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SIMULATION OF INTERMEDIATE ORDER IN POLYMERIC GLASSES

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SUMMARY: The glass phase of most polymers is typically considered amorphous. However, many commercially important polymer glasses do contain a subtle level of structural order intermediate between the crystalline and truly amorphous phases. These include a number of commercially important polymers. This "Intermediate Order" is distributed homogeneously throughout the glass phase and is therefore quite different than the morphology of semi-crystalline materials. Typical computer simulation methods can fail to accurately reproduce the structure of polymers with intermediate order, because they are often based on the assumption that the polymer structure is truly amorphous. Given the subtle nature of this order, computer simulation is important in understanding this structural order and the unique material properties commonly associated with it. We outline the critical issues required for the successful simulation of polymer glasses with intermediate order, and discuss the results of some continuing research designed to improve the accuracy of such simulations.

Introduction

Polymer glasses are typically considered amorphous, however, many commercial polymer glasses contain a subtle level of structural order intermediate between crystalline and amorphous phases. This "Intermediate Order," is not simply a spatial combination of amorphous and crystalline domains as observed in semicrystalline polymers. It includes atomic-level structural correlation that is often difficult to differentiate as separate domains in the polymer glass. A qualitative indication of intermediate order is seen in the Wide Angle X-ray Diffraction (WAXD) pattern illustrated in Figure 1. Unlike the amorphous pattern, which has a single broad peak at $Q \approx 1 \text{Å}^{-1}$, intermediate order usually occurs when this peak is split into two or three broad reflections. Mitchell illustrates this with a comparison of WAXD results for natural rubber and poly(n-butyl methacrylate).[1] Intermediate order also appears to exist in a number of other commercial polymer systems including poly(vinylchloride),[2,3] poly(t-butyl acetylene),[4] cellulose acetate,[5] poly(norbornene),[6] polystyrene,[7] and poly(ethylene terephthalate).[8]

Most polymer glass simulation protocols are derivatives of a method formulated by Theodorou and Suter.[9] This approach assembles one or more polymer chains in a spatially periodic cell, where each torsion angle is chosen from an unperturbed distribution that also accounts for intermolecular interactions. Variations of this procedure exist in commercial

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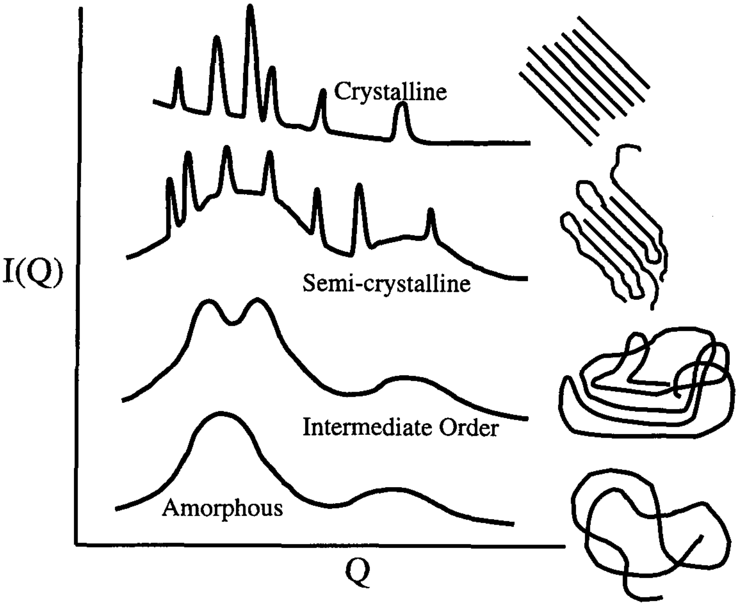

Fig. 1: Schematic of various types of structural order and their representative wide angle x-ray diffraction intensities vs. the magnitude of the scattering vector (Q).

modeling packages.[10] After generating a small ensemble of these initial model conformations, these models are then relaxed using either energy minimization,[9,11-13] or molecular dynamics (MD).[14,15] The models are in local energy minima, not global free energy minima, but this is consistent with the non-equilibrium nature of a glass. Additional information on general issues of glassy polymer modeling is available in two review articles.[16,17] This basic algorithm has been applied to a number of different polymer glasses including atactic poly(propylene),[9] atactic poly(vinyl chloride),[11] aromatic poly(sulfone),[14] cis poly(t-butyl acetylene),[13] bisphenol-A poly(carbonate),[12] and others.[18] This simulation protocol has been successful in reproducing the diffraction patterns of truly amorphous polymers such as atactic poly(propylene)[19] and Bisphenol-A Polycarbonate[20] because they adopt a truly amorphous arrangement in the glassy state.

Intermediate Order from *Inter*molecular Interaction

Poly(vinyl chloride) (PVC) provides a good illustration of the failure of the above algorithm to accurately reproduce intermediate order. It fails because the strong intermolecular interactions that occur in PVC are not properly included in the initial conformation, and the semi-infinite viscosity of the glass phase prevents them from occurring during energetic relaxation. Intermediate order may be responsible for the thermoreversible gelation that occurs in PVC and makes plasticized vinyl tubing possible. This algorithm was applied to atactic poly(vinyl chloride) and the resulting simulated structures were used to calculate the WAXD patterns seen in Figure 2.[2,11] These calculations for two different sized periodic models were compared to the experimentally measured WAXD pattern in Figure 2. The pronounced difference between different sized models indicates a clear dependence on model size. Although the simulations failed to reproduce the experimental WAXD patterns, they produced a non-amorphous pattern. Analysis of the structural order in these models suggested that strong intermolecular electrostatic interactions between the chloromethine groups are responsible for the observed order. We hypothesize that if the initial conformations are generated with enhanced polar interactions the models would more accurately reflect the intermediate order observed in PVC.

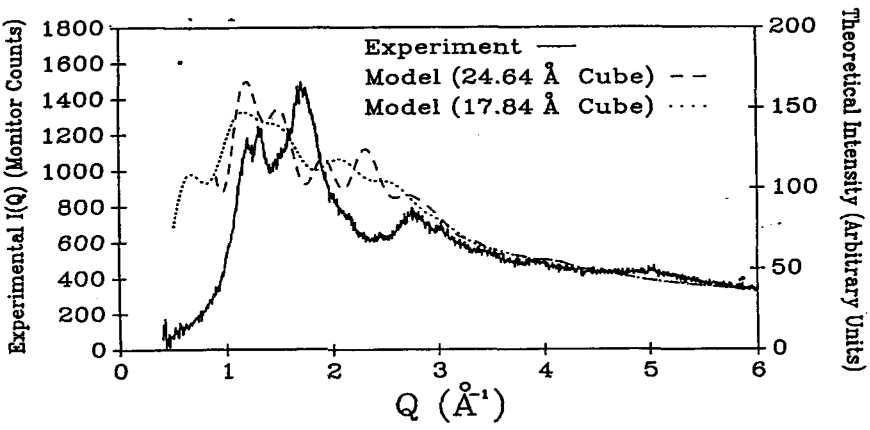

Fig. 2: Simulated wide angle x-ray diffraction intensity for atactic PVC compared to the experimental measurement. The larger model was 1 periodic cube of 200 monomeric units and the small model was 12 cubes of 76 monomeric units.

Improved relaxation algorithms are discussed below, but here we explore the possibility of biasing the initial conformation to more accurately reflect the intermediate order. Figure 3 contains a simulated WAXD pattern obtained from aligning 4 chains with 20 monomers and enhancing the partial charges on the chloromethine groups by a factor of 100 during the initial conformation generation followed by energetic relaxation using the CERIUS^2 program from MSI.[21,22] Although this WAXD pattern compares more favorably to the experimental results than the prediction in Figure 2, the predicted pattern is shifted to higher angle or higher Q values implying that the simulated model density was simply too high. The model used a density averaged from the literature of 1.39 g/cm^3, but subsequent measurement revealed an actual density of 1.35 g/cm^3 for this particular sample.[21] These are encouraging preliminary results but we are now obtaining WAXD patterns based on larger samples of periodic models with biased initial conformations at the correct density.

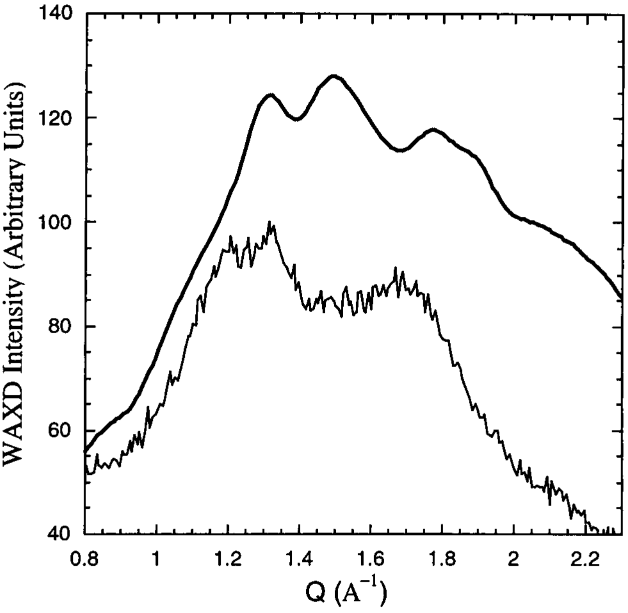

Fig. 3: Simulated WAXD intensity for PVC using biased initial conformation compared to the experimental pattern. The two patterns are offset vertically for clarity.

The experimental WAXD results in Figures 2 and 3 differ because the sample in Figure 3 had relaxed for over 10 years at ambient conditions. The observed increase could be related to an increase in the intermolecular order component of the intermediate order that is discussed below. This is more difficult to observe in high temperature annealing due to the dehydrochlorination reaction that occurs in PVC below its glass transition temperature.

Intermediate Order from *Intra*molecular Interactions

Because the Theodorou and Suter method can properly include intramolecular interactions, it should be effective for polymers that derive their intermediate order from such interactions, provided they are included in the torsional probabilities used to generate the initial conformations. Good examples of this polymer class include erythro di-isotactic poly(norbornene) (PNB) and cis poly(t-butyl acetylene) (PTBA), which posses no strong intermolecular interactions, but have strong intramolecular steric interactions. The steric nature of these two polymers causes them both to have a preferred conformation that is helical. We have simulated this helical conformation in PNB,[15,23,24] and Jacobson has modeled this in PTBA.[13] Both of these polymers exhibit a dominant helical conformation and a split in the amorphous halo of the WAXD pattern.[4,6,13,15,23] The low angle peak appears to be more intermolecular in nature than the high angle peak in the split. The PTBA model included only the helical conformation, whereas the PNB model had an occasional kink in the helix.[23] The helix-kink morphology was able to accurately predict the WAXD pattern for PNB, but the failure to include the kink in PTBA predicted an intermolecular peak too large relative to experiment. We therefore suspect that PTBA and other acetylene derivatives also exhibit this helix-kink morphology which is responsible for intermediate order in these polymers.

Potential Methods for Simulation of Intermediate Order

Because biasing the initial conformation requires some hypothesis of the nature of the intermediate order, a more general method might more broadly sample phase space to properly relax polymers in the glass state. Although stochastic methods such as Monte Carlo algorithms are attempting to address this issue, they require an efficient conformational perturbation that efficiently samples phase space for all classes of polymers. We suggest that increasing the local fluctuations of deterministic methods such as MD may be more general. Our initial algorithm is derived from the Langevin equation (equation 1). The Langevin equation describes the time derivative of the momentum (p_i) of any given atom i

$$\dot{p}_i = F_i + \Gamma_i - \gamma p_i \qquad \text{(equation 1)}$$

where F_i is the force on atom i due to the surrounding polymer, Γ_i is a random stochastic force that is applied to atom i, and γ is a damping factor. The random force is gaussian distributed such that its first moment is zero, but we do not use the generalized Langevin equation to derive the typical relationship between the second moment and the damping factor. Further we use random forces that are not delta-correlated in time. This means that they are applied for more than one integration time step in the dynamics algorithm, making this a colored noise process. Hangii has shown that colored noise can broaden the sampling of phase space relative to the equivalent white noise process.[25] A Nosé-Hoover type controller is applied to the damping parameter (γ) to constrain the system to a constant average temperature (T_{ave}) as seen in equation 2 where Q is a relaxation time.[26]

$$\dot{\gamma} = \frac{1}{Q}\left(\frac{T(t)}{T_{ave}} - 1\right) \qquad \text{(equation 2)}$$

We have carried out some preliminary studies that seem to suggest that this approach may work. Comparing a standard NVT algorithm on a 1 dimensional asymmetric double-well harmonic oscillator to this Modified Colored-Noise Dynamics (MCND) algorithm, we find that the latter algorithm permits sampling of the higher energy well while the NVT simulation did not. Both schemes utilized the same value of the temperature relaxation time (Q) and the MCND algorithm applied the stochastic force over 5 dimensionless time steps. The conformation space plots for the double well system, seen in Figure 4, indicate that the MCND algorithm more broadly samples phase space. Although application of the stochastic force for only 1 time step also allowed some sampling of the higher energy well, the resulting phase sampling was a simple periodic function that clearly did not sample as many conformations as the 5 step simulation. The standard deviation of the MCND simulation, in Figure 4, was equal to10% of the root-mean-square fluctuations in the NVT simulation. Preliminary results on Lennard Jones glasses suggest that the MCND algorithm is more effective than NVT simulation. In addition to colored noise, algorithms such as these can increase fluctuations by decoupling the width of the stochastic force distribution from the damping factor. This potential violation of the fluctuation dissipation theorem is not important given our interest in the final conformation and not the dynamic trajectory.

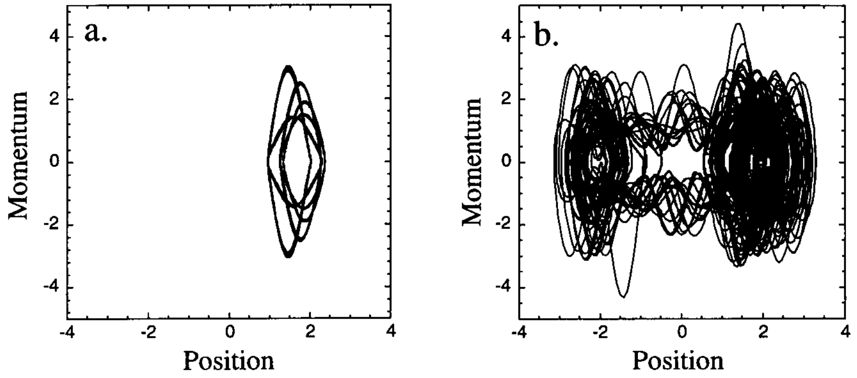

Fig. 4: Phase space maps of NVT (a) and MCND (b) simulations of a particle in an asymmetric double well potential with minima at ±2.

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