Macromolecules **1995,** *28,* 1835−1840 **1835**

Simulations of Induced Orientation in Stretched Polymer Melts[†]

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Received March 18, 1994; Revised Manuscript Received November 19, 1994[⊗]

ABSTRACT: Molecular dynamics simulations of an entangled bead−spring polymer melt were used to study bond orientation induced by uniaxial stretching. Short free "guest" chains added to the melt showed an induced orientation 0.28 times that of the majority "host" chains. This orientation ratio ϵ is comparable to those recently observed in hydrocarbon polymers. For comparison, we oriented the host bonds using an explicit nematic field instead of stretching. The resulting orientation ratio was substantially reduced, to 0.17. This latter ratio was independently obtained using correlation functions of the isotropic, equilibrium liquid. The discrepancy between these two orientation ratios suggests that the widely accepted theory of orientational coupling provides an incomplete explanation of induced orientation under stretching. Other potential mechanisms for induced orientation are discussed.

I. Introduction

A well-known consequence of the theory of rubber elasticity is bond orientation. Elastic deformation of a rubber induces anisotropy of the backbone bonds of the polymer coils. This anisotropy is the basis of the well-known stress-optical law asserting the proportionality of optical anisotropy to stress. As tests of this law have grown in sophistication, puzzles have arisen; such puzzles challenge our understanding of the molecular origin of stress in rubber. One such puzzle is the postulated "orientational coupling" effect in which bonds are assumed to orient because of the orientation in adjacent bonds. This orientational coupling was postulated in order to account for the unexpectedly large optical anisotropy produced by a given stress.[1] One consequence of such a coupling is *induced* anisotropy: trace amounts of free chains in a network or a high molecular weight melt should acquire a bond anisotropy proportional to that of the surrounding host bonds. The constant of proportionality is the "orientation ratio" ϵ. Recent experiments[2] have measured this ϵ explicitly and confirmed that is is often surprisingly large: even simple molecules like poly(ethylenepropylene) show ϵ values of nearly a half.[3] Such large values are puzzling; they suggest that these structureless polymer melts have a strong tendency toward nematic order. In the present study we investigate some of the origins of these large induced anisotropies.

Induced anisotropy under stretch has been demonstrated in a variety of polymer systems. For example, small rigid anisotropic molecules embedded in a strained polymeric medium adopt a preferential orientation in the elongation direction.[4] Flexible oligomers in a homologous host matrix also show induced anisotropy, which is claimed to be stronger for unentangled oligomers than for fully entangled chains.[2] The orientation ratio is almost unity for the unentangled oligomers.[2,5,6] Similar induced anisotropy has been seen in the orientational relaxation of bidisperse polymer melts.[3,7] Orientational order persists in the short chains beyond their stress relaxation time. The residual order is attributed to induced anisotropy. The orientation ratio ϵ varies between 0.26 and 1.0 in different experimental systems.[2]

The induced anisotropy has traditionally been explained by postulating an orientational coupling interaction of a given guest bond to the surrounding matrix.[8,9] The assumed interaction energy has the form

$$U \sim ATr(\check{\mathbf{q}}\check{\mathbf{Q}}) \tag{1}$$

Here the coefficient A is a coupling strength. The tensor

$$\check{\mathbf{q}}_{\alpha\beta} \equiv (3/2)^{1/2}\left(\hat{n}_\alpha \hat{n}_\beta - \frac{1}{3}\delta_{\alpha\beta}\right) \tag{2}$$

is the nematic tensor for a bond with unit vector $\hat{n}$. The tensor $\check{\mathbf{Q}}$ is the analogous average nematic order parameter for the surrounding matrix bonds. Here $Tr(\check{\mathbf{q}}\check{\mathbf{Q}})$ indicates the sum $\Sigma_{\alpha\beta}\check{\mathbf{q}}_{\alpha\beta}\check{\mathbf{Q}}_{\beta\alpha}$. Interactions of this type are plausible, especially if the local structure of the polymer coils is rigid or anisotropic. This type of interaction has also been justified[2,10,11,12] in terms of packing effects using Di Marzio's classic schematic lattice model of the polymer melt. For a simple-cubic lattice the model gives an orientation ratio $\epsilon = 1/2$, in good qualitative agreement with the measurements of refs 2 and 3. It is not clear to what degree this large ϵ arises from lattice effects not shared by real molecules. Indeed bond orientational correlations are rather sensitive to detailed molecular structure, as shown, *e.g.*, by Yoon *et al.*[13] Because of this sensitivity, a quantitative understanding of induced anisotropy requires detailed information about the molecules.

This orientational coupling is not the only possible source of induced anisotropy. One alternative mechanism was proposed by Brereton.[14] His mechanism invokes the anisotropic screening properties of the deformed network chains. The magnitude of this effect is uncertain.

Although the exact value of the orientation ratio ϵ is known to be highly sensitive to chemical detail and geometrical shape, indicating the importance of steric effects, Ylitalo *et al.*[2] in a recent review paper noted that a general trend in the strength of the coupling can be detected. If the size of the molecular probe is increased,

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[†] This paper is dedicated to the memory of Dale S. Pearson, whose encouragement was instrumental in motivating this research.

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

0024-9297/95/2228-1835$09.00/0

so is the orientation ratio. This effect saturates at $\epsilon \approx 1$ for sufficiently long oligomers about a few persistence lengths. These results seem to indicate that the large orientation ratio for these oligomers might have a substantial polymeric part. Our simulations aim to discern how much of the induced anisotropy of polymer liquids arises from their intrinsic chain structure rather than from particular properties of specific monomers. Accordingly, we chose chains with as little extrinsic structure as possible: each chain in the simulation is a sequence of spherical beads connected with ideal springs. It has been shown[13] that the predictions of such a unified atom model for quantities like orientational correlations are approximately a factor 2 too low. Nevertheless, these models have been used very successfully in studying general trends in dense polymeric systems. E.g., similar chains were used to demonstrate reptational motion in simulations.[15] Our system is a bidisperse melt consisting of one long host chain and several short guest chains in a periodic cell. The host chain passes through many spatial periods of the cell and is thus strongly entangled with itself. After this simulated system has come to equilibrium, the cell is rapidly elongated by a substantial factor. After the deformation the short guest chains are expected to relax back to equilibrium much faster than the long chain. Any orientation of the guest chains on time scales much longer than the relaxation time of the guest chains but shorter than that of the host chain should be due to induced anisotropy. As discussed below, we found substantial induced anisotropy. We were able to account for it qualitatively in terms of the packing of segments and the conformational properties of the random-coil chains.

In order to investigate the origin of this induced anisotropy, we used an alternative method for orienting the host bonds. We introduced an artificial nematic perturbation of the form $H' \equiv Tr(\check{\mathbf{q}}_{\mathbf{i}}\check{\mathbf{W}})$ for each host bond i. If the anisotropy in the guest bonds arises from simple orientational interaction U as discussed above, the orientation ratio ϵ would be independent of the means of producing the host orientation. In our simulations this was not the case. Instead, the nematic perturbation produced a substantially smaller ϵ_n than that obtained through stretching. We infer that induced orientation arises in part from properties of the stretched network other than the host bond orientations.

II. Simulations and Results

The simulation method is identical to that used by Kremer and Grest[15] to study polymer dynamics in equilibrium melts. A bead–spring model is used in which each monomer moves according to the equation of motion:

$$m\ddot{\vec{r}}_i = \vec{\nabla}\sum_{j\neq i} U_{ij} - \Gamma\dot{\vec{r}}_i + \vec{W}_i(t) \tag{3}$$

where m is the monomer mass. Here U_{ij} contains a purely repulsive Lennard-Jones potential $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6 + 1/4]$ truncated at $r_c \leq 2^{1/6}\,\sigma$ and a strong attractive potential that acts only between monomers connected along the chain structure. A friction constant Γ and Langevin noise term $\vec{W}$ are introduced to control the temperature and to stabilize the system. They are coupled by the fluctuation–dissipation theorem. The temperature and density are fixed at $k_BT/\epsilon = 1$ and $\varrho\sigma^3 = 0.85$. This temperature is well above the glass transition temperature at this density. Kremer and Grest[15] found that for this system the persistence length (defined as $l_p = C_\infty^{1/2}$) $l_p = 1.32$ and the entanglement length $N_e \approx 35$. The average bond length $l = 0.97\sigma$. The maximum bond length does not exceed 1.2σ, which means that chain crossing does not occur. In our study of binary melts, one long host chain containing 5000 monomers is used, instead of several long chains. The different molecular weights of the guest chains are $N = 5$, 10, and 25. Simulations on longer chains are not possible at the present time due to limitations on computer time. The equations of motion were integrated with a velocity Verlet algorithm[16] with a time step $\Delta t = 0.012\tau$, where $\tau = \sigma(m/\epsilon)^{1/2}$ is the Lennard-Jones unit of time. We use $\Gamma = 0.5\tau^{-1}$.

After equilibration we stretch the system, by an extension ratio $\lambda = \sqrt{2.5}$. The stretch is performed by gradually deforming the original cubical simulation cell into a rectangular cell with a long z-axis λ^2 and short axes $1/\lambda$ times the original axes of the cube cell. The extension rate in the z-direction is $0.025\sigma/\tau$. We checked that within errors the value of the orientation ratio is identical at a lower stretch rate ($0.0025\sigma/\tau$) and for lower extension ratios ($\lambda = \sqrt{1.75}$, $\sqrt{2.125}$). For each bond an order parameter q_{zz} is defined as the second Legendre polynominal:

$$q_{zz} = (3/2)^{1/2}(cos^2\,\theta - 1/3) \tag{4}$$

where θ is the angle of the bond with the stretch (z) direction. Figure 1 shows for two different molecular weight guest chains the bond order averaged over all host ($\langle q_{zz}\rangle_h$) and guest ($\langle q_{zz}\rangle_g$) chain bonds. Data are averaged over a 300τ time interval to reduce noise. All data result from an average over 6 ($N = 5$) or 3 ($N = 25$) runs. Since our $\langle q\rangle$ values are no more than a few percent, it is not surprising that our orientation ratios were observed to be independent of the stretching factor λ. We infer that these $\langle q\rangle$'s represent the linear response of the system so that the same orientation ratios would occur for arbitrarily small elongation. At times much longer than the Rouse relaxation time[15] ($\tau_R \approx 40$, 150, and 1000τ for $N = 5$, 10, and 25, respectively), the bonds of the guest chain are still oriented in the stretch direction. This is similar to the behavior found experimentally. The strength of the orientation ratio is obtained from[3,9]

$$\epsilon = \frac{\langle q_{zz}\rangle_g}{\phi_h\langle q_{zz}\rangle_h + \phi_g\langle q_{zz}\rangle_g} = \frac{\langle q_{zz}\rangle_g}{\langle q_{zz}\rangle_b} \tag{5}$$

where $\langle q_{zz}\rangle_g$, $\langle q_{zz}\rangle_h$, and $\langle q_{zz}\rangle_b$ are the average guest, host, and bulk chain orientations at times longer than twice the relaxation time of the guest chains. ϕ_g and ϕ_h are the volume fractions of the guest and host chains. In the data shown in Figure 1 the guest chain volume fraction equals $^1/_{11}$. Results for the orientation ratio are given in Table 1. The error estimates result from the differences between runs. Identical results within errors are obtained if the average orientations at times longer than 4 times the Rouse relaxation time are used. We conclude that within errors the orientation ratio is independent of the guest chain length and that its average value is $\epsilon = 0.28 \pm 0.01$. For guest chain lengths longer than a few persistence lengths and lower than the entanglement length a molecular weight independent orientation ratio has also been found in

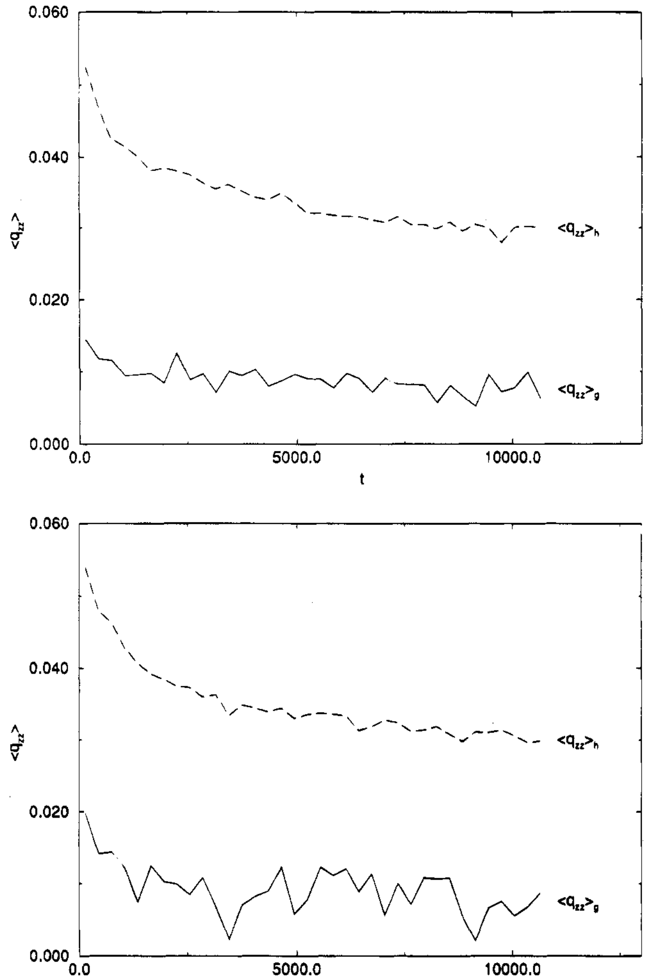

Figure 1. Order parameter $\langle q_{zz} \rangle$ in the stretch direction as a function of time. $t = 0$ corresponds to the moment that we stop stretching. Averages for host and guest bonds are shown separately. The guest chain molecular weights are $N = 5$ (top) and $N = 25$ (bottom).

Table 1. Orientation Ratios ϵ for Different Values of the Guest Chain Molecular Weight N

N	ϵ	N	ϵ
5	0.280 ± 0.003	25	0.282 ± 0.012
10	0.282 ± 0.011		

most experiments[2] and the independence has been attributed to the short range of the orientational coupling interaction.

An additional run at a different guest chain volume fraction was also done. At $\phi_g = 0.4$ we found, as expected, a lower vlaue for $\langle q_{zz}\rangle_g / \langle q_{zz}\rangle_h$. However, the value of ϵ, resulting from eq 5, is 0.28 ± 0.02, identical to the one found at the lower guest chain volume fraction.

Figure 2 shows the bond orientation of the guest chains versus the average bulk orientation at times longer than twice the Rouse relaxation time of the guest chains. Each data point is again an average over a 300τ time interval. Different symbols are for different extension ratios, introduced to obtain a sufficiently large range of host orientation values. From eq 5 a linear relation with slope ϵ and intercept 0 is expected. The data clearly show a correlation between guest chain and bulk orientation. Moreover, a linear least-squares fit gives $\epsilon = 0.29 \pm 0.01$, consistent with the result of the other method. The intercept is 0 within our statistical errors, reinforcing our belief that our ϵ values hold for arbitrarily weak deformation.

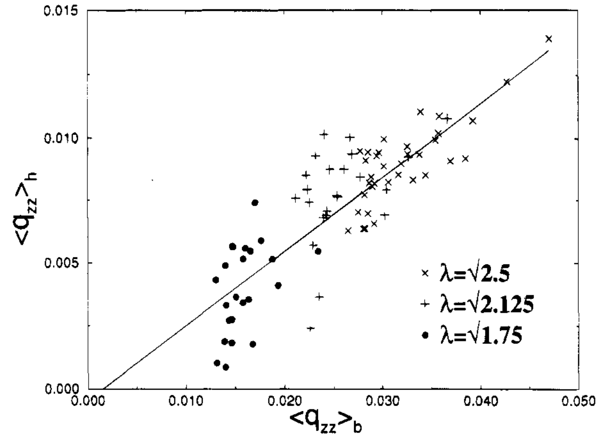

Figure 2. Correlations between the average guest chain bond order and the average bulk bond order. Different symbols stand for different extension ratios λ. The slope of the linear least-squares fit gives the coupling coefficient: $\epsilon = 0.29 \pm 0.1$.

III. Discussion

Having observed an orientational coupling in the nonequilibrium data, one would like to arrive at a better understanding of its origin. Because of the experimentally observed linear relationship between the order parameter of the guest bond chains and that of the surrounding matrix at small strain, one widely accepted explanation[8,9] is that the orientation of the guest chain bonds is due to the fact that the bonds of the surrounding matrix are oriented. Such an explanation gives rise to the introduction of an interaction energy of the form 1. If this is the case for our simulated chains, linear response theory[17] predicts that an orientational interaction between the guest and host chain bonds in the stretched melt is related to the bond orientational correlations in an equilibrium melt at the small extension ratio used. Accordingly, we studied the bond orientational correlations in equilibrated monodisperse polymer melts.[15] The bond orientational correlation function $S(r)$ is defined as

$$S(r) = \langle Tr(\check{\mathbf{q}}(0)\, \check{\mathbf{q}}(\mathrm{r})) \rangle \tag{6}$$

where the brackets indicate an ensemble average over all bonds separated by a distance r. The order parameter tensor $\check{\mathbf{q}}$ of a single bond is defined in eq 2. Figure 3 shows the various orientational correlation functions. The correlation functions are multiplied by the bond distribution functions $g_b(r)$, which is the probability of finding a pair of bonds a distance r apart, relative to the probability expected for a complete random distribution at the same density. Interchain correlations and correlations between all bonds are shown separately. The correlation functions are calculated from the data obtained by Kremer and Grest[15] for chains with molecular weight $N = 150$, but identical correlations are found for $N = 25$. Our equilibrium data for the bidisperse melts give similar results as well. The fact that strong correlations are present only at small length scales (on the order of one bond length), as can be seen in Figure 3, explains why the results are independent of N. In addition to a decaying envelope, oscillations of the correlations around 0 are observed. These oscillations are due to oscillations in $S(r)$. At the shortest length scales the bonds actually tend to antialign, which is indicated by the negative value of the orientational

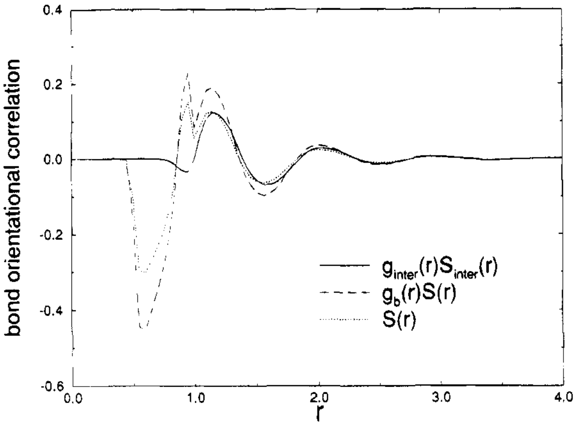

Figure 3. Orientational bond correlation functions $S(r)$ shown separately and multiplied by the bond distribution function $g_b(r)$. Correlations between bonds on different chains ($g_{inter}(r)$ $S_{inter}(r)$) are shown separately. r is in units of the Lennard-Jones length scale σ.

correlation between all bonds. The positive peak at $r \approx \sigma$ indicates a strong alignment. These oscillations in $S(r)$ can be understood as follows. Since the range of the Lennard-Jones potential is approximately equal to the bond length, each bond can be seen as a small halter, with spheres on both sides just touching each other. The closest two such halters can come is by bonds that are perpendicular. The packing at high density of many halters in such a way results in oscillations in $S(r)$. Packing effects similar to those observed here indeed have been found in simulations of diatomic molecules.[18] This antialignment at short distances is absent from the simplest lattice models.[10,11] In the present case, the chain structure adds some interesting features. The first negative peak is almost absent in the interchain correlation, indicating that at typical nearest-neighbor chain separations the orientational correlations are positive. A similar packing structure has been reported for amorphous glassy polymers.[19] We will show that this effect is crucial for understanding the orientational coupling between guest and host chains. On the other hand, the intrachain correlation shows a strong negative peak at the shortest distances. This is accounted for by the fact that two adjacent bonds in the chain have a tendency to anticorrelate.

These correlation functions may be used to estimate the orientation ratio ϵ resulting from aligning the host bonds. In order to make this estimate, we must postulate a form for the aligning perturbation H'. The simplest perturbation that can produce alignment in the host bonds has the form

$$H' = \sum_{i=1}^{M} Tr(\check{\mathbf{q}}_i \check{\mathbf{W}}) \tag{7}$$

where the sum is over all host chain bonds. (To produce alignment in the z direction, the nematic field $\check{\mathbf{W}}$ has the form $W(\hat{z}\hat{z} - \mathbf{I}/3)$.) We suppose that there is one small guest chain in a host matrix containing only long chains. Due to the perturbation of the host bond i at distance r from the origin, the average orientation of the guest chain bond at the origin is[17,20]

$$\langle \check{\mathbf{q}}(0) \rangle = \frac{1}{k_B T} \langle Tr(\check{\mathbf{q}}(0)\ \check{\mathbf{q}}_i(r)) \rangle \check{\mathbf{W}} \tag{8}$$

where the term in brackets is the equilibrium correlation function. The guest bond orientation due to all host bonds is

$$\langle \check{\mathbf{q}}(0) \rangle = \frac{1}{k_B T} \sum_{i=1}^{M} \langle Tr(\check{\mathbf{q}}(0)\ \check{\mathbf{q}}_i(r)) \rangle \check{\mathbf{W}} \tag{9}$$

where the sum is over all host chain bonds. This sum equals $\int d\vec{r}\ \varrho g_{inter}(r)\ S_{inter}(r)$, where g_{inter} and S_{inter} are the interchain bond distribution function and orientational correlation functions, which are used here since the host and guest chain bonds are on different chains. The density of the melt is ϱ. Next, we need to express $\check{\mathbf{W}}$ in terms of the average host chain orientation. Once more using linear response theory, we find that the orientation of an arbitrary host chain bond j due to the perturbation is given by

$$\langle \check{\mathbf{q}}_j \rangle = \frac{1}{k_B T} \sum_{i=1}^{M} \langle Tr(\check{\mathbf{q}}_i \check{\mathbf{q}}_j) \rangle \check{\mathbf{W}} \tag{10}$$

where the correlation functions are again taken at equilibrium. Given the normalization of $\check{\mathbf{q}}$, eq 10 results in

$$\langle \check{\mathbf{q}} \rangle_h = \frac{1}{k_B T} \frac{1}{M} \sum_{i,j} \langle Tr(\check{\mathbf{q}}_i \check{\mathbf{q}}_j) \rangle \check{\mathbf{W}} = \frac{1}{k_B T} \left(1 + \frac{1}{M} \sum_{i \neq j} \langle Tr(\check{\mathbf{q}}_i \check{\mathbf{q}}_j) \rangle \right) \check{\mathbf{W}} \tag{11}$$

The last sum on the right-hand side, that is the sum over the orientational correlations between different host chain bonds, equals $\int d\vec{r}\ \varrho g_b(r)\ S(r)$. We found that in equilibrium the integral of the orientational correlations of all bonds is essentially zero. The same is true for the correlations between different bonds of the host chain in the bidisperse melt. Neglecting the influence of other guest chain bonds, $\langle \check{\mathbf{q}}(0) \rangle = \langle \check{\mathbf{q}} \rangle$, eqs 9 and 11 result in

$$\epsilon_n = \frac{\langle \check{\mathbf{q}} \rangle_g}{\langle \check{\mathbf{q}} \rangle_h} = \frac{\int d\vec{r}\ \varrho g_{inter}(r)\ S_{inter}(r)}{(1 + \int d\vec{r}\ \varrho g_b(r)\ S(r))} \tag{12}$$

The integrals have been calculated from the data shown in Figure 3. The orientation ratio ϵ_n was found to be 0.18 ± 0.01. This value is comparable to, though somewhat lower than, the one found earlier from the bond orientations in the stretched melt.

The large value of ϵ_n is remarkable, considering that the nominal nematic coupling $\int d\vec{r}\ \varrho g_b(r)\ S(r)$ is much smaller than unity: the negative contributions at the shortest distances are nearly cancelled by positive contributions beyond. If the numerator of eq 12 were of comparable size, the resulting ϵ_n would be much smaller than it is. The relatively large size of ϵ_n arises from the significant positive value of the numerator $\int d\vec{r}\ \varrho g_{inter} S_{inter}$. In this integral the negative contributions from the shortest distances are suppressed: g_{inter} is less than g_b here. In physical terms, neighboring bonds at very short distances are less likely to come from other chains than those at longer distances. Other bonds of the guest chain are more likely to take up these nearby, negatively aligned positions. That is, the guest chain *shields* itself from the negatively-aligning tendencies of its surroundings. What remains is a net positive tendency. Thus the large value of ϵ arises because the guest chains are small polymers. Without the mutual

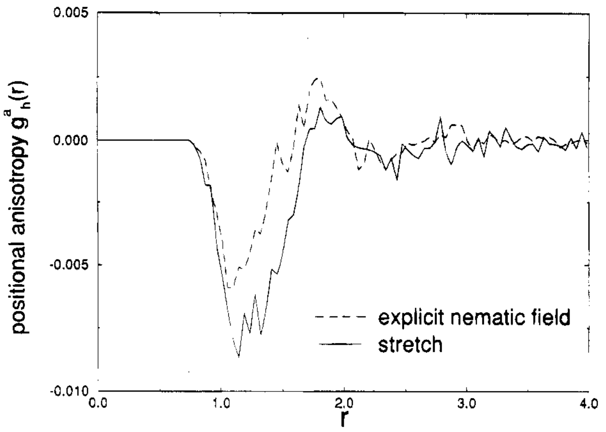

Figure 4. Anisotropy $g_{\mathrm{h}}^{\mathrm{a}}(r)$ in the distribution of host bonds around guest bonds for a stretched melt and a melt perturbed by an explicit nematic field.

shielding effect among the guest chain's bonds, the alignment would be much reduced. This shielding effect suggests that, if the guest chains were replaced by isolated dimers, ϵ would be much reduced. Even for guest dimers some residual coupling is expected, since also in this case g_{inter} is less than g_{b} at the shortest distances, because of the correlation hole effect of the host chain. There is some evidence in the literature that very small guest molecules have weaker alignment.[21]

The predicted $\epsilon_n = 0.18$, though not small, is nevertheless significantly smaller than the $\epsilon = 0.28$ measured under stretching. Given this discrepancy, we decided to investigate the main assumption made in the above derivation, that is, the assumed form of the perturbing Hamiltonian in eq 7. We simulated a bidisperse melt consisting again of a long host chain with molecular weight 5000 and 100 guest chains with $N = 5$. This time the equations of motion for the host chain monomers include a perturbing part H' as given in eq 7. This perturbation orients the host chain bonds in the z-direction. As expected, we observed that, although the equations of motion of the guest chain monomers were not changed, the guest chain bonds orient in the z-direction as well. The orientation ratio was found to be 0.17 ± 0.01. This is consistent with the value ϵ_n obtained in the linear response theory calculation above.

Since the host bond *orientation* causes only part of the guest bond alignment, other anisotropic interactions must take place as well. Among these is the *positional* anisotropy of atoms and bonds in the stretched liquid, where, in the local pair correlation function between guest and host bonds $g_{\mathrm{h}}(r)$, the concentric rings of enhancement are distorted into ellipsoids. This anisotropic density may, in principle, exert an aligning force on guest bonds. The anisotropy might be related to the observed strong compositional fluctuations in the stretch direction. Although the radius of gyration of individual guest chains is slightly (few percent) larger in the stretch direction, clusters of guest chains tend to form and orient perpendicular to the stretch direction. Figure 4 shows the anisotropy $g_{\mathrm{h}}^{\mathrm{a}}(r)$ in the positions of host bonds around guest bonds for the stretched melt and for the melt perturbed by an explicit nematic field. The positional anisotropy is defined as

$$g_{\mathrm{h}}^{\mathrm{a}}(r) = g_{\mathrm{h}}(r)\,\langle cos^2\,\theta - 1/3\rangle \qquad (13)$$

where θ is the angle between the vector connecting the host and guest bonds and the z-axis. The average is taken over all pairs of guest and host bonds that are a distance r separated from each other. In either case the host bond orientation $\langle q_{zz}\rangle_{\mathrm{h}} \approx 0.04$. The data in Figure 4 show that in the stretched melt host bonds around a given guest bond tend to be positioned perpendicular to the stretch direction (negative $g_{\mathrm{h}}^{\mathrm{a}}$), compared to those in the melt perturbed by an explicit nematic field. There the positional anisotropy results from the guest bond orientation, and the $\int \mathrm{d}^3r\,\varrho g_{\mathrm{h}}^{\mathrm{a}}(r)$ vanishes within errors. This integral, which defines an order parameter for the positional anisotropy of host bonds, was -1.0 ± 0.2 for the stretched melt.

Next we want to know if in the stretched melt the host bond's tendency to be positioned perpendicular to the stretch direction is what causes the additional guest bond alignment as observed along the stretch axis. To this end, we study in the equilibrium liquid the correlation between the orientation of an arbitrary test bond and the anisotropy in the bond positions surrounding it, regardless of the orientations of those other bonds:

$$\mathrm{X} = 3/2\sum_j (cos^2\,\theta_{ij} - 1/3) \qquad (14)$$

where the sum is over all bonds j around a test bond i, and θ_{ij} is the angle between the test bond orientation and the vector connecting bonds i and j. The correlation is short ranged, and only bonds that are less than a few bond lengths from the test bond contribute to the sum in eq 14. The sum of eq 14 over all bonds on chains that do not contain the test bond is -2.5 ± 0.3. Its large negative value indicates that the observed anisotropy in the host bond positions in the stretched melt will indeed result in an orientation of guest bonds along the stretch direction. The fact that anisotropy in the positions of host bonds can induced orientation of guest chains has been studied theoretically by Brereton[14] and by Edwards and McLeish.[22]

Another obvious anisotropy in the host is the stress itself. (The bond orientation may be viewed as a byproduct of this stress; the anisotropic density may be viewed as the microscopic manifestation of this stress.) Indeed, anisotropic stress in itself is expected to produce alignment. This is easily seen by considering a rigid, macroscopic ellipsoid in an elastic material such as rubber under uniaxial stress. We suppose that the aspect ratio of the ellipsoid has some finite value greater than unity. The presence of the ellipsoid increases the elastic energy in the vicinity. The increase in energy is roughly the elastic energy in a sphere as large as the ellipsoid. This elastic energy is lowest when the long axis is in the direction of elongation. This energy is increased by a factor of order unity for an ellipsoid in a perpendicular orientation.[23] The energy difference is thus on the order of the strain energy in the ellipse volume.

By treating our guest bonds as inclusions of this type, we estimate alignment effects comparable to those observed. The simulated chains have a plateau modulus of about $kT/35$ per bead.[15] Since in our stretched chains the elastic strain was of order unity, the elastic energy was also some $kT/35$ per bead. We may regard our guest bonds as oblong inclusions in this distorted matrix with anisotropy of order unity. Then the elastic energy near each bond should be lowered by a factor of order unity when the bond is aligned with the stress. The energy difference is roughly the strain energy in the volume of the inclusion—*i.e.*, roughly the energy in a guest–bond volume. Since the number of bonds per unit volume is comparable to the number of beads, this yields an orientation energy of order $kT/35$. Such an energy is expected to produce an alignment $\langle \check{\mathbf{q}} \rangle_g \approx \exp(1/35) - 1$ of a percent or two. This is in reasonable agreement with the 1% induced alignments we observed.

IV. Conclusion

Our simulations suggest that induced anisotropy in stretched polymer liquids is largely an intrinsic consequence of the chain structure of polymers rather than an extrinsic consequence of the structure of particular polymers. Our minimal, bead–spring chains have no local rigidity or anisotropy, yet they show induced anisotropy effects comparable those seen in real polymers. To be sure, these effects are somewhat stronger in real polymers than in our minimal polymers, with orientation ratios ϵ often 2–3 times as large as ours. This seems natural: the extra structure and rigidity in real chains might well be expected to produce extra alignment. Moreover, studies of bond orientational correlation functions by Yoon *et al.*[13] have shown that their magnitude is strongly enhanced if chemical detail is included in the simulations. Therefore, we expect that the orientation ratio for our minimal polymers is lower than that for real polymers.

Part of our observed alignment is attributable to the classical orientational interaction[1] of guest bonds with neighboring host bonds. This part may be accessed by using the explicit nematic field of eq 7 to produce the host alignment. Since all simulations were done in the linear response regime, the orientation ratio ϵ_n is expressible in terms of correlation functions of the isotropic, equilibrium system. In view of the structure of these correlation functions, the net alignment appears to arise from a self-shielding effect. The alignment in the vicinity of a bond has strong negative and positive contributions according to the distance. These opposing contributions cancel nearly completely. But the negative aligned bonds, occurring at the shortest distances, tend to be bonds of the guest chain itself. The remaining, host bonds have a net aligning influence; the antialigning sites are shielded by the guest chain's own bonds.

This orientational coupling, acting alone, produces an orientation ratio ϵ_n of about 0.18—substantially smaller than the orientation ratio produced by stretching. We infer that the guest bonds are influenced not only by the orientation of the host bonds but also by other anisotropic properties of the host. For example, we have measured that, under stretch, the host bonds near a given guest bond are *positioned* anisotropically. Taking a more macroscopic viewpoint, the very presence of anisotropic stress in the host is expected to align an anisotropic inclusion. As argued above, the magnitude of this effect may be sufficient to account for the observed alignment. To account for the interplay between these various anisotropic influences in a stretched polymer liquid is a worthwhile goal for future research. In this way, one may hope to understand, *e.g.*, the observed variations[2] of ϵ with guest chain length.

Acknowledgment. We thank M. Cates, D. Frenkel, J. Kornfield, D. Pearson, and F. Solis for useful discussions. This work was supported by the National Science Foundation through Grant Nos. DMR 88-19860 and DMR 91-10004. A.R.C.B. acknowledges the hospitality of Exxon Research where part of this work was carried out.

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MA941308B