



A molecular scale perspective: Monte Carlo simulation for rupturing of ultra thin polymer film melts



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ABSTRACT

Monte Carlo simulation has been performed to study the rupturing process of thin polymer film under strong confinement. The change in mean square displacement; pair correlation function; density distribution; average bond length and microscopic viscosity are sampled by varying the molecular interaction parameters such as the strength and the equilibrium positions of the bonding, non-bonding potentials and the sizes of the beads. The variation in mean square angular displacement $\chi_\theta = [\langle \Delta\theta^2 \rangle - \langle \Delta\theta \rangle^2]$ fits very well to a function of type $y(t) = A + B * e^{-\frac{t}{\tau}}$. This may help to study the viscous properties of the films and its dependence on different parameters. The ultra thin film annealed at high temperature gets ruptured and holes are created in the film mimicking spinodal dewetting. The pair correlation function and density profile reveal rich information about the equilibrium structure of the film. The strength and equilibrium bond length of finite extensible non-linear elastic potential (FENE) and non-bonding Morse potential have clear impact on microscopic rupturing of the film. The beads show Rouse or reptation motion forming rim like structures near the holes created inside the film. The higher order interaction as dipole–quadrupole may get prominence under strong confinement. The enhanced excluded volume interaction under strong confinement may overlap with the molecular dispersion forces. It can work to reorganize the molecules at the bottom of the scale and can imprint its signature in complex patterns evolved.

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1. Introduction

Thin polymer films are extensively used in various technological applications like insulation and protective coatings, optical coatings, lubricants, adhesive etc. Its study is of great significance in making the nanopolymer films stable in conditions of varying temperature. Only a thermally stable film can maintain the functional properties of the devices intact. The dimensions of the devices used, have become progressively smaller. The thin films have reached to mesoscopic dimensions due to many fold advancement in science and technology. The thermodynamic and transport properties of very thin films show variations from the bulk properties. It is hard to understand the changes that take place at the very molecular scale and the researchers too find it to be a challenging task. The very small sizes of the films and the spatial confinements of the order of few nanometers have made the computational methods play very important role in understanding the structural properties of the films and exploring the underlying physics. Molecular simulation offers full control in precisely

defining our systems of interest without introducing a single trace of impurity. One can alter the chain interaction parameters, chain length, interface parameters, density and temperature etc. in desired and systematic manner, while keeping the other parameters constant. It is possible to single out the effect of each parameter on the properties of the systems, using computational methods. The computational methods and tools not only provide us microscopic to molecular insights but also enable us to test the theoretical concepts in building new models at small scales. Many of the experiments at nanoscale are very hard to perform or even impossible. This makes the simulation methods even more essential.

The effect of geometric confinement on glass transition temperature has earned considerable attention in last two decades [1–5]. Interfacial effect plays an important role in reduction or enhancement of glass transition temperature. The monomers near the attractive surfaces become more immobile, when the surface affinity to the beads is increased. The thin film offers better mobility to the beads inside the film for weakly interacting surfaces. The strong surface potential results in higher glass transition temperatures. The movement of the beads or the segment of polymer chains near a surface is slowed down in comparison to the bulk of the film, but this transition from the interface to the bulk is

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even. This transition yields an inhomogeneous distribution of the particles or beads near the surface in comparison to the bulk and there is a surface excess of the beads near the attractive walls. This surface excess of beads may help in reducing or enhancing the glass transition temperature. The surface effect decreases, as the distance from the surface increases. This is the reason why, under the influence of strong confinement effect, we observe differential behavior of spatial temporal correlation leading to a complex dynamics and equilibrium structure especially in the case of wetting, dewetting or non-equilibrium structures inside thin (glass) films. There have been few published simulation reports for systems under confinements, with bead spring models of polymers, which discuss the interfacial effects on glass transition temperature [6]. But the simulation work dedicated to study of thin film instabilities leading to the rupturing of a film has not been reported much. One of the obvious reasons is that, spinodal theory could get into existence only after 1995 [7]. It has just completed a time line of two decades or so [8–13]. Viscosity, surface tension, thickness of the film, attractive properties of a coated surface etc. are the key parameters, which play important role in dewetting. The onset of an instability caused by the thermal jiggling inside the film or at the surface of the film may amplify or damp, depending on key parameters as discussed in this paper. The confinement and interfacial effects become important because, these may change the key parameters, which in turn can change the dynamics and thus the equilibrium structures of the films. The effect of confinement and interface parameters have been scarcely discussed especially using Monte Carlo simulation technique. Confined polymeric liquids and polymer melts can display complex relaxation behavior and dynamics because of the interplay of bulk properties and interfacial effects [14–19]. Folding of polymers in confinement has been a major challenge, as the presence of interfaces can enhance or retard the mobility of beads near the walls, making these beads different from those immersed inside the bulk [6]. Thus, it can alter the wetting and dewetting behavior of the surfaces. The surface attraction above a certain threshold would prefer to wet the surface partially or completely, and the bulk system may be driven to dewetting like dynamics leading to complex stable structures in ultra thin polymer films. This paper deals with the investigation of parametric dependence on the key parameters leading to the rupturing of thin films, especially by spinodal mechanism.

2. The model and simulation method

Total 120 polymer chains have been taken for all cases of studies in this paper. 20 chains are placed in +Y direction and 6 chains are placed one above other in +Z direction (Fig. 1). Simulation box of the size $22.5\sigma \times 15.0\sigma \times 5.625\sigma$ has been used for all the cases of studies, which corresponds to the dimensions of the box along x, y and z directions respectively. The potential used in this modeling work is motivated by the work of Kurt Binder and his co-workers [20]. Each chain consists of 30 beads, connected by FENE (finitely extensible non-linear elastic) potential, represented as follows [20, 21]:

$$U_r^{\text{FENE}} = -\frac{1}{2}K(l_{\text{max}} - l_0)^2 \ln \left[1 - \frac{(r - l_0)^2}{(l_{\text{max}} - l_0)^2} \right] \quad (1)$$

The potential diverges logarithmically for maximum possible stretching of the bond and for the case of overlap respectively given by $r \rightarrow l_{\text{max}}$ & $r \rightarrow l_{\text{min}} \equiv 2l_0 - l_{\text{max}}$. Thus, the effective length of the bond is limited to the range of $l_{\text{min}} < l < l_{\text{max}}$.

We have $l_{\text{max}} = 1.2\sigma$, $l_{\text{min}} = 0.20\sigma, 0.30\sigma, 0.40\sigma$, $l_0 = 0.70\sigma, 0.75\sigma, 0.80\sigma$; $K = 200, 220, 240$. One may choose a scaling factor as $\sigma = 1.0$ so that all the length scales in this paper have the units

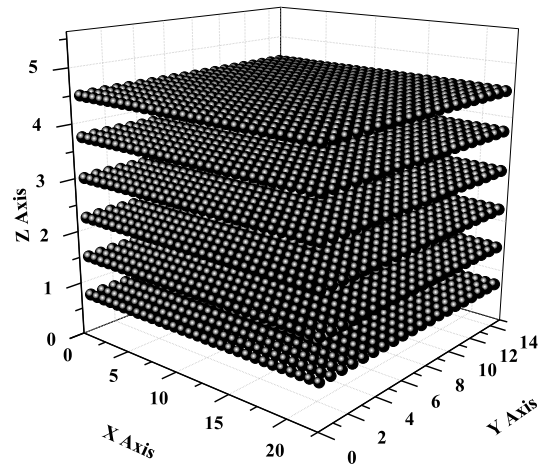


Fig. 1. Shows the initial stage configuration of the polymer film. Simulation box of the size $22.5\sigma \times 15.0\sigma \times 5.625\sigma$ has been used for all the simulation data. The beads are equally spaced in all three dimensions.

of σ . Non-bonded interaction amongst intra-chain and inter-chain monomers are taken into account using Morse potential given by

$$U_M(r) = \varepsilon_M \exp\left(-\frac{2.0}{\xi}(r - r_0)\right) - 2\varepsilon_M \exp\left(-\frac{1.0}{\xi}(r - r_0)\right) \quad (2)$$

The strength of the Morse potential is given by ε_M . It is taken to be 2.0, 4.0, 6.0 & 8.0 for different cases of study in this paper. The equilibrium distance between beads for non-bonded interaction is taken as $r_0 = 0.68, 0.72, 0.76$, for which the interaction potential is minimum as $-\varepsilon_M$. Choosing different values as $l_0 = 0.70$ & $r_0 = 0.68$ for bonded and non-bonded interaction decreases the tendency of crystallization in dense configurations at low temperatures. $1/\xi$ has been taken as 9.0 in this paper for all cases of studies, which makes the potential extremely short ranged i.e. $U_M(r \rightarrow 1.25) = 0$.

The surface affinity to the beads is defined by square well attractive potential as follows in eq. (3):

$$U(r) = \begin{cases} \infty, & \text{if } r < \sigma_0 \\ -\varepsilon, & \text{if } \sigma_0 < r \leq \lambda\sigma \\ 0, & \text{if } r \geq \lambda\sigma \end{cases} \quad (3)$$

Here, the interaction range is λ . For all cases of studies in this paper, λ and ε are taken to be 1.0 and 5.0 respectively. Square well potential has both the repulsive and attractive characters of the Lenard–Jones interaction. It has been used in various simulation reports [20–24] and has yielded correct results. The important thing about choosing surface bead potential as square well, is that it has constant well depth of $-\varepsilon$ for $\sigma_0 \leq r \leq \lambda\sigma$, so the beads remain adsorbed without any change in energy i.e. the beads dwell inside the square well. σ_0 is the dimension of the beads. The hard sphere interaction with the surface of the walls ensures that beads do not penetrate into the surface. Thus, the effect of melting of polymer propagates to the beads in contact of surface at latter stages. The surface induced undulations remain small and do not onset the instability in the film. The graphical representations of the Finitely Extensible Non-linear Elastic potential, Morse potential acting amongst beads and the square well potential for surface–bead interaction for lower substrate are as shown in Fig. 2(a), (b) and (c) respectively.

A generic canonical Monte Carlo simulation program has been developed by the author for this paper. The initial configuration is as shown in Fig. 1. The dimension of the simulation box is taken as $22.5\sigma \times 15\sigma \times 5.625\sigma$ and all the beads are placed at equal distances (0.75 units of length for all cases) in X, Y and Z directions, so that the initial configuration is isotropic, in all three

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