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Competition Between Liquid-Crystalline Ordering and Glassy Freezing in Melts of Semiflexible Polymers: A Monte Carlo Simulation

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SUMMARY: We present results of a Monte Carlo simulation of dense melts of semiflexible polymers using the bond-fluctuation model. The chosen Hamiltonian increases the chain stiffness upon cooling which in turn leads to glass-transition like freezing of the polymer mobility. Employing an efficient simulation algorithm, which is able to equilibrate the simulated systems to lower temperature than the Rouse-type algorithm showing the glassy freezing, we are able to observe an isotropic-nematic phase transition. This transition lies above the glass transition temperature one would extrapolate from the observed freezing behavior.

Introduction

The amorpous state is ubiquitous in polymeric materials and therefore has a longstanding history of experimental and theoretical research. In the last decade there has also been an increased interest in computer simulation studies of the glass transition in polymers, see e.g. the review articles in Chaps. 5 and 6 of [1]. As a rule of thumb these studies have all been limited to a temperature range spanning about $2-3$ orders of magnitude in relaxation time from the high temperature side, as far as the treatment of thermodynamic equilibrium behavior is concerned [2]. The same holds true for simple glass forming systems also [3].

On the other hand it was argued that the excess scattering at small momentum transfers that one observes for some organic glass forming materials [4] may be due to the buildup of orientational correlations between the strongly asymmetric molecules of glass forming systems [5]. Furthermore recent nuclear magnetic resonance experiments on polybutadi-

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ene melts at temperatures well above the glass transition temperature were interpreted as showing unexpectedly strong nematic correlations between neighboring chains [6]. We therefore want to analyze a model with a built-in competition between glassy-freezing and nematic ordering.

Model and Simulation Technique

We use the three-dimensional version of the bond-fluctuation lattice model [7,2]. Each monomer occupies the eight corners of a unit cube on the simple cubic lattice, i.e. its size is $V = 2^3$ in units of the lattice constant. The bonds connecting the monomers are generated out of the set $\mathcal{B} = \{(2,0,0),(2,1,0),(2,1,1),(2,2,1),(3,0,0),(3,1,1)\}$ by all possible lattice symmetry operations. Two monomers whose centers are connected by the largest bond length are still so close, that no other monomer can pass between them (chain connectivity). Temperature is introduced by the following Hamiltonian

$$H(\{l\},\{\theta\}) = \sum_{\{l\}} \epsilon_l \,(l - l_0)^2 + \sum_{\{\theta\}} \epsilon_\theta \cos(\theta)\,(1 + c_0 \cos(\theta_0))^2 \qquad (1)$$

which contains only intramolecular degrees of freedom. $\{l\}$ denotes the set of all bond lengths and $\{\theta\}$ denotes the set of all bond angles. $\epsilon_l = 1$ defines the energy scale of the model (temperatures will henceforth be given in units of ϵ_l) and we choose $\epsilon_\theta = 0.67$, $l_0 = 0.86$ and $c_0 = 0.03$. The Hamiltonian therefore favors short bond lengths ($l_{\text{min}} = 2$) and stretched bond angles ($\theta = \pi$). At high temperatures these chains are known to conform to the Gaussian statistics of polymer chains in the melt [7,2] and the ground state of each chain is a rigid rod with all bonds collinear and of type $(2,0,0)$. The contour length of the chains in the ground state is $2N$ lattice units and its width is that of a monomer, i.e. $d = 2$.

The intermolecular interaction in the model is pure excluded volume interaction, realized in the lattice model by prohibiting double occupancy of lattice sites. We will discuss simulations performed at a constant polymer volume fraction of $\Phi = 0.5$ and for chains of length $N = 20$ and for linear system sizes from $L = 30$ to $L = 130$.

At low temperatures a Monte Carlo simulation using Metropolis rates exhibits an exponentially decreasing acceptance rate and the polymer mobility will even show a Vogel–Fulcher like decrease. One important technical advantage of the bond-fluctuation model at this volume fraction is the ability of the slithering snake reptation algorithm to equilibrate the simulated system much closer to the glass transition temperature [8] , although at the cost of introducing an artificial dynamics into the simulation. Despite the fact that our largest system size $L = 130$ means that we have almost 1.1 million monomers in the system, times of order 10^7 MCS per monomer can be reached.

Glassy Freezing

The high temperature melt dynamics of the short chains we are simulating in this work is well described by the Rouse model [9] describing the entropic motion of one chain in an effective medium (friction ζ, stochastic forces $d\vec{W}_n(t)$).

$$\zeta d\vec{r}_n(t) = \frac{3k_BT}{\sigma^2}\left(\vec{r}_n + 1(t) - 2\vec{r}_n(t) + \vec{r}_{n-1}(t)\right) dt + \sqrt{2\zeta k_BT}d\vec{W}_n(t) \ . \qquad (2)$$

The model contains one length scale, the statistical segment or Kuhn length σ, and one time scale, usually taken as the end-to-end vector decorrelation time,

$$\tau_r = \zeta N^2\sigma^2/3\pi^2 k_BT \ , \qquad (3)$$

where N is the chain length. An equivalent definition of this time scale can be derived from the center of mass motion of the chains.

$$\langle(\Delta R_{cm})^2\rangle(\tau_{msd}) = R_g^2 \Rightarrow \tau_{msd} = \frac{\pi^2}{12}\tau_r \qquad (4)$$

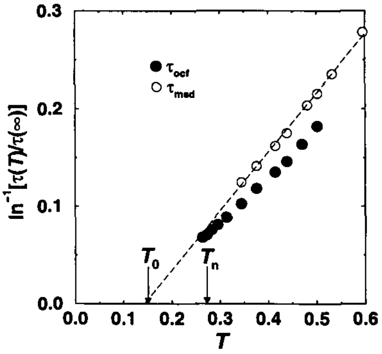

FIG. 1. Longest relaxation time of the chains as obtained from the center of mass motion (open circles) and orientational autocorrelation time of the bond vectors (full circles) as a function of temperature. The chosen form of the plot reduces to a straight line for a Vogel-Fulcher behavior.

This longest relaxation time of the polymer chains is usually found to follow the typical α-relaxation behavior of the polymer glass transition, which is phenomenologically described by a Vogel-Fulcher law

$$\tau_{msd}(T) = \tau_{msd}(\infty) \exp\left\{\frac{E}{T - T_0}\right\} . \tag{5}$$

Figure 1 shows a linearized version of the Vogel-Fulcher behavior, which employs the value of $\tau_{msd}(\infty)$ which we can measure in a Monte Carlo simulation without the employed Hamiltonian. For the center of mass mean square displacement shown by the open symbols we can see a clear signature of the glassy freezing of the melt, at par with other published simulation studies in the literature. The displayed range of relaxation times covers again 2.5 orders of magnitude. The Vogel-Fulcher temperature comes out to be $T_{VFT} = 0.15$.

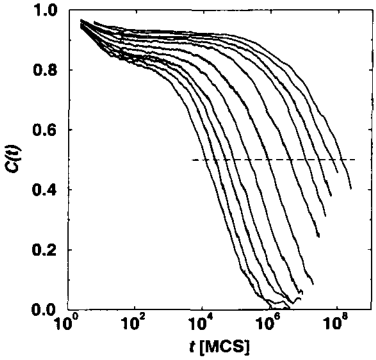

FIG. 2. Second Legendre polynomial of the bond vector autocorrelation for temperatures ranging from $T = 0.5$ for the downmost curve to $T = 0.26$ for the uppermost curve.

We can observe the slowing down in the melt as well, looking at orientational correlation functions. One easily accessible orientational correlation function is the second Legendre polynomial of the bond vector autocorrelation.

$$C(t) = \frac{1}{2}\left[3\left\langle(\hat{u}_i(t)\cdot\hat{u}_i(0))^2\right\rangle - 1\right] \tag{6}$$

Here $\hat{u}_i$ is a unit vector along bond i. This function is displayed in Fig.2 for temperatures between $T = 0.5$ (downmost curve) and $T = 0.26$ (uppermost curve). Through $C(\tau_{ocf}) = 0.5$ we define a typical orientational autocorrelation time. This time scale is also shown in Fig.1. At low temperatures, which were only accessible starting from configurations that had been equlibrated with the slithering snake algorithm, this time scale clearly does not show a Vogel–Fulcher behavior. In this temperature range the dynamics is governed by the isotropic-nematic phase transiton we observe in the model.

Isotropic-Nematic Transition

To monitor an isotropic-nematic transition in a computer simulation one can evaluate the Saupe-tensor [10] to quantify the orientational correlations in the system.

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{N} \left\{ \frac{3}{2} u_{i\alpha} u_{i\beta} - \frac{1}{2} \delta_{\alpha\beta} \right\} \tag{7}$$

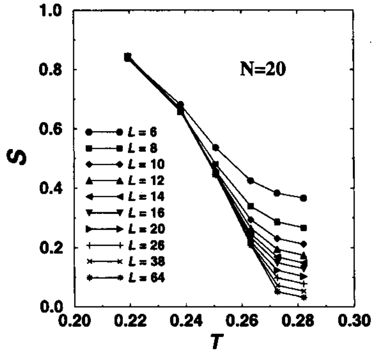

FIG. 3. Nematic order parameter as a function of temperature evaluated for the sub-box sizes of a system of linear dimension $L = 130$ which are denoted in the legend.

The largest eigenvalue of this tensor can be used to define the nematic order parameter, S, which is shown in Fig.3. The different curves show the order paramter evaluated in sub-boxes of the simulation box which had a linear dimension $L = 130$. For temperatures larger than approximately 0.27 the order parameter vanishes with increasing sub-box size, indicating the disordered state. At low temperatures its value is independent of the sub-box size, typical for the ordered state. For a finite size scaling analysis of this first order phase transition one best uses the second order cumulant $g_2^0 = \langle \lambda_0^2 \rangle / \langle \lambda_0 \rangle^2$ of the intermediate of the three eigenvalues of the Saupe tensor [11,12] as shown in Fig.4.

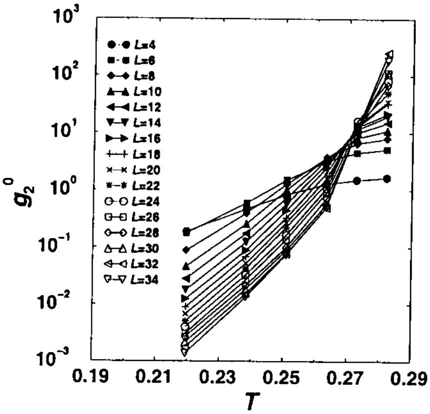

FIG. 4. Finite size scaling plot of the second order cumulant of the intermediate eigenvalue of the Saupe tensor. The intersection points between sizes L and $L+2$ converge to the first order phase transition temperature.

The resulting isotropic-nematic transition temperature $T_n = 0.271$ is sufficiently high above the extrapolated glass transition temperature in this model, that it was possible to observe this purely entropy driven Onsager-type [13] transition in a lattice simulation, contrary to earlier work [14,15]. The temperature dependence of the orientational autocorrelation time can also be consistently understood within the context of this transition as Fig.5 shows.

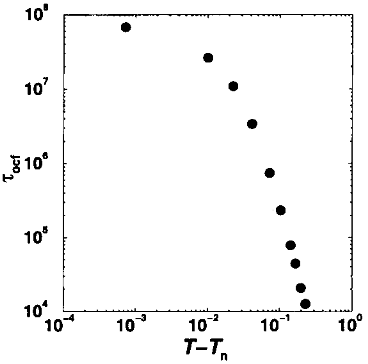

FIG. 5. Rounded algebraic increase of the orientational autocorrelation time as a function of the distance to the isotropic-nematic transition temperature.

Conclusion

We have shown Monte Carlo simulation results for a competition between glassy freezing and liquid crystalline ordering for a model of a melt of semiflexible polymers. The relative order between glass transition temperature and isotropic-nematic transition temperature depends on chain length and density. For our choice of parameters the isotropic-nematic transition occured sufficiently far above the glass transition to be observable in the simulation. For shorter chains, which reach the critical aspect ratio [16] for the transition only at lower temperatures the situation is expected to be reversed, so that the glass transition may mask the orientational ordering.

In this context it is also interesting to note, that an earlier analysis of the Gibbs-DiMarzio entropy theory of the glass transition in a model closely related to the one studied here [17] showed, that the expressions of Gibbs-DiMarzio [18] for the entropy of the supercooled melt and Flory's prediction [19] for the entropy of a disordered polymer melt approaching the isotropic-nematic transition yield identical results when evaluated for a given supercooled polymer melt.

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