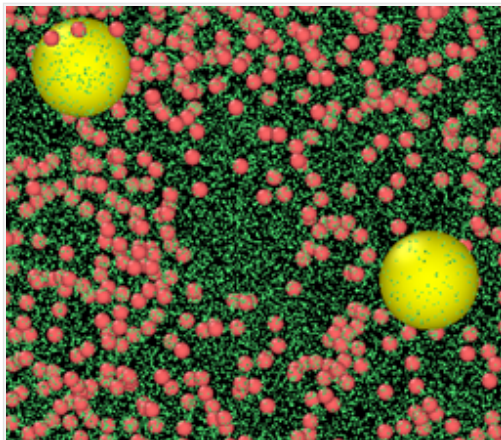


Fig: Yellow balls- nano particles, red balls- monomers, green area represents stochastic solvent

Many-body HI in the nanoparticle–polymer solutions were simulated using the **MPCD** algorithm.

In **MPCD**, meso-particles (polymers and nanoparticles) are immersed in a background solvent, which is modeled explicitly through an ensemble of point particles. These solvent particles exchange momentum with nearby solvent and meso-particles through stochastic collisions, which are designed to ensure that hydrodynamic correlations emerge over sufficiently large length scales. The MPCD simulations for our model were conducted using the existing **SRD** module in LAMMPS.

4 RESULTS AND DISCUSSION

4.1 Purpose

MSD

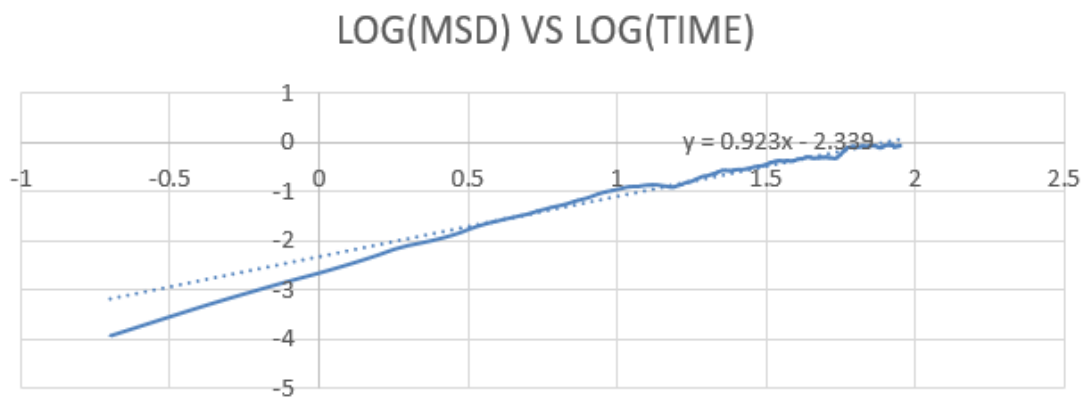
The Mean Square Displacement MSD is defined by the relation:

Where $r_i(t)$ is the position of the atom i at the time t , and the $\langle \rangle$ represent an average on the time steps and/or the particles.

$$MSD(t) = \langle r^2(t) \rangle = \langle |r_i(t) - r_i(0)|^2 \rangle$$

Then in order to find out the sub-diffusive exponent α_{NP} which is defined as $\langle \Delta r^2 \rangle \sim t^{\alpha_{NP}}$

We have plotted log graph between MSD and time and the slope will give us an idea of the sub-diffusive exponent of the nano particles.



5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

From the conducted simulations for a time step of .002 in LJ units, and plotting a log graph between MSD and time, the trend line was plotted using Excel and it was found that for the given conditions the sub-diffusive exponent was still coming out to be way higher than the predictions by the coupling theory. A similar nature has been observed in the previously conducted experiments. The discrepancy though not fulfilling has been attributed to the presence of an additional coupling mechanism between the nanoparticle dynamics and the polymer center-of-mass motion, which differs from the polymer relaxations that control the long-time diffusion. This experiment was also conducted in a polymeric melt and same behavior was observed. Hence, one can also say that, this coupling is retained even in the absence of many-body hydrodynamic interactions when the long-time dynamics of the colloids and polymers are matched.

REFERENCES

1. Coupling of Nanoparticle Dynamics to Polymer Center-of-Mass Motion in Semi-dilute Polymer Solutions, Published: February 22, 2018. Ryan Poling-Skutvik, Arash Nikoubashman, X Michael P. Howard, Jacinta C. Conrad, Jeremy C. Palmer
2. Omari, R. A.; Aneese, A. M.; Grabowski, C. A.; Mukhopadhyay, A. Diffusion of Nanoparticles in Semi-dilute and Entangled Polymer Solutions. *J. Phys. Chem. B* 2009, 113, 8449–8452.
3. Cukier, R. I. Diffusion of Brownian spheres in semi-dilute polymer solutions. *Macromolecules* 1984, 17, 252–255.
4. Phillies, G. D. J. Universal scaling equation for self-diffusion by macromolecules in solution. *Macromolecules* 1986, 19, 2367–2376.
5. Starr, F. W.; Schroder, T. B.; Glotzer, S. C. Molecular dynamics simulation of a polymer melt with a nanoscopic particle. *Macromolecules* 2002, 35, 4481–4492.
6. Malevanets, A.; Kapral, R. Mesoscopic model for solvent dynamics. *J. Chem. Phys.* 1999, 110, 8605–8613.

7. Brown, D.; Mele, P.; Marceau, S.; Alberola, N. D. A molecular dynamics study of a model nanoparticle embedded in a polymer matrix. *Macromolecules* 2003, 36, 1395–1406.
8. MPCD routines and sample input files for LAMMPS are available on GitHub: https://github.com/palmergroup/mpcd_polymer_colloid.
9. Tao, Y.-G.; Götze, I. O.; Gompper, G. Multiparticle collision dynamics modeling of viscoelastic fluids. *J. Chem. Phys.* 2008, 128, 144902.
10. MIT- Introduction to modelling and simulation
11. FENE- <http://web.cecs.pdx.edu/~derek/Classes/ME%20510610%20Non%20Newtonian/FENE%20Dumbell%20model.pdf>
12. Andrew R. Leach- Molecular Modelling
13. Dynamics of Polymeric Liquids- Bird

ACKNOWLEDGEMENTS

Given the current scenario, it almost seemed impossible to do this internship. But the team of SRFP 2020, made it possible and I am therefore very grateful to them for giving me this opportunity. I would like to acknowledge each and every member of SRFP 2020 working in order to help us do our internship. Its because of them I was able to get a one in a lifetime experience.

I would also like to express my sincere thanks to my mentor/ guide **Dr. Alope Kumar**, who guided me through the intern and also **Dr. Gaurav Tomar**, we helped me in understanding major fundamental concepts related to the research. Also, PhD. Student **Prabeen Kumar Pattanaik**. With the compiled efforts of this team I was able to successfully complete my internship.

Lastly, my parents for providing me constant support and motivation during the internship.

APPENDICES

The appendix contains codes involved in the input file-

```
### Define variables ###
```

```
variable Boxsize equal 40.0
```

```
variable dt equal 0.002
```

```
variable N_rotation equal 45
```

```
variable hgrid equal 1.0
```

```
variable cutoff equal 1.122462 # Cut at min energy,  $2^{(1/6)} \cdot \sigma$ 
```

```
variable cc_cutoff equal 6.73477229
```

```
variable delta equal 2.5 #  $R_{np} - \sigma / 2 = 3.0 - 0.5 = 2.5$ 
```

```
variable epsilon equal 1.0
```

```
variable sigma equal 1.0
```

```
variable cc_sigma equal 6.0
```

```
variable kapa equal 30
```

```
variable maxbond_length equal 1.5
```

variable d_monomer equal 0.0

variable m_monomer equal 5.0

variable Temp equal 1.0

variable d_particle equal 6.0

variable m_particle equal 565.486677646

variable N_particle equal 5

variable m_solvent equal 1.0

variable N_solvent equal 320000

variable vcmx equal vcm(all,x)

variable vcmy equal vcm(all,y)

variable vcmz equal vcm(all,z)

variable fout equal 1000

variable runtime equal 500000

variable fremcom equal 10

variable frestart equal 5000

timestep $\{\text{dt}\}$

units lj

boundary p p p

atom_style hybrid bond sphere

pair_style lj/expand $\{\text{cc_cutoff}\}$

pair_modify shift yes

bond_style fene

special_bonds lj 0.0 1.0 1.0

read_data data.equilSys_MPCD

group small type 1

set group small diameter $\{\text{d_monomer}\}$

set group small mass $\{\text{m_monomer}\}$

group solvent type 2

set group solvent diameter 0.0

set group solvent mass 1.0

group big type 3

set group big diameter $\{d_particle\}$

set group big mass $\{m_particle\}$

group solute union small big

atom_modify first solute

pair_coeff 1 1 $\{\epsilon\}$ $\{\sigma\}$ 0.0 $\{cutoff\}$

pair_coeff 1 2 0 $\{\sigma\}$ 0.0 $\{cutoff\}$

pair_coeff 2 2 0 $\{\sigma\}$ 0.0 $\{cutoff\}$

pair_coeff 1 3 $\{\epsilon\}$ $\{\sigma\}$ $\{\delta\}$ $\{cutoff\}$

pair_coeff 3 3 $\{\epsilon\}$ $\{cc_sigma\}$ 0.0 $\{cc_cutoff\}$

```
pair_coeff 2 3 0  $\{\sigma\}$  0.0  $\{\text{cutoff}\}$ 
```

```
bond_coeff 1  $\{\kappa\}$   $\{\text{maxbond\_length}\}$   $\{\epsilon\}$   $\{\sigma\}$ 
```

```
neighbor 1.0 bin
```

```
neigh_modify delay 0 every 1 check yes include solute
```

```
comm_modify mode multi group solute vel yes
```

```
fix BIG big nve
```

```
fix SRD solvent srd  $\{N_{\text{rotation}}\}$  big  $\{\text{Temp}\}$   $\{h_{\text{grid}}\}$  10923 shift yes 77394 rescale no  
collision slip
```

```
fix RMV all momentum  $\{\text{fremcom}\}$  linear 1 1 1
```

```
compute COM all com
```

```
fix COM all ave/time 1 1  $\{\text{fout}\}$  c_COM[1] c_COM[2] c_COM[3] file COM.out
```

```
compute msqd big msd com yes average yes
```

```
thermo_style custom c_msqd[4]
```

```
thermo  $\{\text{fout}\}$ 
```

dump 1 all atom 50 dump.project

dump INIT solute xyz \${runtime} initial.xyz

dump TRJ solute dcd \${fout} SNDPS_1.dcd

dump_modify TRJ unwrap yes

restart \${frestart} polycoll*.restart

timestep \${dt}

run \${runtime}

write_data data*.equil