

Structure of polymer chains around a spherical interface: A Monte-Carlo simulation study

A Project Report

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Abstract

A systematic study of the structure of polymer chains around spherical interfaces, using Monte Carlo simulations has been performed. A Canonical ensemble (NVT - Number of Molecules, N , Volume, V , and Temperature, T , constant) is used for this purpose. The spherical interface is modelled as a large Yukawa sphere, whereas the polymer chains are treated as freely jointed chains interacting through Yukawa potentials. Variations in singlet density profile of the polymer chains around the interface have been analysed to obtain the effect of the size of the central spherical interface, the effect of the chain size, and the effect of the attractive potentials between the interface and the chains and amongst the chains themselves, for varying bulk densities of the polymer solutions. The configurational and packing entropic effects compete to produce density profiles analogous to those for the structure of polymer chains near walls in slit like pores. The presence of attractive potentials between the interface and the chains, between the chains themselves, and both, give expected results, i.e. there is a marked increase in density near the interface when attractive potentials are between the interface and the chains, and vice versa.

Introduction

Over the past several decades, polymers and polymer solutions have been of continued interest to the scientific community, across varying disciplines. Polymers have found applications in fields as varied as energy conversion and storage, in photovoltaics and supercapacitors, in adsorptions and membrane separation technology, in cybernetics, nanotechnology, and catalysis.¹ Polymers continue to be of interest due to the widespread in their inherent characteristics, physical and chemical. This uniqueness can be attributed to their fundamental structural differences i.e. the long chain structure, from other materials like, say, metals. This responsiveness of properties to structural changes such as repeat units and chain length has been the focus of several intriguing studies. Study of polymer systems has therefore, been a continuously expanding area of research.

A basic understanding of the behaviour of polymer systems under different constraints and conditions is as important,² if not more so, as is their technological applications. A variety of techniques, viz., experimental, theoretical and computational methods have been employed over the years, to gain insight into this behaviour. These efforts have further been boosted by technological innovations in general, especially advanced microscopy and scattering instruments, enabling experimental studies through techniques like ellipsometry, atomic force microscopy and small angle scattering. Exponential increase in the computational power readily available to researchers has also led to a spurt in advanced and more accurate simulation studies. There have been several major advancements in theoretical treatment³ of these systems as well: development of semi-analytic theories, especially for long chain and high-density polymers, such as the integral equation theory, the density functional theory and amalgamations of these two theories, being of prime importance.

The density functional theoretical approach to understanding polymer systems has been successfully applied to problems spanning binding of salts to DNA, polyelectrolyte solutions, as well as polymers at interfaces. The basic premise in this approach is the expression of the grand potential of the system as a functional of the density distribution. This information works since the density distribution is unique for each type of external potential and reaches a minimum at equilibrium. A number of studies have been carried out using variations of this approach, differences being in the approximation of free energy functional. Several quantitatively accurate theories (in comparison with computer simulation results) have been developed, particularly those by Yethiraj and Woodward.⁴

The Integral Equation approach builds off the polymer reference interaction site model (PRISM)⁵ to calculate the intermolecular radial distribution function, which is not only of structural importance but also simplifies the calculation of thermodynamic properties, including an equation of state. This approach too has been worked on over time to result in computationally convenient methods with results comparable to simulation results. A number of amalgamated methods which utilise the interrelations between approximation techniques utilised in DFT and IET, have also been developed from time to time.⁶

Experimental techniques,⁷ such as Cryo-TEM (Tunnelling Electron Microscopy) can be performed on polymer solutions to view the actual microstructural state of the system. SANS (Small Angle Neutron Scattering) data can also be analysed to obtain structural models of the systems with quantitative data as well. SAXS (Small Angle X-ray Scattering) data, along with fits from electron modelling data can also reveal important characteristics of the polymer systems under study. Adsorption behaviour of natural and synthetic macromolecules at interfaces can also be studied by ellipsometry. AFM (Atomic Force Microscopy) and XPS (X-ray photoelectron spectroscopy) studies of polymer blend systems have also been performed to gain insights into complex configurations.

Generation of new and innovative simulation techniques,⁸ a lot of these as a result of, and utilising, the spurt in computational capability, have made a large amount of data available for analyses. Interest in simulation studies can be attributed to their capacity to be specifically tuned for a given model, and the fact that they provide exact results for any particular configuration. Systems where carrying out experiments will be technologically challenging, such as for high temperature conditions, or when the material itself would be rare and difficult to synthesize, can be comfortably simulated. The idea in this approach is usually to extrapolate the macroscopic properties of the system, via. Statistical mechanics,⁹ from the data for microscopic states obtained from simulation.

Simulation studies of systems can be time dependent or cycle dependent, the former being referred to as Molecular Dynamics simulations and the latter as Monte Carlo simulations. Molecular Dynamics studies approach the system with basic initial data for the positions, velocities and forces/potentials, and then simulate the system over several very small time steps, under the effect of aforesaid force/potential, until equilibrium is achieved, at which point final state is recorded. These studies are very comprehensive and computationally intensive. Monte Carlo simulations on the other hand are more focussed on obtaining an

overall picture of the system, which they obtain by disregarding the time factors, and allowing the system to reach equilibrium over several runs and averaging properties over the entire set of cycles. This difference in the MD and MC approaches can be understood mathematically as follows:¹⁰

For MD simulations,

$$\langle A \rangle = \frac{1}{t} \int_0^t A(\tau) d\tau,$$

whereas, for MC simulations,

$$\langle A \rangle = \lim_{t \rightarrow \infty} \frac{\sum A_i}{\sum i},$$

where A is any property that is being studied in the simulation process.

Monte Carlo simulations themselves have evolved over the years into several types depending upon the target systems vis. a vis. the physical quantities to be calculated. MC simulation relates to the stochastic sampling in a chosen ensemble. An initial configuration for the system is generated and within certain constraints of energy and samplings, the system is allowed to reach equilibrium. The equilibrium state is then analysed, and properties averaged out to generate the Markov chain. The acceptance probability for any MC move is given as:

$$P_{acc} = \text{Min}[1, \exp(-\beta \Delta U)],$$

where ΔU is the difference in energy between the final and the initial state and β refers to the inverse temperature.

For systems like polymer solutions, MC simulations can also be sub divided as Lattice and off lattice MC simulations, the primary difference between the two being that the positions that the units can take in the former is limited to the lattice points whereas in the latter no such restriction is placed on the polymer chains. Several properties like finite size effects and ergodicity of the system need to be taken into account to ensure accurate simulations. Finite size effects originate when the system configuration under analysis is too small to mimic real life systems, and hence the properties obtained as simulation results may differ substantially from experimental results. P_{acc} is kept between 0.2 to 0.4 to satisfy ergodicity criteria of the chain.¹¹

Previous Studies

A number of studies have been carried out over the years to study the behaviour of polymer chains at interfaces through theoretical studies and computer simulations.

Following the pioneering work by Dickman and Hall¹² on obtaining the bulk equation of state and density profile near walls through high density Monte Carlo simulations of chain molecules, Kumar, Vacatello and Yoon¹³ performed off-lattice MC simulations of polymer melts confined between two plates. Kumar et al. used¹³ a Lennard-Jones type potential in their simulations and obtained interesting results for a film-like polymer melt confined between impenetrable walls. Yethiraj and Hall¹⁴ performed a systematic study of systems comprising chain molecules and monomers in hard slit like pores, to understand the effect of the presence of solvent molecules on the structure of chain fluids. This work provided a detailed analysis of the effect of density, pore size, chain concentration and chain length on chain conformations and density profiles.

Patra, Yethiraj and Curro¹⁵ studied the effect of attractions on the structure of fused sphere chains confined between surfaces. The model choice is to investigate the system on a length scale in addition to the size of the spheres. This was also followed by a generalised van der Waals density functional theory by Patra and Yethiraj¹⁶ and was found to be in good agreement with the simulations. A density functional study^{of} the effect of attractions on the structure of polymer solutions confined between surfaces was also done followed by an MC study of a similar system by Patra.⁶

Motivation

A number of studies have been carried out investigating the structure of polymer chains confined between planes, viz. in slit like pores, and against planar interfaces. This work is an attempt to study the behaviour of polymer chains at interfaces in spherical geometries, with and without the effect of attractive/repulsive potentials.

Behaviour of simple fluids at interfaces is of prime concern, whether it is readily recognisable or not. The same drop of liquid when dropped onto a glass surface behaves differently as compared to when dropped onto a sheet of paper. The difference is in the interactions between the fluid and the interface. Application of paints onto surfaces is an example of polymer chain interaction with planar surfaces on a macro scale. We intend to investigate the structure of polymer chains around a spherical interface at the atomic scale. A practical application of such a scenario would be the effect of micelles in a soap solution on dissolved polymers. Dissolution of C_{60} like molecules into a polymer solution would also be another hypothetical example where the current study can shed some light. To gain an in-depth understanding of such systems, a simulation study like this one is essential.

Current Model and Simulations

For the current work, the polymer chains have been modelled as hard sphere chains similar to a pearl necklace defined as freely jointed chain model. The only restriction being the diameter of the hard sphere as this is the minimum approach distance. The spherical interface is placed at the centre of the simulation cell and is also assumed to be a hard sphere of fixed radius. This choice of model is primarily out of simplicity of execution and also should provide the trends of the static structural behaviour of polymers.

For the present work, MC simulations are being performed in the canonical ensemble (number of molecules, N , volume, V , and temperature, T , constant). The simulation cell is a rectangular parallelepiped with a spherical bead of fixed radius placed at its centre. Programs for generation of initial configuration of the system for the MC simulation are written in FORTRAN 77. Simulations are being performed for three chain lengths, $n=4, 8, 16$; three radii of the central sphere, $\sigma_s=\sigma, 1.5\sigma, 2\sigma$, where σ is the diameter of the beads of the chain; and three volume fractions, $\eta=\pi\rho\sigma^3/6=0.1, 0.2, 0.4$. Attractions between the central sphere and the chains, and among the chains themselves have also been incorporated into the programs. For chain lengths of 4 and 8, number of chains (N) is set to 400 and 200 respectively. For 16-mers, number of chains is limited to 100, keeping in mind the computational power needed. The periodic length is accordingly calculated for each of the cases, from the void fractions required. Periodic boundaries will be in all three directions as the system is radially symmetric and there are no boundary constraints.

The site-site interaction potential between any two sites on the chains is a sum of hard sphere and Yukawa potential, given as

$$\beta u_{ff}(r) = \begin{cases} \infty, & \text{for } r < \sigma, \\ -\epsilon_{ff} \frac{\exp[-\kappa(r/\sigma - 1)]}{r/\sigma}, & \text{for } r > \sigma, \end{cases}$$

where r is the distance between any two beads, $\beta = 1/k_B T$, k_B is Boltzmann's constant, T is the temperature, ϵ_{ff} is the (dimensionless) strength of fluid-fluid interactions and κ is the inverse range of the Yukawa potential (here $\kappa = 2.5$). The spherical interface is also modelled as an attractive Yukawa surface with the external potential $u_{sf}(r)$ between the sphere and any chain monomer is given by

$$\beta u_{sf}(r) = \begin{cases} \infty, & \text{for } r < \sigma_s, \\ -\epsilon_{sf} \frac{\exp[-\kappa(r/\sigma - \sigma_s)]}{r/\sigma}, & \text{for } r > \sigma_s, \end{cases}$$

where σ_s is the diameter of the central sphere, ϵ_{sf} is the (dimensionless) strength of sphere-fluid interactions and all other notations are the same as in the previous equation.

For generation of the initial configurations, we use a growth and equilibration algorithm. Initially single beads equivalent in number to the number of chains needed, are placed inside the simulation cell using the 'move and insert' strategy. Configurations are checked for overlap i.e. centres of any two beads cannot come closer to one another beyond a fixed minimum distance of approach, which in this case is the diameter of a single bead. The single beads are then converted to chains, employing one of three possible movements, *Dickman* moves, *CCB* (*Continuum Configurational Bias*) and *Reptation* for each move followed by addition of bead to chain, until maximum lengths are achieved. Details on how these moves are executed and how this combination of moves does not violate ergodicity criteria for the system can be found elsewhere. If the percentage of accepted moves out of the total number of attempted moves is above a given threshold, the simulation is assumed to be fairly representative of a real system. Overlap of the polymer chains with the central spherical interface also needs to be monitored, which is done by not allowing any insertion of a bead within a fixed distance (equivalent to sum of radii of the central sphere and of the smaller bead) of the centre of the simulation cell.

Simulations are performed for 10^9 moves in one run with sampling at every 10^3 moves. The probability of one of the three moves taking place at every step is kept equal. Various combinations of values of ϵ_{ff} (0.0, -0.2 and -0.5) and ϵ_{sf} (0.0, -0.2, and -0.5) are taken to analyse the effect of attractive potentials on the system. The results are obtained as number density profiles found by a block averaging scheme over four successive runs for each set of initial parameters, final configuration from one run being used as the initial configuration for the next. The number density profile is calculated by dividing the region around the central sphere radially into spherical bins each of equal thickness. After a certain specified number of attempted moves, the number of sites in each bin is recorded. This value is then used to obtain the number density in each bin which is then graphed over the length of the simulation cell.

Results and Discussion

The density profiles obtained as simulation results are plotted and analysis is reported in the subsequent sections. All plots, except those where effects of attractive potentials are being explicitly compared, are for systems of athermal chains, where attractions have been set to zero ($\epsilon_{ff}=\epsilon_{sf}=0$).

A. Effect of Central Sphere Size

Graphs in Figure 1 for packing fractions (η) 0.2 and 0.4, depict the density profiles for 8-mers, for central sphere size (σ_s) of σ , 1.5σ and 2σ , respectively. The shift in the peaks of the curves away from the origin is a direct result of the no overlap criterion employed for the central sphere. The slight increase in the peak of the density, just at the interface as one moves from central sphere of size σ to 2σ is a result of the change in the total available volume for arrangement of the chains around the central sphere.

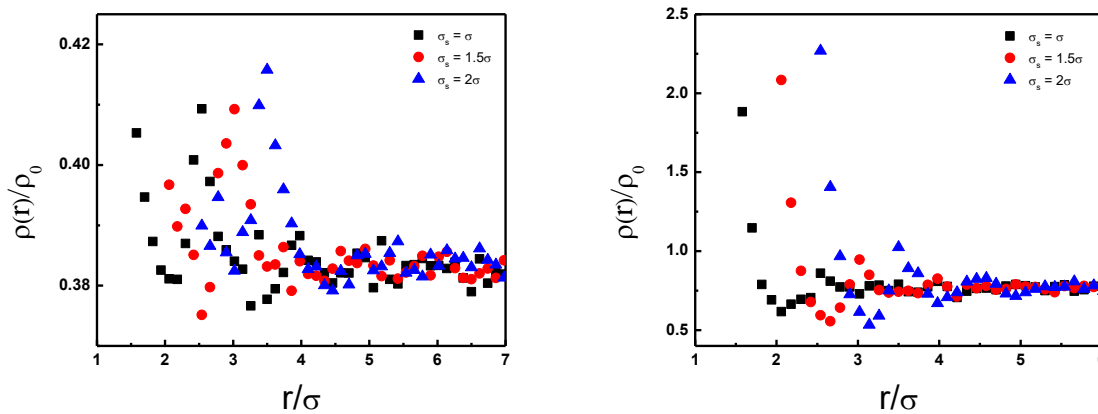


Figure 1 - Density profiles for 8-mers at packing fraction (η) 0.2 and 0.4

Characteristic feature of these profiles is the subsequent crests and troughs in the profile, which emerge out of the packing tendencies of the chain around the central sphere.

B. Effect of Chain Length

Graphs in Figure 2 for packing fractions (η) 0.2, depict the density profiles for central sphere size of 1.5σ and 2σ , for 4-mers, 8-mers and 16-mers, respectively.

The constraints placed on configurational freedom of polymer chains due to their length are clearly visible in these plots. As the length of chains increases from 4-mer to 8-mer to 16-mer, the freedom of arrangement progressively decreases and so, packing closer to the interface

becomes entropically more difficult. Hence the decrease in the number density of the polymer chains. This effect become clearer as the size of the central sphere increases.

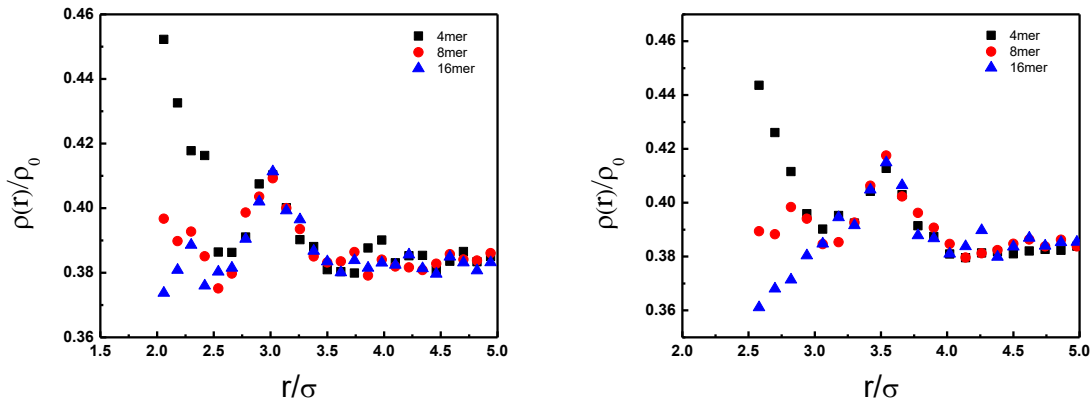


Figure 2 - Density profiles at packing fraction 0.2, for central sphere size 1.5 and 2.0

C. Effect of Packing Fraction

Graph in Figure 3 depicts the density profiles for central sphere size of 1.5σ , for 8mers for various values of packing fraction.

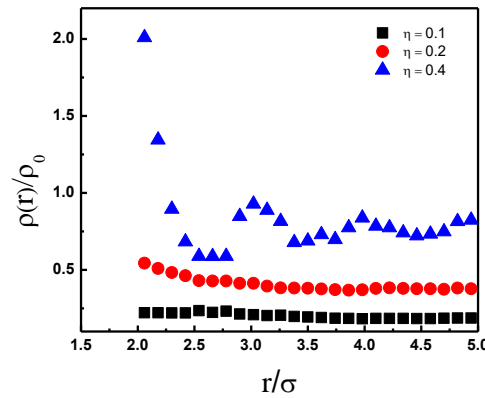


Figure 3 - Density profiles for 8mers for central sphere size of 1.5

In the absence of attractive potentials, density near the interface rapidly increases as the packing fraction increases. While this may seem counter intuitive for larger chain lengths, the results clearly indicate that packing entropic effects dominate over configurational difficulties.

D. Effect of Attraction Parameter

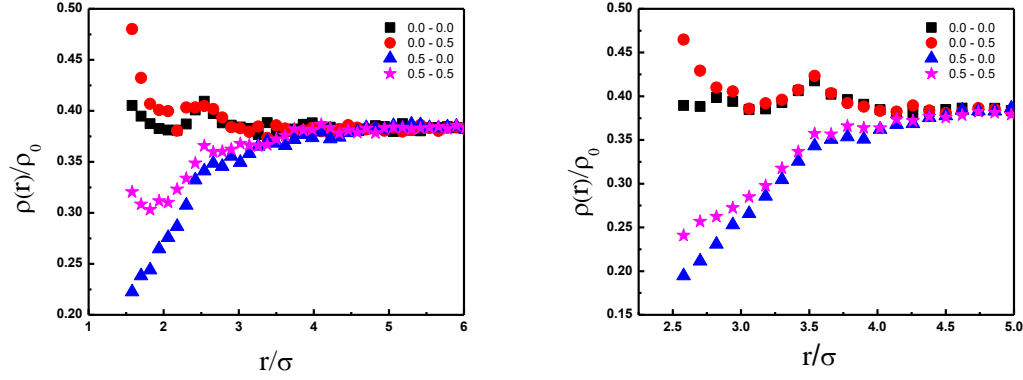


Figure 4 - Density profiles for 8mers for a packing fraction (η) of 0.2, and central sphere sizes of 1.5σ and 2σ at different (ϵ_{ff} , ϵ_{sf}).

Graphs in Figure 4 for packing fractions 0.2, depict the density profiles for central sphere size of 1.5σ and 2σ , for various combinations of values of ϵ_{ff} (0.0 and -0.5) and ϵ_{sf} (0.0 and -0.5). As is clearly visible, attractive potential between the spherical interface and the chains results in an increase in the number density of beads at the interface. The '0.0 - 0.0' curves are for the case when no attractive potential is active. The marked increase in the curve for '0.0 - 0.5' shows the effect when $\epsilon_{sf} = 0.5$ and $\epsilon_{ff} = 0.0$; i.e. attraction is active between the interface and the chains but not so between the chains themselves. In such a case, it is obvious that the chains will accumulate close to the interface. In the case when $\epsilon_{sf} = 0.0$ and $\epsilon_{ff} = 0.5$; i.e. attraction is active between the chains themselves but not between them and the interface, the system tends to equilibrate in such a way that the chains pack amongst themselves instead of around the interface. When $\epsilon_{sf} = 0.0$ and $\epsilon_{ff} = 0.5$; i.e. both the attractions are active, the results are more interesting. The number density close to the interface does increase as compared to the values in the previous case, but still the attraction between the chains appears to dominate and the net effect is a decreased number density at the interface in comparison to the '0.0 - 0.0', i.e. no attraction case. With increase in the central sphere size, these effects get compounded, and hence the packing near the interface further decreases.

It may however be noted that at even higher packing fractions, say 0.4, the effect of attractive potentials is visible but not on a long length scale, i.e. immediately at the interface, increase and decrease in the number density for corresponding values of ϵ_{sf} and ϵ_{ff} respectively, are visible, but quickly converge to a similar profile. In such cases the packing effects seem to dominate over the attractive potential effects.

Conclusion

A systematic Monte Carlo simulation study has been carried out to study the behavior of polymer chains around a spherical interface. Effects of the chain length of polymers, size of the spherical interface, packing fraction of the polymer solution, and the attractive potentials in play in the system, have been analyzed using the obtained density profile data.

Results are as expected; packing, attraction and configurational entropic effects compete to produce a range of density profiles. Further details about the structural features of the system can be obtained from further analysis of the mean square radius of gyration and mean square end-to-end distance data for these simulations. Theoretical studies can also be performed on the system to obtain further depth for such systems.

Polyelectrolytes¹⁷ are polymers having embedded charges on all beads. It would be interesting to see how the effect of charge can be brought out systematically into the neutral or Yukawa systems. In fact, because of its utmost use in day-to-day activities, a comprehensive study on polyelectrolytes from simulation and analytical point of view may provide sufficient information for modification of these systems for use in public and private lives of humankind.

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