Dynamics near the glass transition in two-dimensional polymer melts: a Monte Carlo simulation study

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Abstract. The glass transition in a lattice model (bond-fluctuation model) of a dense two-dimensional polymer melt has been studied using the Monte Carlo technique. Temperature is introduced in this model by associating energies with the bonds connecting the monomers in the chains. This creates competition between the energetic and geometric constraints within the system at low temperatures and the system becomes frozen. The frozen monomers and the persistence of such states are investigated in terms of an appropriately defined autocorrelation function. Attention has been paid to the various relaxation processes at different length scales. In particular, the global relaxation by the diffusion of the polymers, the Rouse relaxation at the scale of the chain length and the relaxation of the above-mentioned autocorrelation function involving the frozen monomers have been studied. The system is equilibrated at various temperatures down to $T = 0.22$ K and the results thus correspond to those in the limit of an infinitely slow cooling rate. No phase transition is observed in the temperature range studied. On all length scales the relaxation times exhibit a crossover from an Arrhenius behaviour at high temperatures to a behaviour closely fitted to the form $\tau \sim \exp(A/T^2)$ at low temperatures, where A is a constant independent of the relaxation processes. The increase of the relaxation times does not seem to be fast enough to explain a finite-temperature transition observed on quenching the system.

1. Introduction

Although much experimental and theoretical work has been carried out in order to understand the physical phenomenon behind the glass transition [1–3], it still remains highly controversial whether the transition can be characterized as a thermodynamic phase transition. A characteristic feature of the glass transition is the sharp rise of the transport coefficients, such as viscosity, inverse diffusion constant or relaxation times, in a narrow temperature range near the transition temperature T_g. This sharp rise, which is often fitted by the Vogel–Fulcher law [4], makes the glass transition very difficult to study. In most experiments and computer simulations the time scale is much smaller than the intrinsic relaxation time of the glass former and the system rapidly falls out of equilibrium. Hence, the study of any underlying thermodynamic transition, if there is one, is blurred by the non-equilibrium effects close to T_g and becomes almost impossible.

There have been many attempts (see [5, 6] and references therein) to search for the development of a structural order near the glass transition comparable to that near a second-order phase transition point [7]. However, none of the attempts have been successful up to now, which shows that the order in a glass, if there is any, is much more subtle and hidden than that of a conventional phase transition. According to the mode-coupling theory [3] of the glass transition, there may not be any growing static correlations as the transition

is approached, the overall structure of the glass former relaxes to a glassy phase with a drastic slowing down of the relaxation processes. A major prediction of the theory is that the dynamical correlations are completely decoupled from any static correlations near the transition (it is worth mentioning that the transition temperature in the mode-coupling theory is situated well above the calorimetric glass transition temperature). On the other hand, in spin glasses [8] the slowing down is always linked to the growth of static correlations related to the Edwards–Anderson (EA) spin-glass order parameter, and this has been observed experimentally by the analysis of a (diverging) static non-linear susceptibility. While it is believed [8] that the Ising spin glass in $d = 3$ dimensions does have an underlying static phase transition at a nonzero freezing temperature, other models such as isotropic spin glasses are believed to have a static phase transition at zero temperature only. Although in these latter systems the static length scale (meaning glass-like correlations) diverges at zero temperature only, the relaxation times become very large at much higher temperatures and the system falls out of equilibrium at some 'dynamic' freezing temperature. This makes the observable glass transition in isotropic spin glasses a purely dynamical phenomenon. In case of the structural glass transition of undercooled fluids, the situation is more difficult since in this case it is not obvious which type of static correlation one should look for. Recent molecular-dynamics simulation studies [6] of density and bond-angle correlation functions on a Lennard-Jones mixture have failed to see any growth of glass-like correlations even in the region of non-Arrhenius slowing down. But it must also be emphasized that the time scale accessible to such molecular-dynamics studies [5, 6] is very short, and in order to equilibrate the systems properly a very slow cooling is required; otherwise, if one cools the system too fast, both static [9] and dynamic [10] correlations are strongly suppressed.

Therefore we do not consider the issue of a growing static length underlying the glass transition as easy to settle. In the present paper, we approach the problem indirectly focusing attention on the dynamics near the glass transition. Our model system is a very simplified lattice model of a two-dimensional polymer melt. Unlike previous studies [11, 12] of the same model we make a great effort to equilibrate the system at all temperatures that are studied. Thus we probe the glass transition of an undercooled polymer melt in thermal equilibrium. Very low temperatures are inaccessible because equilibrium cannot be established within the available computer time. We have been able to go down to the temperature $T = 0.22$ K. There are many length scales in the system and we have studied suitable dynamical correlation functions and the corresponding relaxation behaviours at these different length scales. Our results are compatible with a gradual freezing in; a thermodynamic glass transition does not occur at nonzero temperatures. But the divergence of the relaxation times seems to be stronger than the Arrhenius law, namely $\tau \sim \exp(A/T^2)$ as $T \to 0$, where the constant A is independent of the type of quantity that is being studied.

2. The model and simulation

Our method of simulation is similar to that used by Wittmann *et al* [11] in order to study the glass transition in polymer melts. We use the bond-fluctuation model [13] on a square lattice, where a monomer is made up of a unit cell of the lattice, occupying four lattice positions, and the polymer chains consist of a number N of such monomers connected by bond vectors. The polymer chains are self- and mutually avoiding, so that no two monomers occupy the same position on the lattice and no two bonds cut each other. The lengths of the bond vectors connecting the monomers are restricted to lie in the range from $L(\pm 2, 0) = L(0, \pm 2) = 2$ to $L(\pm 3, \pm 2) = L(\pm 2, \pm 3) = \sqrt{13}$, where (x, y) in the symbol $L(x, y)$ stand for the x and the y components of the bond of length L which are measured

in units of the lattice spacing. The smallest length guarantees the local self-avoidance of the monomers and the selected value for the largest length prevents the chains from crossing each other, even in the course of their motion. The selection of the bonds allows us to have 36 bond vectors of six different lengths (see, e.g., [11]) and a rich bond-angle spectrum where the angle between two successive bonds can have 41 different values. This makes the model more realistic and much closer to off-lattice models.

In order to study the glass transition in this model we have followed [11] and introduced the energy

$$\epsilon_b = \epsilon_0 (L(x, y) - L_0)^2 \qquad (1)$$

with the bond vector b which depends only on the length $L(x, y)$ of the bond. We chose $\epsilon_0 = 1/(2 - L_0)^2$ and $L_0 = \sqrt{10}$, so that $0 \leqslant \epsilon_b \leqslant 1$ for any bond b and the bonds $L(\pm 3, \pm 1)$ or $L(\pm 1, \pm 3)$ of length $L = \sqrt{10}$ have the minimum energy which is zero. The prefactor ϵ_0 sets the scale for the temperature (Boltzmann's constant is unity).

In the course of the Monte Carlo simulation a monomer is selected at random and a move is attempted by one lattice spacing in one of the randomly chosen directions $\pm x$, $\pm y$ with a transition probability

$$W = \begin{cases} \exp(-\delta H/k_B T) & \text{if } \delta H \leqslant 0 \\ 1 & \text{otherwise} \end{cases} \qquad (2)$$

where δH is the difference in energy between the initial polymer configuration and the final one resulting from the displacement of the monomer. The move is accepted if the condition of self-avoidance is satisfied (i.e., the sites in the jump direction are empty) and the new bond vectors still belong to the allowed set of bond vectors as has been mentioned before (see figure 1).
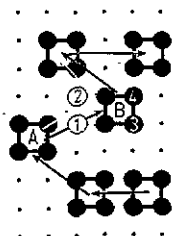

Figure 1. Illustration of the bond-fluctuation model on a square lattice. A monomer is made of four lattice points of an elementary plaquette and the arrows indicate the bond vectors connecting the monomers. In the hopping process a monomer jumps from a plaquette to a neighbouring one if the two lattice sites along the jump direction are free. This is shown for the monomer B which has for example the lattice points highlighted by the open circles free to its left. If the monomer B moves to the left in course of random hopping, sites 1 and 2 will be blocked and sites 3 and 4 will be free. For this move the new bond vectors are shown by the open arrows.

As the temperature is lowered, the energy of the melt is reduced by releasing the energy out of the bonds. The bonds stretch out to attain the minimum energy (see equation (1)) and such a stretched bond blocks a site of a plaquette of the lattice which becomes inaccessible to a monomer. So, the free space where a monomer can jump reduces with lowering of the temperature. If the density of the monomers ϕ is sufficiently high, the geometrical constraints will suppress the tendency of the melt to go to the minimum-energy state at low temperatures. In addition, if the chain length (degree of polymerization N) is not too small, a typical configuration of the melt will have the chains circling round each

other (in two dimensions chain entanglement is absent) and such a state will have an enormous relaxation time at low temperatures. The system cannot satisfy both the energetic and geometric conditions simultaneously, giving rise to 'frustration' and this together with randomness exhibits the glassy behaviour at low temperatures when the configuration of the melt becomes frozen (at least in the time scale of the simulation). Thus, we see that in order to obtain the glass transition we need long chains and sufficiently high density of the monomers in addition to the bond energies. What 'sufficiently high' means in this context was discussed in [11] and it found that a possible choice was $N = 10$ and $\phi = 0.8$. With this choice, it was shown [11] that even with a slow cooling, the system exhibits a glass transition at low temperatures. Moreover, this value of N ensures the expected Rouse dynamics of the chains in the athermal limit. Square lattices of size 100×100 with periodic boundary conditions are used throughout the simulation and 64 statistically independent systems of the same kind are simulated in parallel (involving 12 800 monomers) to obtain a good accuracy. A highly optimized version of the bond-fluctuation model suitably designed [14] for use on a vector supercomputer has been used. In what follows, the time unit is always given in terms of one attempted move per monomer or MCS (Monte Carlo step).

The starting point of our simulation is the stacking of the polymers onto the lattice in a completely random way and it is very difficult to achieve this. The problem is tackled by filling the lattice with ordered arrays of chains and the system is then relaxed in the athermal condition until the chains are moved for a period of several Rouse times (see, e.g., [13]). This takes typically $\sim 10^5$ MCS for our system. Cooling of the system (which is carried out at constant volume) is accomplished by lowering the temperature with a constant quench rate γ:

$$\beta(t) = \beta_f \gamma t \tag{3}$$

where β is the inverse temperature and t is the time measured in MCS. In our simulation the quenching rate is 4×10^{-5} MCS^{-1} and we have gone to the lowest temperature $T_{min} = 1/\beta_f = 0.01$ in 2.5×10^5 MCS.

In the cooling process configurations at several temperatures are stored. They are used as starting states for long canonical runs at the respective temperatures in order to equilibrate the melt. During these runs various quantities are monitored and studied, which will be discussed in the next section. In this respect there is an important distinction between our simulation results and those of Wittmann *et al* [11] where at low temperatures averages were taken on unrelaxed configurations which hence were not in equilibrium.

3. Transport and relaxation

In order to illustrate the effect of the chosen Hamiltonian on the state of the melt during the cooling process, we show in figure 2 the variation of the average bond energy ϵ_b with temperature in our system. The averaging is performed over the bonds in all the polymers and configurations. We see that ϵ_b initially reduces with temperature, but instead of going to zero, which represents the ground state of the bond energies, it levels off in a narrow temperature range around $T \sim 0.$ to a value ~ 0.15. It shows that the system becomes locked to a state whereupon any further lowering of temperature does not influence the distribution of the bond vectors among the energy levels. This 'locked' state represents the glassy state whereas the high-temperature state ($T \gg 0.1$), where the average bond energy can still relax with temperature, represents the liquid state. The non-zero value of the mean bond energy in the glassy region exemplifies the effect of geometrical frustration: the bonds cannot all go to the ground state simultaneously. If one compares the energy value of the

low-temperature glassy phase, i.e., $\epsilon_b \simeq 0.15$ with that of the corresponding system in [11] one finds that the energy value in this simulation is higher. This can be explained by the fact that we are working with a cooling rate that is one order of magnitude faster than that used in [11]. However, the smaller the cooling rate is, the more time the system gets to relax and thus the more bonds succeed in reaching the ground state. Therefore the residual energy in the low-temperature phase has to be larger the faster the quench rate is, a result which has also been obtained and extensively analysed for the glass transition in the three-dimensional bond-fluctuation model [10].
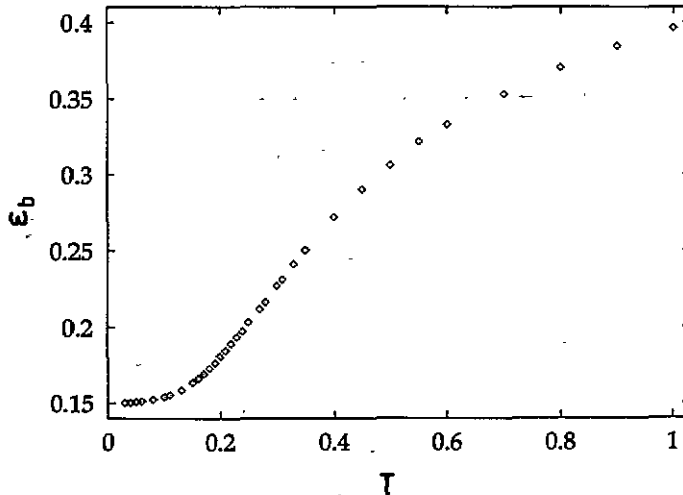

Figure 2. The mean bond energy ϵ_b as a function of the temperature T during the cooling process.

The main feature of the glass transition is the drastic slowing down of structural relaxation processes which eventually leads to a total arrest of the dynamics in the system. In Monte Carlo studies there is no microscopic dynamics in the sense of equations of motions derived from a Hamiltonian; it is the hopping that gives rise to a stochastic dynamics in the system. We follow Carmesin and Kremer [13] to investigate the dynamics in the melt and measure $g_1(t)$, the mean square displacement of the monomers with time; $g_2(t)$, the mean square displacement of the monomers in the centre-of-mass system and $g_3(t)$, the mean square displacement of the centre-of-mass of the polymers. The behaviours of these three quantities are shown in figure 3 both in the athermal limit and at $T = 0.22$ K. At early times, we find that $g_3(t)$ is very small and $g_1(t)$ and $g_2(t)$ are almost the same. With time, $g_3(t)$ develops and ultimately coincides with $g_1(t)$ while $g_2(t)$ becomes constant with time. The melt can then be considered to have attained the diffusive limit where the chains behave like a single object and diffuse like a Brownian particle. This feature is prominent in the athermal melt, while at low temperature there is a big jump in the time scale as can be seen in figure 3(b). The behaviour of these g functions in connection with Rouse dynamics has been discussed in detail in [13].

At sufficiently large times $g_1(t) \propto g_3(t) \propto t$, so that the polymers behave like Brownian particles. The diffusion constant D of the polymers can then be related to the infinite time limit of the relaxation function $g_3(t)$, as (in two dimensions)

$$D = \lim_{t \to \infty} \left[g_3(t)/4t \right]. \tag{4}$$
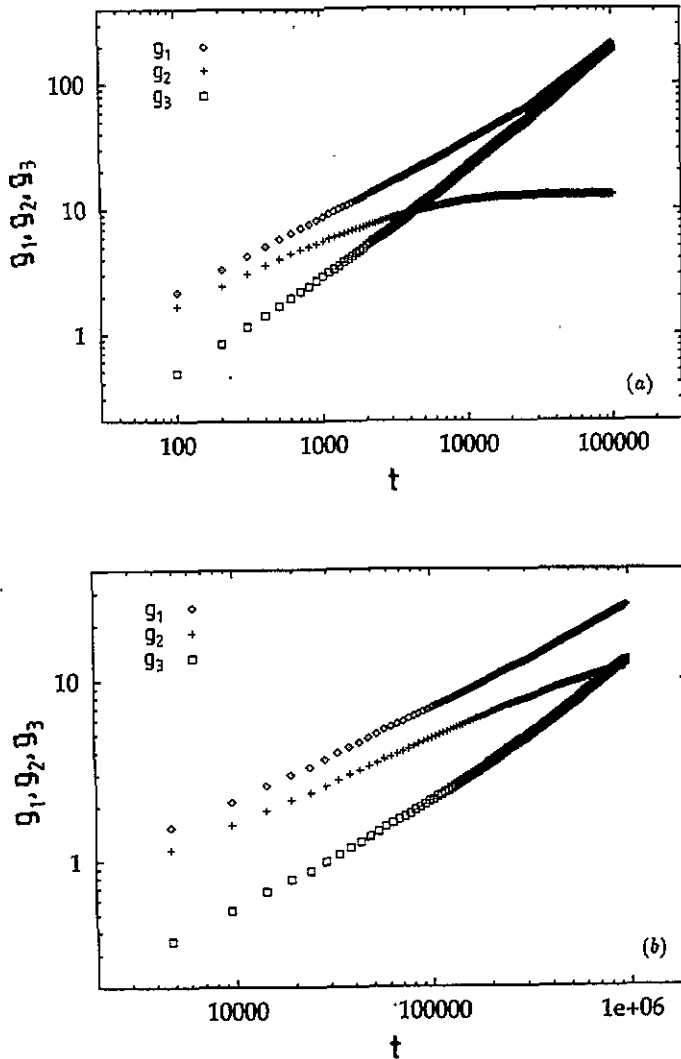
Figure 3. Plot of g_1, g_2, g_3 against time t in terms of MCS (a) in athermal limit and (b) for T = 0.22 K.

In figure 4, $g_3(t)/4t$ is plotted against $1/t$ in the logarithmic scale. The curves attain constant values at large times which increase with the lowering of the temperature. The diffusion constant D is approximated by this constant value of $g_3(t)/4t$. At lower temperatures, the curves seem to have attained the plateau at $t \simeq 10^6$ MCS and lower values of D cannot entirely be ruled out. Figure 5 shows $1/\ln(D_a/D)$ against T, where D_a is the diffusion coefficient in the athermal limit. The low-temperature data do not span a large temperature range and can be simultaneously fitted to the Vogel–Fulcher law $D \propto D_a \exp[b/(T - T_{VF})]$, with $a \simeq 1.76$ and the Vogel–Fulcher temperature $T_{VF} = 0.09$, and to the form $D \propto D_a \exp(a/T^2)$ with $b \simeq 1.76$. The latter fitting seems to be more convincing, which shows no sign of any finite-temperature transition.

At any temperature the relaxation time τ_D corresponding to this global diffusive motion can be obtained by arguing that it is the time needed for the polymers to diffuse to a distance of the average end-to-end distance R_{EE} (the largest length scale in the system) of
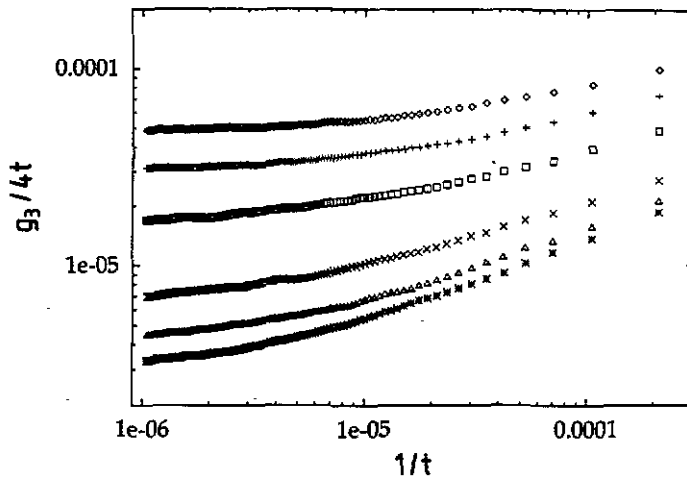
Figure 4. $g_3(t)/4t$ is plotted against $1/t$ (both in logarithmic scale) for temperatures 0.40 ($\Diamond$), 0.35 (+), 0.30 ($\Box$), 0.25 ($\times$), 0.23 ($\triangle$) and 0.22 ($*$) K. The values of the diffusion constant $D(T)$ are given by the constant values of the curves attained at the long-time limit.
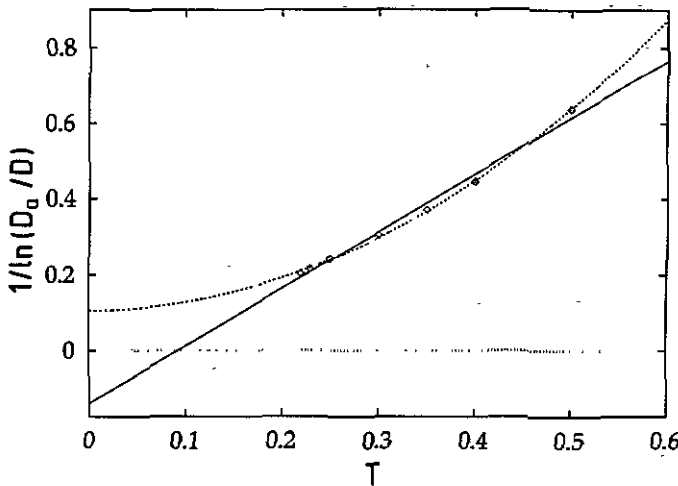

Figure 5. $1/\ln(D_a/D)$ is plotted against T. The low-temperature data are fitted to the form $D \sim D_a \exp[b/(T - T_F)]$ (the full curve) and to $D \sim D_a \exp(a/T^2)$ (the dotted curve). We have taken $a = 0.1406$, $T_{VF} = 0.093$ and $b = 1.76$.

the polymers at that temperature [15, 16]. This gives

$$\tau_D = \langle R_{EE}^2 \rangle / 4D \tag{5}$$

where $\langle \bullet \rangle$ denotes the averaging over all the polymers in the system. In figure 6, $1/\ln\tau_D$ is plotted against T. At high temperatures, the behaviour of τ_D is of Arrhenius type but the low-temperature data can be fitted to a form $\tau_D \sim \exp[A/T^2]$ (Bässler showed [17] that the viscosity data for some supercooled liquids obey this form), where $A \simeq 0.18$. The crossover temperature between the two relaxation regimes is around $\sim$0.3 K.

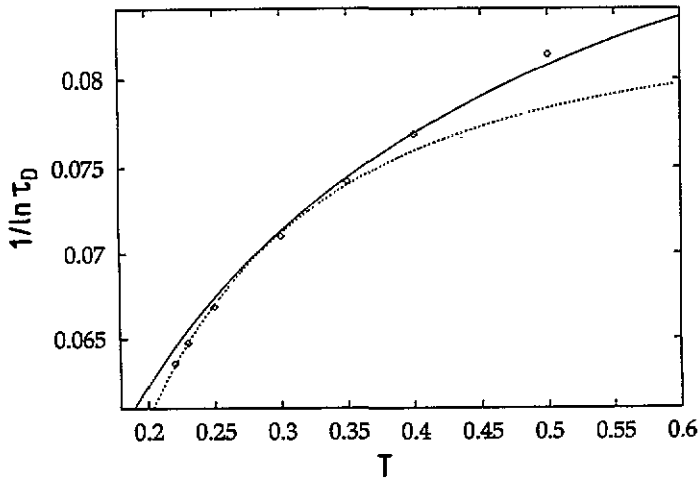The value of t where $g_2(t)$ cuts $g_3(t)$ (see figure 3) provides a measure of the Rouse

Figure 6. $1/\ln\tau_D$ is plotted against T. The data are fitted to the Arrhenius law (the full curve) and to the form $\tau_D \sim \exp(A/T^2)$ with $A = 0.18$ (broken curve).

relaxation time τ_R [16]. τ_R is the relaxation time associated with the rotational motion of the polymers and can be defined as the longest relaxation time associated with the autocorrelation function of the average end-to-end distance of the polymers [15]. τ_R is found to rise sharply as the temperature is lowered. Figure 7 shows the behaviour of $1/\ln\tau_R$ with T for our system. We find that the behaviour of τ_R is very similar to that of τ_D. The high-temperature Arrhenius behaviour crosses over at around $T \sim 0.3$ to the $\tau_R \sim \exp[B/T^2]$ behaviour at low temperatures, with $B \simeq 0.19$.
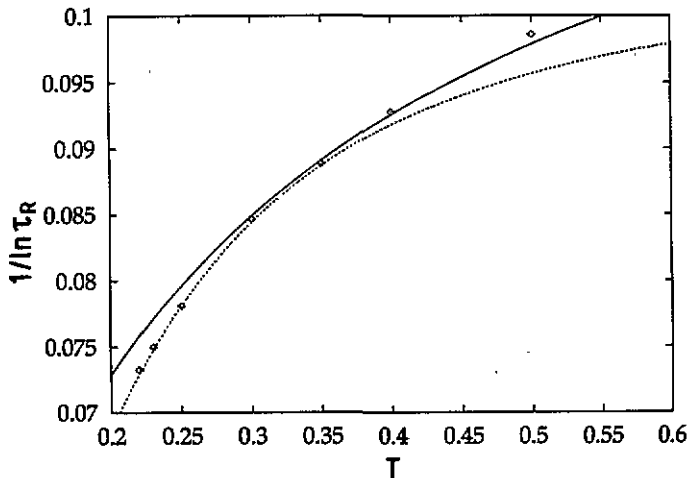

Figure 7. $1/\ln\tau_R$ is plotted against T. The data are fitted to the Arrhenius law (the full curve) and to the form $\tau_D \sim \exp(B/T^2)$ with $B = 0.19$ (the broken curve).

Information on the dynamics on the local scale of the monomers is conveniently extracted from the autocorrelation function defined in the following way. We associate a lattice-gas variable s_i with all monomers i. $s_i(t) = 1$ for the monomers which are completely

blocked at time τ_0 (in terms of MCS) whereas for all others $s_i(t) = -1$. We measure the autocorrelation

$$q(t) = \langle s_i(t_0) s_i(t_0 + t) \rangle_m \qquad (6)$$

where $\langle \bullet \rangle_m$ denotes the averaging over the monomers and the time t_0. $q(t)$ is very much similar to the EA order parameter in spin-glass systems [8]. The initial time t_0 should be so chosen that the system is relaxed at least on the scale of the individual monomers. We chose $t_0 \simeq \tau_R$, as the relaxation at the scale of the monomers is much faster than the Rouse relaxation of the chains. $q(0)$ is trivially unity by definition. For $t \to \infty$, $q(t) \to m_0 = \langle s_i \rangle_s^2$, where $\langle \bullet \rangle_s$ is the statistical-mechanics average. It is to be noted that $m_0 \neq 0$ since in the dense melt the probability of finding a monomer to be blocked is much higher than to find it otherwise. Also in our model the value of m_0 depends on temperature, as with the lowering of temperature the polymers swell out and the volume available to the monomers becomes less.
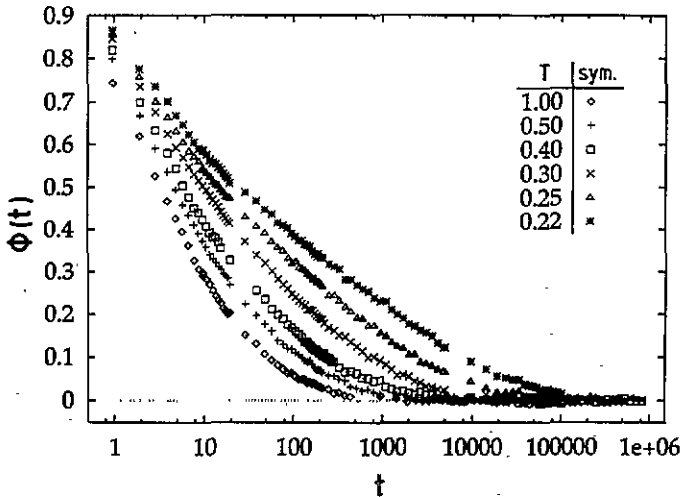

Figure 8. The autocorrelation function $\phi(t)$ is plotted against t (in the logarithmic scale) for different temperatures.

From this autocorrelation function the non-linear relaxation function is constructed as

$$\phi(t) = (q(t) - m_0)/(1 - m_0). \qquad (7)$$

In figure 8, $\phi(t)$ is plotted against t (in the logarithmic scale) for different temperatures. The decay of $\phi(t)$ is certainly not exponential. If we represent the decay by a spectrum of relaxation times $P(\hat{\tau})$ so that

$$\phi(t) = \int_0^\infty P(\hat{\tau}) \exp(-t/\hat{\tau}) \, d\hat{\tau} \qquad (8)$$

then the average relaxation time $\tau = \int_0^\infty \hat{\tau} P(\hat{\tau}) \, d\hat{\tau}$ can be extracted from

$$\tau = \int_0^\infty \phi(t) \, dt. \qquad (9)$$

In figure 9, $1/\ln\tau$ is plotted against T. Interestingly, we find that the dependence of τ on T is very similar to those of τ_D and τ_R, namely high-temperature Arrhenius behaviour and a crossover to a behaviour given by $\tau \sim \exp[C/T^2]$ around $T \sim 0.3$ with $C \sim 0.17$.
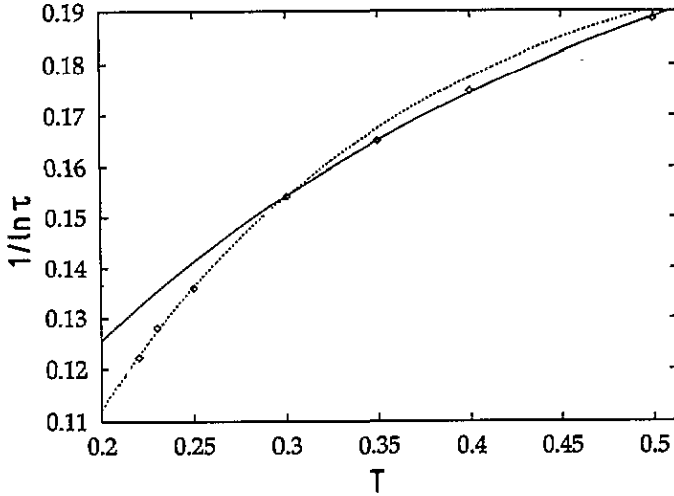
Figure 9. $1/\ln\tau$ is plotted against T. The data are fitted to the Arrhenius law (the full curve) and to the form $\tau_D \sim \exp(C/T^2)$ with $C = 0.17$ (the broken curve).

4. Discussion

We have studied the dynamics in a two-dimensional polymer melt at different temperatures and at different scales of the system. The melt is equilibrated at the temperatures studied. The equilibrated results correspond to those obtained in the limit of infinitely slow cooling rate. The lowest temperature at which the system could be equilibrated is 0.22 K; further low-temperature equilibrium configurations are inaccessible within a reasonable computer time. The smallest scale in the system is the local scale of the monomers. The dynamics at this scale is conveniently extracted from the relaxation of the autocorrelation function $q(t)$. We have also considered the Rouse relaxation which has a scale of the order of the average end-to-end distance of the polymers. It can be thought of as the relaxation of the wriggling motions of the chains. The largest scale is however associated with the global relaxations of the system brought by the diffusion of the chains. We find that though the relaxation times of these various relaxations at different scales differ in absolute magnitude (the largest relaxation time is associated with the relaxation at the largest scale), their dependence on the temperature T is remarkably similar. The relaxation times follow Arrhenius law at high temperatures and crossover to the behaviour $\tau \sim \exp(A/T^2)$ at low temperatures. In each of the relaxation processes the crossover temperature between the two relaxation regimes seems to be the same (~ 0.3 K) and the value of the constant A, which is a measure of the activation energy, is $\simeq 0.18$ for each of these relaxation processes. The relaxation time seen on large length scales hence is essentially the same as that of the local monomeric hopping motion! Interestingly this fact that the relaxation characteristics are independent of the scale does agree with the corresponding experimental findings ([18] and references therein) in polymer glasses (in three dimensions).

Another quite general question is the state of the time–temperature superposition principle regarding the isotherms in figure 8. The principle suggests that the relaxation functions at different temperatures and at long times can be superposable on a single curve so that the relaxation functions are not functions of two variables but only a combination of both. One could have expected that the natural scales for the time at different temperatures are the relaxation times $\tau(T)$. However, figure 10 shows that scaling the time by τ does
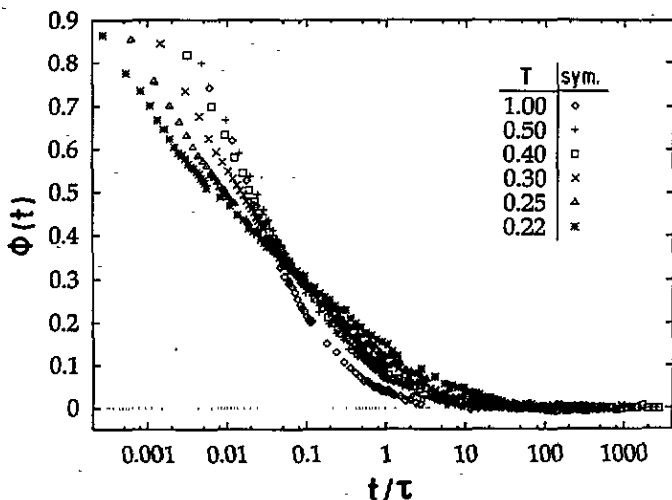
Figure 10. The autocorrelation function $\phi(t)$ for different temperatures are plotted against t/τ (in logarithmic scale). The curves splay out systematically at early and late times.

not lead to the collapse of all the data points to a single curve; rather they splay out systematically at both early and late times. This can be explained by the fact that we have determined the relaxation time by using equation (9) and integrating the relaxation function over the entire time range. This may involve other relaxation processes. On the other hand, figure 11 suggests that the late-time data are indeed superposable by proper rescaling of the time axis. We find that the lower the temperature, the larger is the time zone over which the scaling is valid.
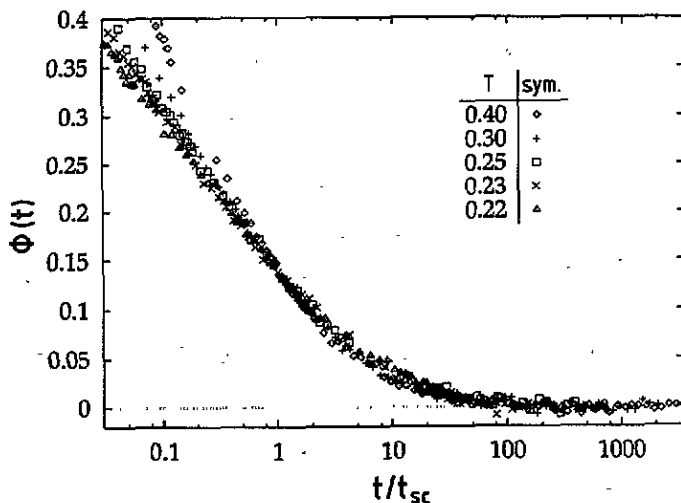

Figure 11. The autocorrelation function $\phi(t)$ for temperatures $T = 0.40, 0.30, 0.25, 0.23$ and 0.22 K are plotted against t/t_{sc} (in logarithmic scale) where $t_{sc} = 130, 400, 1160, 2260$ and 3700 for the respective temperatures. All the curves collapse on to a single curve at longer times. The corresponding relaxation times at these temperatures, as determined by equation (9), are $\tau = 306.5, 657.1, 1562.7, 2459.9$ and 3563.2 respectively.

Our study shows that although fast quenching of the system results in a glass transition at a non-zero temperature, in the limit of infinitely slow cooling rate the system only exhibits the tendency of a gradual freezing in; a thermodynamic glass transition does not seem to occur at non-zero temperatures. The fast increase of the relaxation time over a narrow temperature range can be thought of as a result of strong cooperative effects among the monomers. However, this increase does not seem to be sufficiently rapid to explain the possibility of a non-zero freezing temperature but sufficient enough to show a dynamic freezing at a non-zero temperature when the system is cooled fast. The result is similar to what has been found in the study of isotropic spin-glass systems [8]. It is to be noted that the strong temperature dependence of the form $\tau \sim \exp(A/T^2)$ has been observed in supercooled liquids [17] and in other systems [19] and has also been discussed in the context of the short-range spin glass models [8].

Acknowledgments

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