

# Glass Formation in a Lattice Model for Living Polymers

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We study glass formation in a lattice model for living, semiflexible polymers. Our model exhibits logarithmically slow relaxation out of quenched, metastable configurations, a frustration-driven glass to crystal transition, and an exotic lamellar glass. We propose a Monte Carlo analog of scanning calorimetry and use it to study these glasses. We discuss the relevance of our work to experiments and to some theories of the glass transition in model systems.

Strongly viscoelastic, glassy states have been found in water-surfactant mixtures with threadlike micelles [1]. These micelles are "living" polymers: Unlike conventional polymers, their lengths fluctuate leading to a temperature-dependent equilibrium length distribution. Dilute systems of living polymers were studied first [2]; systems dense enough to yield solid assemblies are being investigated now [1,3,4]. These living polymers are semiflexible since it costs energy to bend them: at low temperatures ( $T$ ) they straighten and favor the formation of ordered phases, but, given laboratory cooling rates, entangled gels (or glasses) form more readily. It has been suggested [5] that liquid sulfur and selenium, poly( $\alpha$ -methylstyrene), and protein filaments are also living polymers. In this Letter we present the first study of glass formation in a model for semiflexible, living polymers [5].

Given the complexity of polymeric melts, it is customary to follow Flory [6] and use lattice models [3,7] for them. We study a three-dimensional version of a lattice model proposed by us [3]. Our model, unlike Flory's, allows for polydispersity, vacancies, and closed rings. We concentrate on glass formation in our model; its equilibrium behavior is given elsewhere [3].

In our simple-cubic model, occupied links are monomers (at most 1 per link). They fuse to form self-avoiding polymer chains (only two monomers can merge at a site). Semiflexibility is built in via an energy  $e > 0$  for every site with a right-angle bend in a chain. An open chain end costs an energy  $h$ , a vacancy chemical potential  $\mu$  is associated with a site at which all bonds are vacant, and  $J > 0$  is an attractive interaction between next-nearest-neighbor, parallel monomers [8]. We choose  $e = 1$  to set the energy scale, use  $J = 0.3$  and  $\mu = 2$  for specificity, and vary  $T$  and  $h$ . The low- $T$  ordered state is characterized by three order parameters:  $M_{xy} = (N_y - N_x)/N_L$ ,  $M_{yz} = (N_y - N_z)/N_L$ ,  $M_{xz} = (N_z - N_x)/N_L$ , where  $N_x$ ,  $N_y$  and  $N_z$  are, respectively, the numbers of occupied links in the  $x$ ,  $y$ , or  $z$  directions, and  $N_L$  is the number of links occupied in the triply degenerate ground state (all polymers along the  $x$ ,  $y$ , or  $z$  directions).

Our extensive Monte Carlo simulations reveal a variety of interesting behaviors: In equilibrium our model has a first-order transition from a high- $T$  disordered state to a low- $T$  ordered one. The order parameters, internal energy ( $E$ ), and mean polymer size ( $\ell_{av}$ ) are discontinuous at this transition [3]. Quenches from the disordered phase to low  $T$  yield metastable states which are disordered for large  $h$  ( $> 3$ ) or partially ordered "lamellar glasses" (a one-dimensionally disordered stacking of ordered layers of polymers) for  $1 < h < 3$ . These metastable states relax slowly: For large  $h$  ( $> 3$ ) local rearrangements are suppressed and the temporal evolution of  $E$  [Fig. 1(a)] is logarithmic. Data for the vacancy concentration  $N_v$  and order parameters are similar, though noisy for the latter. For intermediate  $h$  [Fig. 1(b)] quenched configurations evolve into a lamellar glass over a time  $\tau_{lg}$  [ $\sim \exp(2\beta/h)$ , where  $\beta = 1/T$  (Boltzmann constant  $k_B = 1$ )]. Figure 2(a) shows the system falling out of equilibrium as it is cooled at a finite rate, and Fig. 2(b) shows a Monte Carlo analog of scanning calorimetry. Figures 2(a) and 2(b) are in qualitative accord with the behavior of real polymeric glasses [9]. Order-parameter autocorrelation functions are slowly decaying exponentials for shallow quenches, but for deeper ones these decays are too slow to obtain reliable fits. Lowering  $h$  eases the frustration in the disordered network obtained on quenching; this induces a glass to crystal transition (apparently continuous for the scans in Fig. 3), but one that is not related to an underlying equilibrium phase transition (see below).

We use lattices of (linear) size  $L = 16$  (i.e.,  $3 \times 16^3$  links), and the algorithm of Metropolis *et al.* [10], with single-link updates and, at intervals of 10 Monte Carlo steps per link (MCS), multilink moves [3] that help low- $T$  equilibration. Our updates do not conserve monomers, vacancies, or order parameters. Nonetheless, glassy behavior obtains when we quench from high  $T$  to  $T < T_c$  (the equilibrium crystallization temperature = 1 — 1.3 for our parameter values) or even when we cool from high to low  $T$  at steady, but not too slow, rates.

For quenches we start with short chains ( $\ell_{av} = 4$ ), obtained by equilibration at  $T = 10$  and  $h = 1.2$ , and

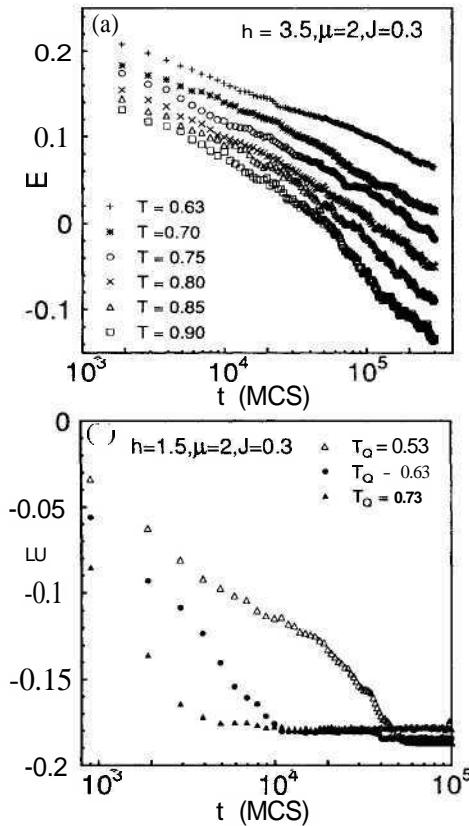


FIG. 1. The energy  $E$  vs time  $t$  after a quench to  $T = T_Q$  for  $L = 16$  showing (a) a logarithmic decay at large  $h$  and (b) a somewhat faster decay at intermediate  $h$ . In (b) the system eventually becomes a lamellar glass and  $E$  does not evolve over our  $t$  range.

reduce  $T$  in one step to  $T_Q < T_c$ . We compute  $E, N_v$ , etc., at a time  $t$  (in MCS) by averaging over 20 measurements, centered at  $t$ ; each measurement is made every 10 MCS; we follow the time evolution for  $(3 - 6) \times 10^5$  MCS. Different initial configurations, including ones at  $T = \infty$ , yield qualitatively similar results.

For small  $h$  ( $< 1.5$ ) quenches yield configurations that evolve over 100-1000 MCS to the equilibrium crystal. For intermediate values ( $1.5 < h < 3$ ) the quenched system evolves, in a time  $\tau_{lg}$ , to a lamellar glass; order parameters saturate to values between 0 (the high- $T$  value) and 1 (the perfect crystal). Our data [Fig. 1(b)] are consistent with  $\tau_{lg} \sim \exp(2\beta h)$ . Once formed, these lamellar glasses do not evolve substantially even if annealed for  $\sim 10^6$  MCS, since a large number [at least  $O(L^2)$ ] of local updates are required to align all planes.

At large  $h$  ( $> 3$ ), quenches yield complex, disordered structures, which evolve slowly: Order parameters,  $E$ , and  $N_v$  all vary logarithmically, especially for the deepest quench [ $10^3 < t < 2 \times 10^5$  MCS in Fig. 1(a)]. Such logarithmic behavior often occurs in disordered systems. However, in our model disorder does not arise because

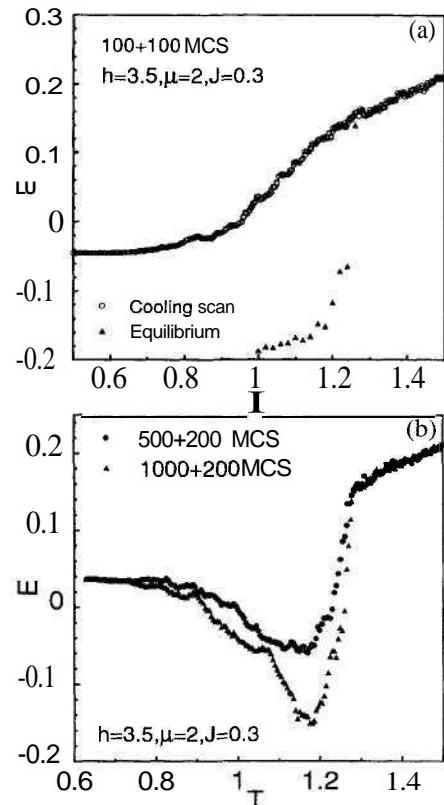


FIG. 2. (a) The evolution of  $E$  with temperature  $T$  on steady cooling (circles) to  $T < T_c$  at large  $h$  [ $= 3.5$  here with annealing and recording times (see text)  $t_a = t_r = 100$ ] and in equilibrium (triangles). (b)  $E$  vs  $T$  for our Monte Carlo scanning calorimetry (see text) after a quench to  $T_Q = 0.63$ . We use two heating rates indicated by circles ( $t_a = 500$  and  $t_r = 200$ ) and triangles ( $t_a = 1000$  and  $t_r = 200$ ). At the slower heating rate (triangles), the glass transforms more effectively into a crystal (the flat minimum in the curve with  $E = -0.17$ ; for the ordered crystal  $E = -0.2$ ) before it melts eventually into the disordered high- $T$  phase.

of random couplings but is generated dynamically by the quench, as in conventional glasses. The slow decrease of  $N_v$  is reminiscent of the volume contraction seen during the aging of polymeric glasses [11], normally ascribed to decreasing "free volume" as in some theories [12].

A glass also forms if we cool the system at a finite rate (not slow enough for equilibration) through  $T_c$ : We begin with equilibrated configurations at  $T = 1.5$  and lower  $T$  in steps of 0.005. The time  $t$  (MCS) that we spend at a particular  $T$  (or  $h$  in Fig. 3) in our scans is divided into an annealing time  $t_a$  ( $\approx 200 - 1000$  MCS), during which we do not record data, and a recording time  $t_r$  ( $\approx 100 - 200$  MCS), in which we collect data for averages every 10 MCS. Cooling or heating rates for Figs. 2 and 3 follow from  $t$ , given as  $t_a + t_r$  MCS. The  $h$  dependence of the morphologies of these glasses is similar to those obtained in our quenches: For  $h < 1.5$  our system can be supercooled just a little before it crystallizes. For  $1.5 <$

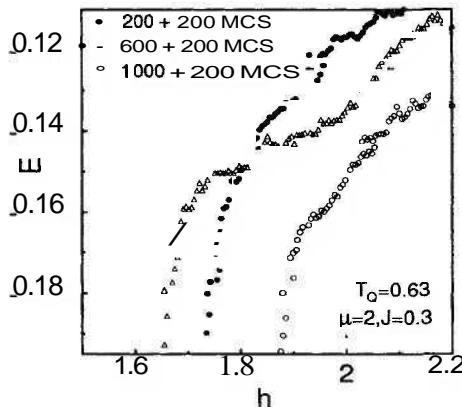


FIG. 3.  $E$  versus the frustration parameter  $h$  at three scanning rates (see text) with  $t_r = 200$  but  $t_a = 200$  (filled circles), 600 (triangles), and 1000 (open circles). As  $h$  is lowered from 3.5, its value when we quench to  $T_Q = 0.63$ , an apparently continuous glass-crystal transition occurs and  $E$  flattens out. The value of  $h$  at the transition depends on the scanning rate.

$h < 3$  the system falls out of equilibrium ( $E$  drops with  $T$  but not as sharply as in equilibrium [Fig. 2(a)]) to form lamellar glasses; for  $h > 3$  it freezes into a completely disordered configuration, but with slightly larger ordered patches than for instantaneous quenches.

We also study our model via a Monte Carlo analog of scanning calorimetry, which yields successive glass-crystal and crystal-liquid transitions by a steady heating of our glasses. As far as we know this is the first time scanning calorimetry has been adapted to Monte Carlo studies of glassy states. We quench the system from  $T = 10$  (see above) to  $T_c/2$ , anneal it for  $6 \times 10^5$  MCS, and then increase  $T$  at  $10^{-6}$  per MCS. We concentrate on large  $h$  ( $> 3$ ); for small and intermediate  $h$  we get crystals or lamellar glasses which melt directly to the disordered phase. Our data for large  $h$  show that heating transforms the glass into a crystal, which, on further heating, melts into the disordered phase.  $E$  drops sharply at the glass-crystal transition [Fig. 2(b)]; the range of  $T$  over which the crystal appears increases with decreasing heating rate. For sufficiently slow heating rates [triangles in Fig. 2(b)], both these transitions appear to be discontinuous. From Fig. 2(b) one can obtain  $d\langle E \rangle/dT$  (numerically); this yields the analog of an experimental differential-scanning-calorimetry plot [9] and shows both an exotherm (because of relaxation out of a high fictive-temperature state formed by the quench) and a sharp overshoot, as is often seen in rapidly cooled, annealed, and slowly reheated glasses [9,13]. The crystal-liquid transition resembles equilibrium melting. In some scans more complicated transitions obtain: the glass transforms to a crystal which reforms at a slightly higher temperature into a glass. This glass then becomes a crystal which melts to the disordered phase.

Glass formation occurs in our model because of local frustration induced by self-avoidance (which restricts updates involving the addition of monomers to the melt) coupled with a large barrier for the removal of a link (whose scale is set by  $h$ , for large  $h$ ). Thus  $h$  plays a crucial role in slowing down the kinetics; but, for large  $h$ , it plays a relatively minor role in determining the equilibrium  $T_c$  [3]. Hence we interpret  $h$  as a "frustration parameter" (like size ratios in a Lennard-Jones mixture [14]) and study  $E$ , etc., as  $h$  is changed: We prepare glassy configurations by annealing quenched configurations for  $6 \times 10^5$  MCS at  $T_c/2$ , and large  $h$  ( $h = 3.5$  in Fig. 3). We then decrease  $h$  in steps of  $5 \times 10^{-3}$ ; annealing and recording times  $t_a$  and  $t_r$  are as in Fig. 2. On decreasing  $h$  we get an apparently *continuous* transition:  $E$  decreases monotonically and smoothly to a value characteristic of the crystal. Figure 4, a smoothed numerical derivative of one of the curves (triangles), is similar to a susceptibility at a continuous, equilibrium transition. Such transitions have been invoked in some scenarios for the glass transition [15]. However, in our model there is no *equilibrium* transition underlying this frustration-driven transition. Firstly, the transition is not reversible: no crystal to glass transition occurs on increasing  $h$ . Secondly, our results depend on the rate at which  $h$  is changed; slower scans than those of Fig. 3 would make the transition disappear, for the glass would become a crystal at higher and higher values of  $h$ .

We have also studied temporal autocorrelations in the glasses obtained by annealing quenched configurations at different  $T < T_c$ . Autocorrelation functions like  $A^{(x)}(t) = \frac{1}{L^3} \sum_i [\langle \rho_x(i, t_0 = f_{\text{typ}}(i, t_0 = t) \rangle - \langle \rho_x(i, t_0) \rangle^2]$  and its  $y$  and  $z$  analogs can be fit to exponentials with large autocorrelation times, which increase as  $h$  is increased or as  $T$  is decreased. For  $h = 3.5$  and  $T = 0.7$ , these autocorrelation times are  $\approx 500$  MCS. For lower  $T$  or higher  $h$  our data indicate decays too slow and noisy to yield

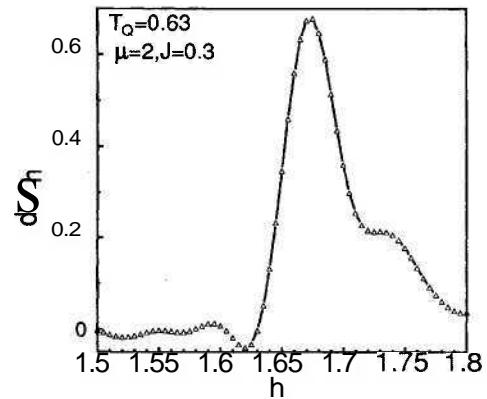


FIG. 4. A smoothed numerical derivative  $dE/dh$  vs  $h$  for the data of Fig. 3 for  $t_a = 600$  shows a peak at the apparently continuous glass-crystal transition.

meaningful fits, leaving open the possibility of nonexponential large- $t$  behaviors.

Lattice models for glass formation in polymer melts go back to Gibbs and DiMarzio [16], who extrapolated Flory's mean-field expression for the configurational entropy below its equilibrium transition temperature. They found a continuous transition to the glass; however, their work relies on the Flory approximation (inadequate in many cases, e.g.,  $d = 2$ ), and the (implicit) assumption that the low- $T$  extrapolation is meaningful. As mentioned above, our simulations show no underlying equilibrium glass transition. In recent MC simulations of glasses in a two-dimensional lattice model for a conventional polymeric melt, Ray and Binder [17] find glassy states with non-exponential decays of autocorrelation functions at low  $T$ . However, their model has an equilibrium transition only at  $T = 0$ , so it cannot yield scanning-calorimetric plots like ours, nor does it have a simple frustration parameter that can be varied. But since their simulation conserves the number of monomers, they can obtain diffusion constants which we cannot. Our model and the spin-facilitated model of Fredericksen and Andersen [18] have interesting connections, for, in both, relaxation at low temperatures occurs via highly cooperative moves. However, our model has the advantage that it yields both equilibrium freezing and glass formation. Of course, to model glass formation in real polymeric melts, we should, ideally, use a continuum description and enforce the relevant conservation laws. Conservation laws will, in general, lead to longer equilibration times and slower relaxation than in our model, in which no quantity is conserved.

Our study of a simple model shows how an interplay of semiflexibility, self-avoidance, and the energy cost for breaking chains leads to the vitrification of a melt of living polymers. Furthermore, our model is a good testing ground for theories of the glass transition, since frustration can be tuned easily. In a more general context, our model can be thought of as a spin model (or lattice gas) *without* quenched disorder which exhibits a transition to a glassy state at low temperatures [19]. It would be interesting to see whether lamellar glasses form in real polymeric melts or are merely an artifact of our lattice model. We hope our work stimulates experimental studies of glasses and gels in melts of living polymers.

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