

Polymer Communication

Time scales for three processes in the interdiffusion across interfaces

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Abstract

The complete cohesion of two thin films composed of melts of $C_{99}H_{200}$ has been achieved by simulation. The simulation employs a new 'mapping/reverse mapping' technique that is orders of magnitude more efficient than conventional molecular dynamics simulations of fully atomistic models. Three distinct processes, each with its own time scale, can be resolved. From fastest to slowest, these are:

1. the healing of the density profile between the two films,
2. the redistribution of chain ends, and
3. the complete intermixing of the segments from the original two films.

This simulation has the capability of producing new insights into the mechanism of interdiffusion across an interface and the mechanism of the development of cohesive strength at the interface. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Simulation of the cohesion of an interface between two similar films is of interest because of unanswered questions about the mechanism by which interdiffusion occurs and the development of cohesive strength at the interface. The time and distance scales involved in the complete removal of any trace of the initial interface make the simulation extremely difficult. A conventional molecular dynamics simulation with a fully atomistic model of the chains is not an attractive option, because of the outrageous amount of computer time required for calculation of a trajectory of sufficient length to produce complete cohesion. The problem can be addressed with accessible time (but still large, on the order of 10^4 h CPU time on a Cray T3D), using coarse-grained models of the chains on a lattice [1]. This type of simulation is useful for the study of general trends shared by many types of real polymers. However, comparison with the results of a specific experiment, such as those performed by i.r. microdensitometry [2], secondary ion mass spectroscopy [3], or neutron reflectivity [4,5], is often ambiguous because of the enormous simplification in the molecular structure in the simulation. The experiment is performed with a real polymer, and not with generalized coarse-grained chains on a lattice.

Here we describe preliminary results, obtained by a different method, for the simulation of the cohesion of two films. This simulation retains the computational advantages of a simulation of a coarse-grained model on a sparsely occupied lattice, but under constraints that allow precise specification of the chemistry and molecular weight of the chains.

Recently Rapold and Mattice developed a Monte Carlo simulation method on a high-coordination lattice (the 2nd lattice) derived from an underlying diamond lattice [6]. The short-range intramolecular interactions from the Rotational Isomeric State model [7,8] can be incorporated in the simulation, forcing the coarse-grained chain on the high coordination lattice to retain the short-range conformational characteristics of the real chain of interest [9]. The long-range interaction, which is responsible for the cohesion of the multichain system, is derived from an adaptation of the potential energy function describing the interaction of two monomers in the gas phase. The interaction is mapped onto the discrete space of the 2nd lattice to describe the long-range interaction of pair beads [10]. The coarse-grained system can be 'reverse mapped', which regenerates the fully atomistic model in continuous space [11]. The reverse mapping recovers excellent local intrachain (population of torsion angles) and interchain (pair correlation functions) properties [11]. The simulation also produces excellent longer range properties, such as cohesive energy density

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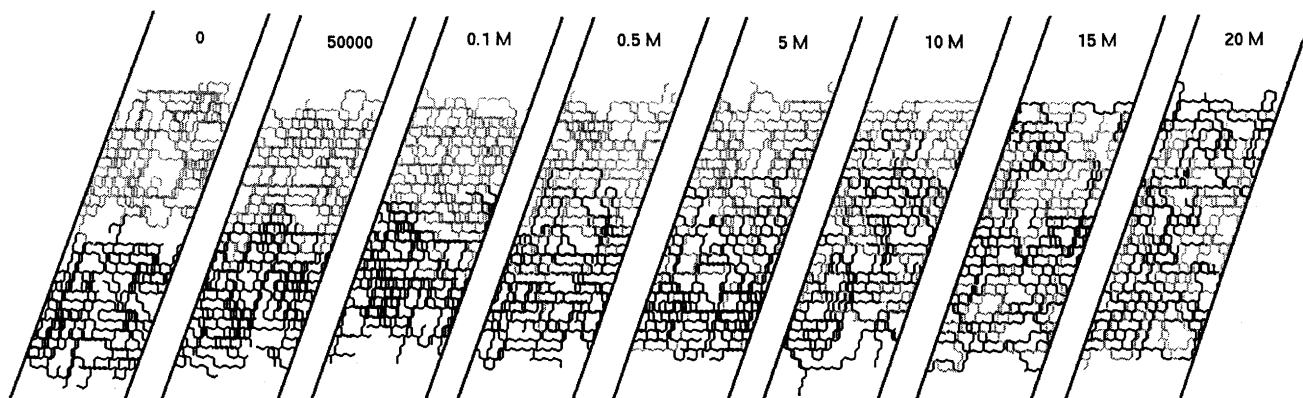


Fig. 1. Projection onto the xz plane of snapshots in the initial state (0 steps), after complete intermixing (20×10^6 MCS), and at six intermediate times (0.05 , 0.1 , 0.5 , 5 , 10 , and 15×10^6 MCS). The contrast in darkness distinguishes the coarse-grained C_{99} chains that were in the two original films.

in the bulk [10,11] and surface energies of thin films [12], both when in the coarse-grained representation on the 2nd lattice, and also after reverse mapping back to the fully atomistic structure in continuous space. The efficiency of the simulation on the lattice provides the possibility of the study of diffusion of the centre of mass over a distance greater than the radius of gyration of the chains. This efficiency, along with the ability to create thin films with excellent surface properties, suggests the method can be applied to the study of the mechanism of cohesion of two films. The preliminary demonstration of the successful application of the method to this purpose is presented here, using two thin films composed of melts of $C_{99}H_{200}$ (C_{99}).

2. Computations

A periodic box containing a monodisperse melt of nine parent chains of C_{99} was mapped onto the 2nd lattice. The periodicity along the three axes of the 2nd cell was $13 \times 13 \times 15$ steps (measured in terms of the step length, 2.50 \AA , on this lattice [9]), giving a density of 0.74 g cm^{-3} . The mapping discards all of the hydrogen atoms and every second carbon atom, so that each parent chain of C_{99} is represented by 50 beads. This film was relaxed at 443 K, using the single bead moves described previously [9–11]. The bulk structure was converted to a thin film by the method of Misra et al. [13], which involves expansion of the periodicity along the z

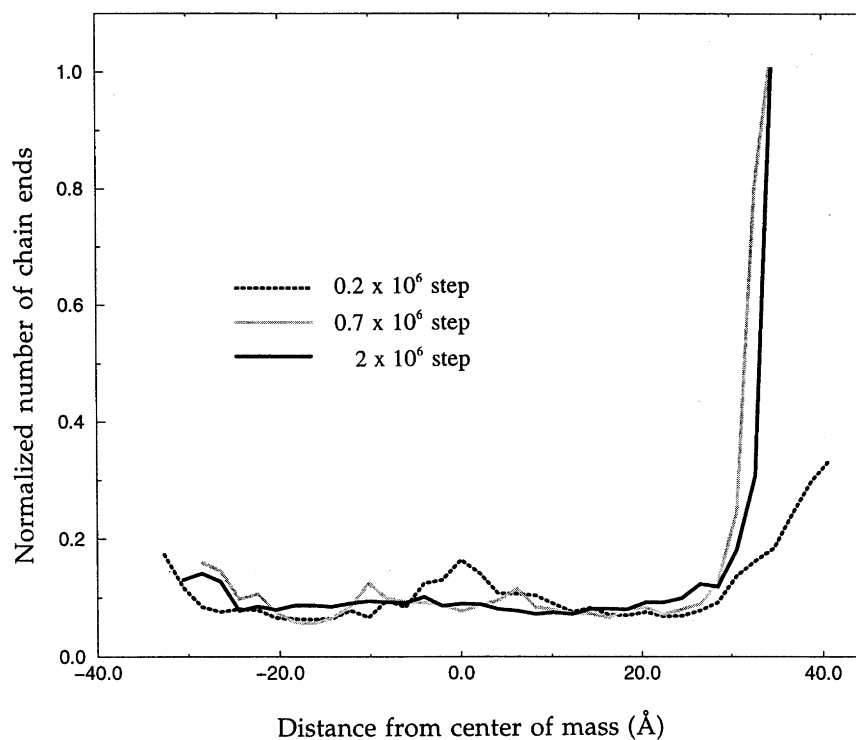


Fig. 2. Distribution of chains ends (normalized by the total number of beads at that z) at 0.2 , 0.7 and 2×10^6 MCS. The original interface is at 0.0 on the horizontal axis.

axis to $13 \times 13 \times 120$, followed by a new relaxation. This method produces a thin film with a surface energy in excellent agreement with experimental values [12]. Images of two such films, previously equilibrated with both surfaces exposed to a vacuum, were placed in a single periodic cell of size $13 \times 13 \times 120$, such that the two films were as close to one another as possible without generation of repulsive interaction between any pair of beads. This structure was used as the starting point for a simulation of 40×10^6 Monte Carlo steps (MCS) on a R10000 Silicon Graphics workstation.

3. Results and discussion

Fig. 1 depicts several snapshots from the beginning of the simulation of the two separate films to their complete intermixing. The 'reverse mapping' procedure allows conversion of each of these replicas of the coarse-grained chains on the 2nd lattice into a relaxed replica of the fully atomistic chain in continuous space [11]. The snapshots are left on the 2nd lattice in Fig. 1 because that representation makes it easier to appreciate the extent of interpenetration of the chains from the two films.

At least three processes, occurring on distinctly different time scales, can be identified in the simulation. The fastest process is detected by examination of the density profile along the z axis (normal to the surfaces of the two films). Initially there is a minimum in density at the region of contact between the two films, due to their placement so that none of the beads from one film overlaps a bead from the other film. This region of low density is apparent in the first snapshot in Fig. 1. The rapid movement of the two films toward one another, and rearrangement of their structures, heals this density profile within 0.5×10^6 MCS, after which the original minimum in density is no longer evident. This process is sensitive to redistribution of chain segments on distance scales much smaller than the radius of gyration of the chains.

The chain end reveal another process, which occurs on a slower time scale. The population of chain ends is enriched at both surfaces of an equilibrated thin film [12]. Therefore, the starting structure has an excess of chain ends at the position of the original minimum in the density profile along the z axis, because this position corresponds to one of the two surfaces of each of the original films. The excess of chain ends is still apparent after 0.2×10^6 MCS, as shown by the local maximum at the position of the interface in Fig. 2. After 0.7×10^6 MCS, there is no longer an excess of chain ends at the precise position of the original interface, but two smaller maxima, located roughly 6–10 Å on either side of the position of the original interface, can be seen. The profile in the vicinity of the original interface is flat after 2.0×10^6 MCS, and there is no evidence of an excess of chain ends inside the new film. This process is determined by the rate at which the chain ends diffuse substantial

distances along the z axis. Their diffusion may occur within one of the original thin films; the chains (or chain ends) do not need to move across the original interface. The curves in Fig. 2 could be made smoother by averaging over more snapshots near the specified time (by opening the time window for each curve). The data in the two wings, near ± 30 Å, is especially susceptible to statistical inaccuracy due to the small number of beads at these edges of the film.

The slowest process is detected by monitoring separately the centres of mass of the beads from the two original films. In the starting structure, these two centres of mass were separated by about 43 Å along the z axis. Intermixing of the chains from the two films causes these centres of mass to approach one another as the simulation progresses. The two centres of mass become coincident, at the midpoint of the newly equilibrated thin film, by 20×10^6 MCS. The last snapshot in Fig. 1 provides a visualization of the completion of the mixing of the chains at this stage of the simulation. This process is controlled by the rate at which entire chains diffuse along the z axis (and across the interface) over a distance exceeding the radius of gyration. The time for completion of the mixing will depend on the thickness of the two original films. The simulation reported here started with two films that each had a thickness of nearly 40 Å. Thicker films can be simulated with this method [12].

The translational diffusion coefficient of C_{99} at 443 K can be obtained from the simulation in units of $\text{cm}^2 (\text{MCS})^{-1}$. The conversion of the Monte Carlo step into real time can be achieved by comparison of this diffusion coefficient from the simulation with the one from the experimental study of self-diffusion for small n -alkanes, reported by von Meerwall et al. [14]. On this basis, one Monte Carlo step in the specific simulation in Fig. 1 is equivalent to 10^{-14} s. This time step can be varied over a rather large range in the simulations of amorphous polymers in the bulk, depending primarily on the number of shells included in the description of the intermolecular interaction and the extension of the chain produced by the parameters in the Rotational Isomeric State model. A recent analysis gives an accessible range of 1–171 fs per MCS for polyethylene melts [15].

Detailed analysis of simulations such as the one described here should produce a description of the mechanism by which cohesion occurs in systems that are on the verge of being entangled. The efficiency of the Monte Carlo simulation on the coarse-grained lattice may also permit simulation of this process in films composed of longer chains, where entanglement effects may become important.

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