

## Small-Angle Excess Scattering: Glassy Freezing or Local Orientational Ordering?

H. Weber, W. Paul, W. Kob, and K. Binder

*Institut für Physik, Johannes-Gutenberg-Universität, Staudingerweg 7, D-55099 Mainz, Germany*

(Received 17 December 1996)

We present Monte Carlo simulations of a dense polymer melt which shows glass-transition-like slowing down upon cooling, as well as a buildup of nematic order. At small wave vectors, this model system shows excess scattering similar to that recently reported for light-scattering experiments on some polymeric and molecular glass-forming liquids. For our model system we can provide clear evidence that this excess scattering is due to the onset of short-range orientational order (in our case of nematic type) and is not directly related to the glass transition. [S0031-9007(97)02585-4]

PACS numbers: 61.25.Hq, 61.20.Ja, 64.70.Pf

The glassy freezing of supercooled fluids has been a long-standing topic of research in a wide range of disciplines from engineering to theoretical physics. Despite these efforts, no agreement concerning the basic physical mechanisms of the transition has emerged [1–4]. A particularly puzzling experimental finding is the onset of some large-scale correlations in various supercooled molecular and polymeric glass-forming fluids [5–7]. The evidence for these correlations consists of excess scattering at small wave numbers  $q$  seen in light scattering experiments, which by far exceeds the value to be expected from the compressibility of the system. The  $q$  range corresponds to distances of several hundreds to thousands of Å, depending on the material.

This finding is completely unexpected from the point of view of theories that treat the glass transition as a purely kinetic phenomenon, such as, e.g., mode coupling theory [4]. The only relevant length scale in this theory is the typical interparticle distance, that is, the diameter of the “cages,” the decay of which is described self-consistently by the theory.

There are, however, theories postulating an underlying second-order phase transition (possibly kinetically masked) [2], which therefore would imply the existence of a growing—and ultimately diverging—intrinsic length scale associated with the glass transition, although most existing theories along such lines seem questionable [3]. Furthermore, direct evidence for such a length scale from computer simulations of simple models undergoing a glass transition is rather scarce [8–10] and any such lengths detected so far are quite small and cannot be connected with the large lengths seen in scattering experiments [5–7] far above the glass transition.

In the present work we show that this surprising scattering behavior of some supercooled liquids can possibly be attributed to local orientational ordering in these systems. We will present a Monte Carlo simulation of the bond fluctuation model of a polymer melt [11,12] with some orientational ordering tendency. In this lattice model each repeat unit of the chains occupies the eight vertices of a unit cube on the three dimensional simple cubic lattice.

Each unit is connected to its neighbors along the chain with bonds fluctuating in length between 2 and  $\sqrt{10}$ . The stochastic dynamics—single monomer hopping or slithering snake moves—obeys connectivity and excluded volume constraints [12,13]. Using a Hamiltonian that favors long bonds, this model has been extensively used to study the glass transition in polymer melts and has been shown to reproduce much of the phenomenology that is observed in experiments [14].

For the present study we employ a Hamiltonian which incorporates both bond length and bond angle energies [15]. The bond length energy favors short bonds,  $b = 2$ , and the bond angle energy favors stretched angles,  $\theta = 180^\circ$ . Details are given in [16]. This model system is cooled down in a stepwise fashion and is equilibrated at each temperature with the highly efficient slithering snake algorithm [17]. After equilibration the dynamics of the chains is studied with the single monomer hopping algorithm which is known to reproduce the Rouse dynamics for short chains in the melt [12].

To study the freezing behavior we analyzed the mean square displacements of the centers of mass of the chains in the long time limit. The simulation data are for a system of linear dimension  $L = 31$  containing 93 chains. A measure of the longest relaxation time of the chains can be defined as the time for which this mean square displacement is equal to the mean square radius of gyration of the chains in the melt. Figure 1 shows a plot of this relaxation time, divided by its infinite temperature limit, for chains of length  $N = 20$  in the form of an inverse activation plot. In the temperature range investigated we observe a slowing down of the chain dynamics by 2 orders of magnitude which is described well by a Vogel-Fulcher law with a Vogel-Fulcher temperature of about  $T_0 = 0.144$ . This result would suggest the existence of a glass transition in the melt somewhere around  $T = 0.2$ .

In Fig. 2 we show the scattering intensity  $S(q)$  at small wave vectors. The data are for a system of 13 732 chains of length  $N = 10$  in a cubic box of linear size  $L = 130$ . All curves are obtained by averaging  $S(q)$  over

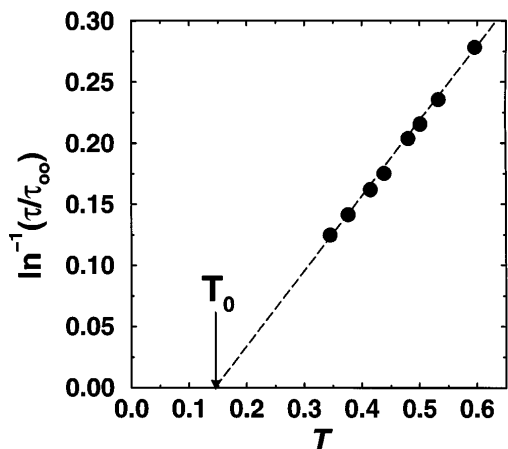


FIG. 1. Longest relaxation time of chains of length  $N = 20$  normalized to the infinite temperature value as a function of temperature. The dashed line shows a Vogel-Fulcher fit giving a Vogel-Fulcher temperature of  $T_0 = 0.144$ .

about 100 statistically independent configurations. The curve at  $T = 0.376$  is flat and its value is the one to be expected from the compressibility of the model system [14]. Excess scattering can be found starting at temperatures around  $T = 0.313$  and its intensity increases by almost a factor of 4 upon decreasing  $T$  to 0.219. The  $q$  range where this effect occurs corresponds to distances of 10–60 lattice constants. Qualitatively this effect is similar to what was observed experimentally in certain glass-forming materials [7].

In this temperature range, however, another property of our model system comes into play: the Hamiltonian we used favors stretched bond angles and short bonds. The conformations of the polymer chains therefore gradually change from the Gaussian coil limit at high temperatures

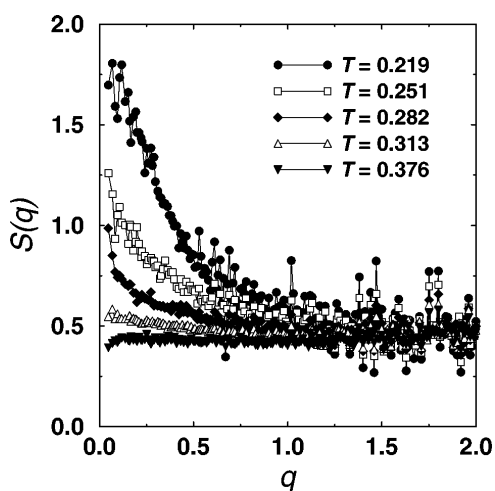


FIG. 2. Scattering intensity at small wave vectors for a system of chains of length  $N = 10$ . The different curves cover the temperature range over which one observes the buildup of local orientational order.

to the rigid rod limit at very low temperatures. In the temperature region where they can be considered to be almost rod-like objects they should therefore display a tendency for liquid crystalline ordering. According to Onsager theory [18] this tendency should depend on the aspect ratio (length/width) of the chains in their rod-like state. It can be quantified by the behavior of the nematic order parameter  $P_2$ , which is defined as the largest eigenvalue of the Saupe tensor [19]

$$Q_{\alpha\beta} = \frac{1}{M} \left( \frac{3}{2} \left\langle \sum_{i=1}^M u_{i\alpha} u_{i\beta} \right\rangle - \frac{1}{2} \delta_{\alpha\beta} \right), \quad (1)$$

where  $\hat{u}_i$  is a unit vector along bond  $i$  and the sum is over all bonds in the system. Figure 3 shows that we observe exactly this behavior. At temperatures around  $T \approx 0.27$  the system starts to develop nematic order. The chains of length  $N = 10$  show only a small increase in the value of the order parameter which is due to a buildup of merely local nematic order [16]. Thus the nonzero value of the order parameter for  $N = 10$  is just a finite size effect. As demonstrated below, this local ordering is, however, sufficient to produce the excess scattering shown in Fig. 2 for the chains of length  $N = 10$ . On the other hand the chains of length  $N = 20$  with their larger aspect ratio develop long-range nematic liquid crystalline order at temperatures below  $T = 0.26$  [16]. For this system the excess scattering occurs in the same  $q$  range and temperature range as for the one with  $N = 10$  but has a larger amplitude. In this case the isotropic-nematic transition preempts the glass transition, which would occur at a lower temperature.

To demonstrate the connection between the excess scattering and the local nematic order, we first of all note

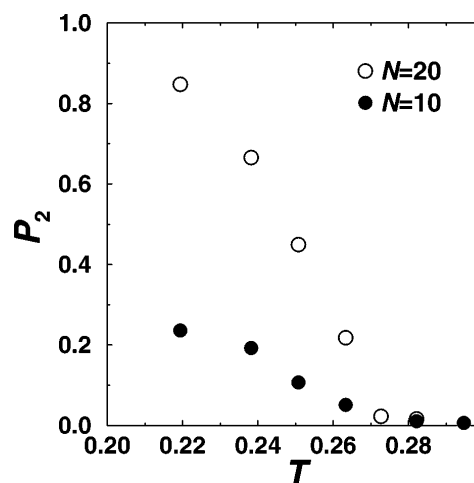


FIG. 3. Nematic order parameter  $P_2$  as a function of temperature. The open circles denote systems of 6866 chains of length  $N = 20$  and the filled circles denote systems of 13 732 chains of length  $N = 10$ . The linear dimension of the box is  $L = 130$  in both cases.

that the temperature dependence of the excess scattering is the same as that of the nematic short-range order. To make this link more quantitative we consider the following approximation to the scattering function. At  $T = 0$  the ground state of the system consists of perfectly aligned rigid rods. In this case the scattering function exactly factors into a contribution from the positional correlation of the rods,  $S_{\text{cm}}(q)$ , and a contribution from the intramolecular correlations, which is just the form factor of the rods,  $f(q)$ :

$$S(q) = S_{\text{cm}}(q)f(q), \quad (2)$$

where the form factor of the rods is given by [20]

$$f(q) = N_{\text{scatt}} \left[ \frac{2}{ql} \int_0^{ql} dz \frac{\sin z}{z} - \left( \frac{2}{ql} \sin \frac{ql}{2} \right)^2 \right]. \quad (3)$$

Here  $N_{\text{scatt}}$  is the number of scatterers per rod and  $l$  is its length. We now approximate our scattering intensity at finite temperatures by Eq. (2), thus neglecting fluctuations of the local director and approximating our chains as rigid rods ignoring their finite flexibility. To calculate the form factor of the rods equivalent to our chains we set  $l$  equal to the end-to-end distance of the chains  $\sqrt{\langle R_e^2 \rangle}$  and set  $N_{\text{scatt}}$  equal to  $\sqrt{\langle R_e^2 \rangle} / \langle b^2 \rangle$ , where  $\sqrt{\langle b^2 \rangle}$  is the mean bond length. If we divide the scattering function for the systems with chains of length  $N = 10$ , presented in Fig. 2, either by the form factor of the rods determined in this way (Fig. 4) or alternatively by the directly measured form factor of the chains, we see that the excess scattering completely vanishes. This clearly shows that the excess scattering is due to the occurrence of orientational order in our system and that it is even sufficient to have only *local* orientational order to reproduce this effect.

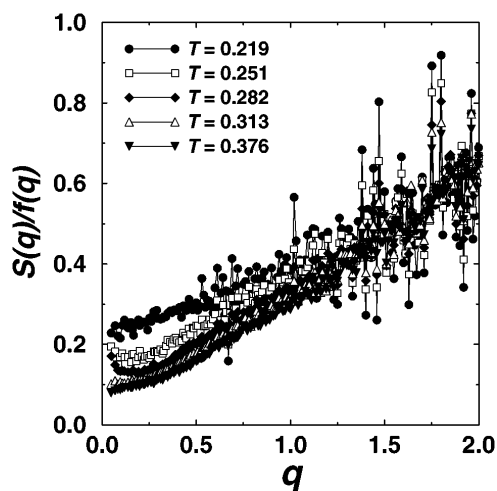


FIG. 4. Scattering intensity at small wave vectors divided by an equivalent rigid rod form factor of the chains for different temperatures as shown. The results are for chains of length  $N = 10$ .

Thus we have demonstrated that for our model system which exhibits on the one hand slowing down typical for a polymer melt undergoing a thermal glass transition and on the other hand a transition from random coil to semi-flexible and finally rigid rod behavior of the chains and an accompanying (local) nematic ordering, the excess scattering intensity at small wave vectors can be unambiguously ascribed to the development of the local orientational order and *is not directly connected* with the glass transition in the system. Since it is sufficient to have a tendency for *local* nematic ordering for this effect to occur, the question arises whether this mechanism may also be responsible for the excess scattering experimentally observed for some glass-forming systems. All of these systems are either polymers or consist of highly anisotropic molecular liquids with the accompanying highly anisotropic interactions. While in our model the local orientational order is associated with local chain stretching and is of uniaxial nematic type, it is very plausible that other systems (like, e.g., orthoterphenyl) may have other types of local orientational ordering, developing from a dense packing of anisotropic molecular groups. This local ordering should show up in qualitatively similar excess scattering. It would therefore be very interesting to reexamine the local orientational properties of these experimental systems and look at the effects of external orienting fields on the excess scattering.

We thank Professor E. W. Fischer for stimulating discussions and gratefully acknowledge support by the EU under Grant No. CIPA-CT93-0105 for one of us (H. W.). We also thank the Sonderforschungsbereich 262 for support.

- 
- [1] *Proceedings of the 2nd International Disc. Meeting on Relaxation in Complex Systems*, edited by K.L. Ngai [J. Noncryst. Solids **172–174** (1994)].
  - [2] J. Jäckle, Rep. Prog. Phys. **49**, 171 (1986).
  - [3] M. Wolfgangt, J. Baschnagel, W. Paul, and K. Binder, Phys. Rev. E **54**, 1535 (1996).
  - [4] W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).
  - [5] B. Gerharz, G. Meier, and E. W. Fischer, J. Chem. Phys. **92**, 7110 (1990); E. W. Fischer, Physica (Amsterdam) **201A**, 183 (1993).
  - [6] T. Kanaya *et al.*, Acta Polymerica **45**, 137 (1994); Macromolecules **28**, 7831 (1995); A. Patkowski *et al.* (to be published).
  - [7] E. W. Fischer, E. Donth, and W. Steffen, Phys. Rev. Lett. **68**, 2344 (1992).
  - [8] P. Ray and K. Binder, Europhys. Lett. **27**, 53 (1994).
  - [9] J. Baschnagel and K. Binder, Macromolecules **28**, 6808 (1995).
  - [10] W. Kob, in *Annual Reviews of Computational Physics*, edited by D. Stauffer (World Scientific, Singapore, 1995), Vol. III, p. 1.
  - [11] I. Carmesin and K. Kremer, Macromolecules **21**, 2819 (1988).

- 
- [12] H.P. Deutsch and K. Binder, *J. Chem. Phys.* **94**, 2294 (1991); W. Paul, K. Binder, D.W. Heermann, and K. Kremer, *J. Phys. II (France)* **1**, 37 (1991).
- [13] H. Weber, Ph.D. thesis, Johannes-Gutenberg-University, Mainz, 1997.
- [14] W. Paul and J. Baschnagel, in *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, edited by K. Binder (Oxford University Press, New York, 1995), and references therein.
- [15] H. Weber and W. Paul, *Phys. Rev. E* **54**, 3999 (1996).
- [16] H. Weber, W. Paul, and K. Binder (to be published).
- [17] M. Müller and K. Binder, *Comput. Phys. Commun.* **84**, 173 (1994); M. Wolfgardt, J. Baschnagel, and K. Binder, *J. Phys. II (France)* **5**, 1035 (1995); V. Tries, W. Paul, J. Baschnagel, and K. Binder, *J. Chem. Phys.* **106**, 738 (1997).
- [18] L. Onsager, *Ann. N.Y. Acad. Sci.* **51**, 627 (1949).
- [19] A. Saupe, *Z. Naturforsch.* **19A**, 161 (1964).
- [20] B.J. Berne and R. Pecora, *Dynamic Light Scattering* (Krieger Publishing Company, Malabar, FL, 1990).