Anomalous pressure dependence of the structure factor in 1,4-polybutadiene melts: A molecular dynamics simulation study

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Neutron scattering has shown the first diffraction peak in the structure factor of a 1,4-polybutadiene melt under compression to move to larger q values as expected but to decrease significantly in intensity. Simulations reveal that this behavior does not result from loss of structure in the polymer melt upon compression but rather from the generic effects of differences in the pressure dependence of the intermolecular and intramolecular contributions to the melt structure factor and differences in the pressure dependence of the partial structure factors for carbon–carbon and carbon–deuterium intermolecular correlations. This anomalous pressure dependence is not seen for protonated melts.

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Complex liquids such as polymer melts exhibit a rich variety of relaxation processes [1]. Improved understanding of these phenomena can only come about through detailed analyses of the correlations between the underlying structure of the polymer melt and the fundamental chain dynamics (torsional transitions, segmental relaxation, normal mode relaxation, etc.) that lead to these processes. This is particularly true for the glass transition of polymer melts [2] where mode-coupling theory [3], which predicts the glass transition to be solely a consequence of packing, has been used to interpret experiments [4] as well as simulations [5]. Another area where local structural correlations are thought to play a central role in determining the dynamics are miscible polymer blends [6,7]. While significant effort has been dedicated to understanding the temperature dependence of structure/dynamic correlations in polymer melts and blends [2–7], only recently has a series of investigations focused on understanding the influence of pressure on structure/dynamic correlations in polymer melts [8–11].

One of the most striking results of these measurements is the behavior of the static structure factor $S(q)$ of 1,4-polybutadiene (PBD) melts under pressure [9]. In these investigations, it was found that the first sharp diffraction peak (amorphous halo), which is generally believed to originate primarily from intermolecular positional correlations, shifts to larger momentum transfers and reduces in intensity with increasing pressure. While the shift in position is expected due to the increase in density upon melt compression and has been similarly found upon reducing the temperature at fixed pressure [12], the reduction in intensity was completely unexpected and could not be explained on the basis of the experimental data alone. In this situation, molecular dynamics (MD) simulations of chemically realistic models provide a unique tool for a detailed investigation of the atomistic structure in the polymer melt and allow us to determine the origin of the surprising pressure dependence of the structure factor.

Although, in this paper, we focus on understanding the anomalous features in the structure factor of a PBD melt, the conclusions will turn out not to be specific to this system but of general relevance to the understanding of polymer melt structure.

We have undertaken MD simulations of PBD with a microstructure of 40% *cis*, 50% *trans*, and 10% vinyl, agreeing with typical experimental samples [13], using a carefully validated chemically realistic united atom model [14]. This model has been shown to quantitatively reproduce experimental measurements of relaxation processes in PBD melts as probed by ^{13}C nuclear magnetic resonance spin-lattice relaxation, [15] dielectric spectroscopy, [16] and dynamic neutron scattering [17]. In this work, we have performed MD simulations of the PBD melt along the 293 K isotherm that was also studied experimentally [9]. (Note that the exact temperature in the experiments was 295 K.) The melt contained 40 PBD chains each consisting of 30 repeat units. Simulations were performed in the NpT ensemble at p =0.001, 0.25, and 2.72 GPa. The melt was equilibrated for 3 ns at each pressure, with production runs of 10 ns ensuring sufficient sampling of the static structure. After the trajectories were generated, the hydrogen (deuterium) atoms were reinserted for each saved snapshot (every 1 ps) in their mechanical equilibrium positions that are uniquely determined by the positions of the backbone carbon atoms (united atoms) [18]. This allowed us to calculate an atomistic structure factor $S(q)$ as well as to analyze its various partial contributions. While we anticipate that bond lengths and bend angles involving inserted hydrogen (deuterium) atoms can slightly change upon compression, we believe that this will only slightly influence all structural properties discussed below.

In Fig. 1, we show the behavior of the PBD melt total structure factor $S(q)$ obtained from simulations at various pressures and defined as
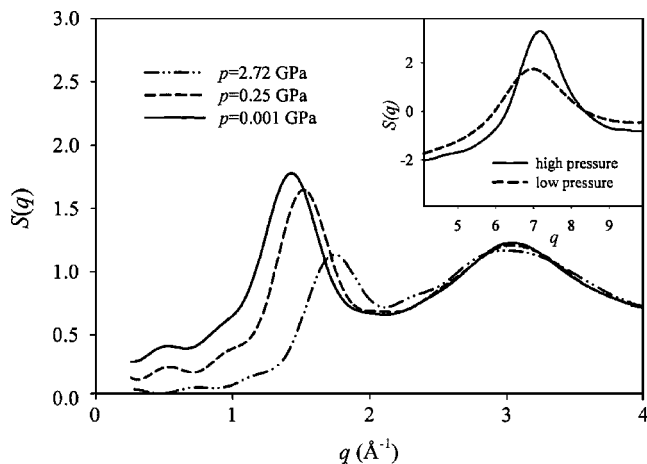
FIG. 1. Static structure factor of the deuterated 1,4-polybutadiene melt in the vicinity of the first sharp diffraction peak at 293 K from MD simulations. The inset shows the behavior of a bead-spring (chain length 20) polymer melt at $T^* = k_B T / \varepsilon = 1.0$ for $\rho^* = N_{beads}\sigma/V = 0.8$ (low pressure) and $\rho^* = 1.0$ (high pressure). Polymer bead–bead interactions were described by standard Lennard-Jones potential with ε and σ parameters defining energy and length scales, respectively. Bond lengths between neighboring beads in the chains were constrained at σ.

$$S(q) = 1 + \frac{n}{\langle |b_\alpha|^2 \rangle} \sum_{\alpha\beta} x_\alpha b_\alpha x_\beta b_\beta \int_0^\infty (g_{\alpha\beta}(r) - 1) \frac{\sin qr}{qr} 4\pi r^2 dr. \tag{1}$$

In Eq. (1) $g_{\alpha\beta}(r)$ is the radial distribution function between atoms of type α and β, n is the total number density of scattering centers, b_α is the coherent scattering length for atoms of type α, x_α is the fraction of atoms of type α in the system, and $\langle |b_\alpha|^2 \rangle \equiv \Sigma_\alpha x_\alpha |b_\alpha|^2$. In complete agreement with the experiment, we find a shift of the first sharp diffraction peak to larger momentum transfer q and a strong reduction in intensity with increasing pressure. Intuitively, one would expect the local structure in the compressed system to become better defined, i.e., interatomic correlations to become stronger, which should lead to an increase in the intensity of the first peak. This intuition is confirmed by the behavior of hard-sphere liquids, colloids and coarse-grained polymer models such as melts of bead-spring chains, shown in the inset of Fig. 1. In this model, the first sharp diffraction peak moves to larger q, increases in intensity, and becomes narrower with increasing pressure. However, real polymer melts have a very different local structure from all of these systems. The local packing of linear polymers can be better visualized as a packing of spaghetti than the packing of billiard balls. In real polymers, the chemical bond lengths are much smaller than the size of the atoms as manifested by the nonbonded Lennard-Jones interactions. It has been shown in simulations of a coarse-grained bead-spring model that the ratio of bond length to atomic radius strongly influences the melt structure [19]. Pursuing the picture of the local packing of spaghetti, we can anticipate that the nearest-neighbor
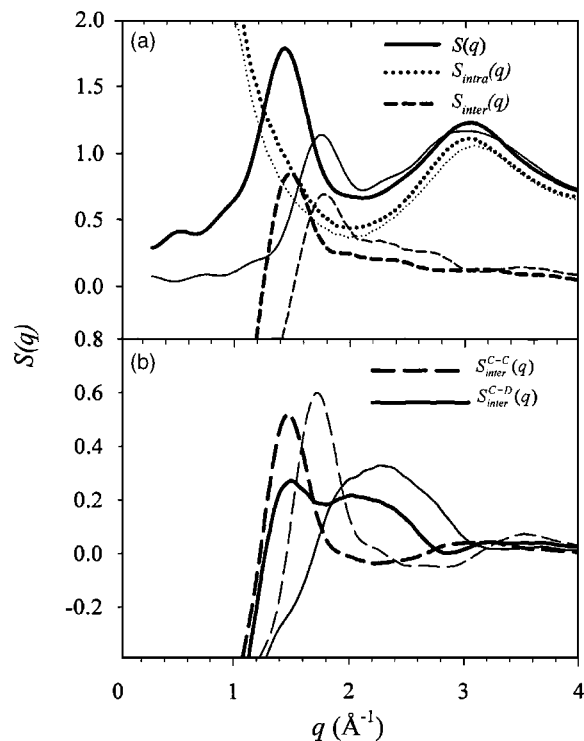

FIG. 2. (a) Inter- and intramolecular contributions to the total structure factor $S(q)$ for the deuterated 1,4-polybutadiene melt shown and (b) intermolecular partial structure factors $S_{inter}^{C-C}(q)$ and $S_{inter}^{C-D}(q)$. Structure factors correspond to $p = 0.001$ GPa (bold lines) and $p = 2.72$ GPa (thin lines).

packing distance between noodles should decrease and become better defined upon compression. This structural information, buried in the total $S(q)$ (determined either experimentally or from simulations), can be extracted from the analysis of various partial contributions to the total structure factor easily obtainable from simulations.

The inter- and intramolecular contributions to $S(q)$ can be calculated as

$$S_{intra}(q) = 1 + \frac{n}{\langle |b_\alpha|^2 \rangle} \sum_{\alpha\beta} x_\alpha b_\alpha x_\beta b_\beta \int_0^\infty (g_{\alpha\beta}^{intra}(r)) \frac{\sin qr}{qr} 4\pi r^2 dr, \tag{2}$$

$$S_{inter}(q) = S(q) - S_{intra}(q), \tag{3}$$

where $g_{\alpha\beta}^{intra}(r)$ denotes the intramolecular radial distribution function normalized the same way as the total $g_{\alpha\beta}(r)$ used in Eq. (1). In Fig. 2(a), we show $S_{inter}(q)$ and $S_{intra}(q)$ for two pressures. $S_{intra}(q)$ decreases monotonically in the q range defining the first peak in $S(q)$, i.e., between 1.0 and 2.0 Å^{-1}, and is nearly independent of pressure. $S_{inter}(q)$, as expected, shows a well defined peak in this q range. The peak position for $S_{inter}(q)$ coincides closely with the position of the peak in $S(q)$ and shifts to larger q values with increasing pressure. The reduction in peak intensity for $S_{inter}(q)$ is significantly less than that observed for the corresponding peak in $S(q)$

upon compression. Figure 2(a) clearly illustrates that the majority of the reduction in the intensity of the first peak in $S(q)$ with increasing pressure is due to shifting of the $S_{inter}(q)$ peak to larger q where it is summed up with a nearly pressure independent $S_{intra}(q)$ that drops sharply in this range with increasing q. Hence, the first sharp diffraction peak in $S(q)$ cannot be interpreted in terms of intermolecular correlations only: The pressure and q dependence of the intramolecular contributions can play a key role in determining the behavior of $S(q)$ in the range of the first diffraction peak.

While Fig. 2(a) reveals that the majority of the reduction in the total $S(q)$ is not due to the loss of intermolecular structure upon compression, there is still some reduction in the intensity of the first peak in $S_{inter}(q)$ that can be interpreted as "anomalous" reduction in the intermolecular structure as pressure increases. In order to better understand this behavior, we have analyzed contributions of the partial structure factors due to carbon–carbon, $S_{inter}^{C-C}(q)$, and carbon–deuterium, $S_{inter}^{C-D}(q)$, correlations to the total $S_{inter}(q)$. These are shown in Fig. 2(b). The partial structure factors due to deuterium–deuterium correlations were featureless in the q range of interest and therefore are not shown. The first peak in $S_{inter}^{C-C}(q)$ becomes sharper and increases in intensity with increasing pressure, therefore indicating that the intermolecular correlation between backbone atoms becomes stronger upon compression as expected. For $S_{inter}^{C-D}(q)$, the pressure dependence is much more dramatic and complex. In the vicinity of the first diffraction peak, we find two humps at low pressure. As pressure increases, the first hump largely disappears while the second hump increases in magnitude and shifts to larger q. Analysis of the intermolecular carbon–deuterium radial distribution functions (not shown) reveals that the second (larger q) hump corresponds to carbon–deuterium correlations between nearest-neighbor chains where a deuterium of one chain is orientated toward the nearest-neighbor chain. As a result, this hump occurs at a larger q value (shorter distances) than that for the first peak in $S_{inter}^{C-C}(q)$. The q value for the first hump in the $S_{inter}^{C-D}(q)$ peak corresponds closely to that for the first peak in $S_{inter}^{C-C}(q)$, indicating that the deuterium atoms involved in these correlations have no net orientation with respect to nearest-neighbor chains. It is the dramatic decrease in the contribution from these "unoriented" deuterium atoms with increasing pressure, and the increase in the contribution due to "oriented" deuterium atoms, that leads to the dramatic pressure dependence of $S_{inter}^{C-D}(q)$. The disappearance of scattering intensity due to carbon–deuterium correlations in the vicinity of the first peak in $S_{inter}(q)$, i.e., the first hump in $S_{inter}^{C-D}(q)$, is also responsible for the decrease in peak intensity of $S_{inter}(q)$ with increasing q despite the fact that the peak intensity for $S_{inter}^{C-C}(q)$ increases with pressure. Clearly, even when it is possible to differentiate between intramolecular and intermolecular contributions to the total $S(q)$, the knowledge of various partial contributions may still be necessary in order to correctly interpret the dependence of the structure on thermodynamic conditions.

The relative importance of the different atom–atom correlations to the structure factor depends on the values of the scattering lengths of the atoms involved [see Eqs. (1) and
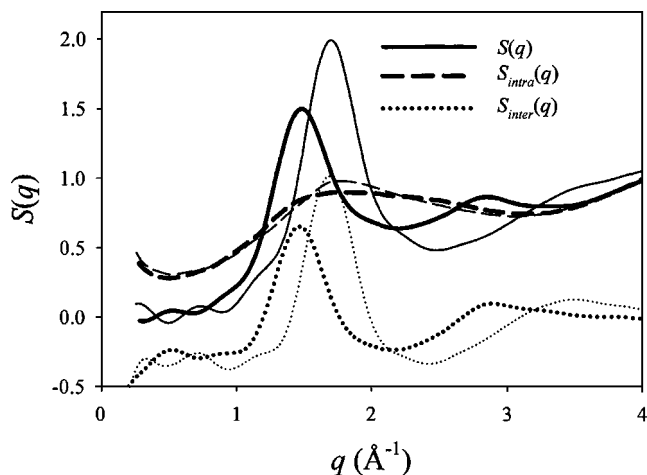

FIG. 3. Inter- and intramolecular contributions to the total structure factor $S(q)$ for the protonated 1,4-polybutadiene melt shown at $p=0.001$ GPa (bold lines) and $p=2.72$ GPa (thin lines).

(2)]. We therefore have calculated $S(q)$ as well as its inter- and intramolecular contributions for the same PBD melts but protonated chains. We used exactly the same trajectories and replaced deuterium atoms with hydrogen atoms. The resulting $S(q)$ and its contributions are shown in Fig. 3. Unlike the deuterated melt, $S_{intra}(q)$ for the protonated melt is very flat in the q range between 1.0 and 2.0 Å^{-1} and therefore does not induce a decrease in peak intensity with shifting of the intermolecular peak to larger q values. In the deuterated sample, where scattering lengths of carbon and deuterium atoms are positive, all partial contributions (carbon–carbon, carbon–deuterium, and deuterium–deuterium) to the intramolecular structure factor steeply decrease in the q range between 1.0 and 2.0 Å^{-1} [see Fig. 4(a)] resulting in the strong q dependence of the total $S_{intra}(q)$ in this q range. In the protonated melt, the negative value of the scattering length for protons results in a sharp increase in the $S_{intra}^{C-H}(q)$ in the q range between 1.0 and 2.0 Å^{-1} while the contributions from carbon–carbon and hydrogen–hydrogen correlations decrease sharply in the same range, as seen from Fig. 4(b),
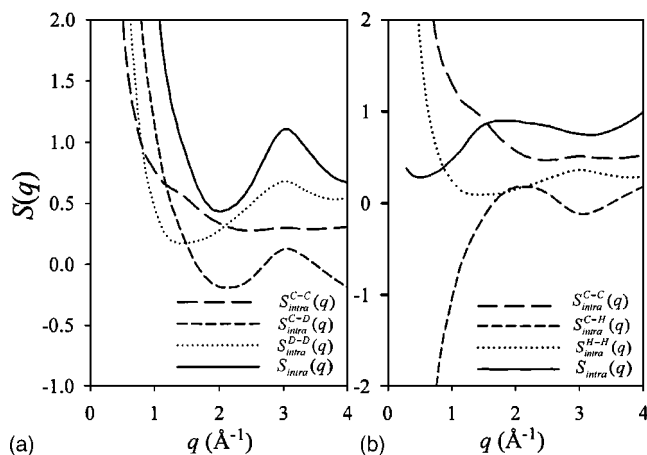

FIG. 4. Intramolecular partial structure factor contributions at $p=0.001$ GPa for (a) deuterated 1,4-polybutadiene and (b) protonated 1,4-polybutadiene.

yielding a relatively q independent $S_{intra}(q)$ in the q range corresponding to the amorphous halo. Additionally, the coherent scattering length for hydrogen is quite different from that of deuterium and therefore the partial scattering due to intermolecular carbon–hydrogen correlations is relatively insignificant in comparison to that from carbon–carbon correlations, while intermolecular carbon–deuterium correlations contribute significantly to the scattering in the q range corresponding to the amorphous halo, as shown in Fig. 2(b). As a result, the pressure dependence of $S(q)$ in the protonated PBD melt is dominated by the pressure dependence of intermolecular carbon–carbon correlations and consequently shows the expected behavior as pressure increases.

In conclusion, we have shown that what appears to be anomalous pressure dependence of the static structure factor obtained from neutron scattering measurements on a perdeuterated PBD melt is not indicative of any loss of intermolecular structure. MD simulations of the PBD melt revealed that the observed decrease in the intensity of the first sharp diffraction peak in $S(q)$ is due primarily to shifting of the intermolecular contribution $S_{inter}(q)$ to larger q values where it is summed up with sharply decreasing and largely pressure-independent intramolecular contribution $S_{intra}(q)$ as well as decreasing contributions of intermolecular carbon–deuterium correlations in the range of the first sharp diffraction peak with increasing pressure. Intermolecular correlations between backbone atoms in the PBD melt were found to become stronger and better defined with increasing pressure. Our simulations also revealed that the structure factor for protonated PBD shows the expected pressure dependence due to a largely q-independent intramolecular structure factor $S_{intra}(q)$ in the relevant q range as well as a dominance of the carbon–carbon correlations in the intermolecular structure factor. This work clearly illustrates that experimentally obtained structure factors can be a quite complex combination of the various partial contributions and that additional information that allows for the determination of those contributions is necessary for the correct interpretation of structural changes.

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