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Comparison of Monte Carlo and quasi-Monte Carlo technique in structure and relaxing dynamics of polymer in dilute solution

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ABSTRACT

Structure and dynamics of polymer in solvent solution is an important area of research since the functional properties of polymer are largely dependent on the morphology of the polymers in solution. This structure related properties are especially important in case of surface science where the phase-separated morphology in the micro/nano scale dictates the properties of the product. Modeling polymers in solution is an efficient way to determine the morphology and thus the properties of the products. It saves time as well as helps to design novel materials with desired properties. Polymers in solution systems are generally modeled with bead spring model and Monte Carlo or importance sampling Monte Carlo simulations is used to find the optimal configuration where the energy of the system is minimized. Often in these simulations, random numbers are used in the Monte Carlo steps. Normally random numbers try to form clusters and do not cover the entire dimension of the system. Thus the minimum energy structures obtained from simulations with random numbers are not optimal configuration of the system. In the present work a lattice-based model is used for polymer solution system and importance sampling Monte Carlo is used for simulation. Quasi-random numbers generated from Hammersley sequence sampling (HSS) are used in the simulation steps for stochastic selection polymers and its movements. Quasi-random numbers obtained from HSS are random in nature and they have *n*-dimensional uniformity. They do not form clusters and the structural configuration obtained using quasi-random numbers are optimal in nature. The optimal configurations of the polymers as obtained from random number and quasi-random number are compared. The result shows that simulation with HSS attains a lower energy state after initial quench. At the late stage of spinodal decomposition, the structure factor decrease-showing Ostwald ripening which is not observed from simulation with random numbers.

1. Introduction

The performance of various polymer products for nanotechnology, biomaterials, paints and coatings is largely governed by the characteristics of their surfaces and interfaces. For example, polymer solar cells where the structure of the interphase plays significant role in charge transfer and determines the properties (Watkins et al., 2005), polymer blends where the interphase of different polymers determines the strength of the materials (Stamm, 2008), paints and coatings where characteristics of the molecular interfaces and surface morphologies determines corrosion and scratch resistance properties (Brune et al., 1997). Thus, understanding the surface and interfacial characteristics at the micro and nano scales is essential for analyzing the performance of a polymer device. In this effort, molecular simulation can also provide information related to the surface characteristics underscoring the physical, chemical and thermodynamic mechanisms involved in fabrication of the material (Hill et al., 2005). The simulations can replicate the fabrication conditions and aid the development process by exploring the effects of manufacturing parameters on surface characteristics without the actual fabrication steps. The key to control the fabrication of polymer products whose performance matrix is governed by surface and interfacial features is to optimize the thermodynamic condition that gives desired characteristics.

Polymer surface and interface is created by polymeric solution mainly containing polymer, solvents and some other reinforcements or polymer blend containing multiple polymers or copolymers. Molecular simulations can be used to replicate surface characteristics at different process conditions (Schmid et al., 2004). In those simulations, the effects of different process parameters on

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the interfacial features as well as surface roughness are monitored. In our previous paper (Mukherjee et al., 2009), a coarse-grained lattice based importance sampling Monte Carlo (MC) simulation is used to investigate the behavior of a polymer and its interactions with solvents in the formation of a spinodally decomposed phase-separated morphology. Computer generated pseudo random numbers are used in the Monte Carlo steps. In this paper, we have simulated a polymer solution system with quasi-random numbers as well as pseudo random numbers and compared the results from the both. The goal of the research is to show the advantage of quasi-random numbers over pseudo random numbers in molecular simulation of a polymer solution system.

The underlying physico-chemical mechanism of the molecules in the polymer solution system is the key to decide the appearance of a surface and interfaces. The characteristic features of polymer surfaces lie in the nano scale. Therefore in our simulations we have adopted a simple, coarse-grained representation of different chemical components of polymer solution system. Our models are simple enough to allow us to deal with relatively large systems, without completely losing all details at the nanometer length scale. The coarse-grained molecular simulations provide a better understanding of the surface phenomena and its relation with the performance metrics. The molecular configuration in our simulation uses the Metropolis criterion that creates a Markov chain of states to reach the minimum energy state. Metropolis criterion uses importance sampling Monte Carlo. The Markov chain of states biases the generation of molecular configurations that allows the low energy configurations to be sampled more efficiently. At every step of the simulation a stochastic movement of the polymer is created. The movement of the polymer generates a new state with a probability $\exp\left(\frac{-\Delta E}{k_b T}\right)$. The ΔE is the change in energy from the step, k_b is the Boltzmann constant and T is the absolute temperature.

Simulation of polymer solution system generally starts with random distribution of polymers and solvents. The simulation starts with an initial quench. The polymers and solvents move to form two phase in equilibrium. One phase is rich in solvent and the other one is rich in polymer. For stochastic sampling of polymer movement, uniformly distributed random numbers are used. In this paper we have used random number generated by computer (pseudo random numbers) as well as a quasi-random numbers generated from Hammersley sequence sampling (HSS) for this purpose. HSS is an efficient sampling technique developed by Diwekar and co-workers (Kalagnanam and Diwekar, 1997). It uses Hammersley points to uniformly sample a unit hypercube and invert these points over the cumulative probability distribution to provide the sample set for the variable. This enables the sampling to be uniformly distributed in n-dimensions. Because of the n-dimensional uniformity of HSS, it is expected that simulation with HSS will not only result in faster conversion but also reach those sites that are not assessable by pseudo random numbers. This will lead to an optimized configuration that is not achievable by pseudo random sampling.

The paper is oriented as follows. In Section 2 details about modeling polymer in solution is given that includes description of the thermodynamic phenomena in a polymer solution system. This is followed by Section 3 where description of the molecular simulation is given that includes simulation procedure and sampling techniques used in simulation. Section 4 presents the results of the simulation and describes them. Finally Section 5 gives the conclusions from present analysis with the application of pseudo random numbers and quasi-random numbers in polymer simulation systems.

2. Polymer solution systems

Experimental evidence shows that due to the composition and polydispersity of the polymers and their difference in solubility with the non-theta solvents, polymers in solution try to aggregate forming granules or clusters (Yamaguchi et al., 1997). As an example we can look into photoresist polymers used in the process of lithography. During photolithography, photoresist polymer coatings are done on metal wafer from polymer solution systems. Photoresist polymers form granules in the solvents. The granules present in the polymer cause the surface to be rough, and are also the main cause of the line edge roughness (LER), surface roughness (SR), line width fluctuations and critical dimension (CD) fluctuations. From the experimental evidences we can see that it is essential to understand the thermophysical feature of the polymers in solution and mechanical process through which polymer coatings are done in order to understand the morphology formation. A mesoscale simulation of the polymer performance is found to be appropriate to identify the cause of the physical features of polymer surfaces and interfaces (Schmid et al., 2004).

In the present study we have performed coarse-grained lattice based model of a polymer solution system and importance sampling MC simulations is performed in order to investigate the chemical and thermodynamic mechanisms involved in the morphology formation. Monte Carlo steps use random numbers. In the present simulation we have used pseudo random numbers as well as quasi-random numbers generated from Hammersley sequence sampling (HSS). The effect of random number generated by computer and quasi-random number in simulation of a polymer solution system are observed in the structural differences.

A high volume percentage of solvents are used in the polymeric system to replicate the polymer in solvent systems. High volume of solvents are generally used to increases the viscosity during polymer processing. Polymer in solution undergoes a phase separation through spinodal decomposition. The phase separated morphology causes clusters granules responsible for the LER and SR and other morphological properties. We have investigated the effect of pseudo random number and quasi-random number through Hammersley sequence sampling in simulated morphology and measured the effect on SR, LER, radial distribution function (RDF), structure factor (SF). Usually random numbers are used for these simulations. From our simulation, we have got a first hand knowledge of the use of quasi-random numbers in finding the structure and dynamics of a polymer solution system.

2.1. Thermodynamics of polymer solution system

The thermodynamics of the solution system used in our simulation has an upper critical solution temperature (UCST) (Yamaguchi et al., 1997; Mukherjee and Romagnoli, 2010). At high temperature, the polymers are randomly distributed in the solution matrix forming a single phase. When it is allowed to equilibrate at a lower temperature, say room temperature (298 K), the polymer undergoes a critical quench phenomenon and moves from stable region to unstable region of the phase diagram through the critical point or around the critical point (Fig. 1). The system enters the spinodal decomposition region. This region is unstable and the mixture decomposes spontaneously and results in microphase separation in the form of spinodal decomposition. The system forms two phases that are at equilibrium. One phase is rich in polymer and other is rich in solvent. This is seen from the morphology formed after equilibrium. The spinodal decomposition gives a metastable phase separated morphology and does not reach the ultimate equilibrium morphology. In the late stage of spinodal decomposition process each phase has the respective equilibrium concentration that yields a rough morphology of the polymer structure at the surface and the edges. The Ostwald ripening process follows the spinodal decomposition where the coarsening of the spinodally decomposed polymer occurs leading to the ultimate equilibrium morphology. This process further reduces the energy of the system