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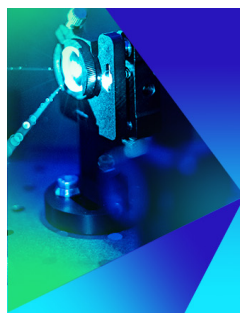


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The intermolecular hydrogen–hydrogen structure of chain–molecule liquids from neutron diffraction

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Neutron diffraction isotopic substitution experiments on liquid *n*-decane (C₁₀H₂₂) and *n*-eicosane (C₂₀H₄₂) are described. The intermolecular H–H structure function $h_{HH}(Q)$ and the intermolecular H–H correlation function $g_{HH}^{inter}(r)$ are obtained without recourse to models of the intramolecular structure. The structure of the $g_{HH}^{inter}(r)$ found at 2.5, 5.0, and 7.0 Å corresponds to different shells in the H–H pair correlation function. In addition, $g_{HH}^{inter}(r) < 1$ for a considerable range, due to the screening of intermolecular correlations by intramolecular correlations. This “correlation hole” effect is accentuated by extrapolation of the structure functions to the expected infinite wavelength limit, and shows good agreement with values determined from small-angle neutron scattering (SANS) data. All of these features are in good agreement with the results of molecular dynamics simulations for the closely related system C₁₃H₂₈.

INTRODUCTION

The method commonly used to arrive at the intermolecular structure function $h(Q)$ of a molecular liquid from scattering data, x-ray data in particular, is from an estimate of the intramolecular structure function $\omega(Q)$, and via the following expression:

$$\rho h(Q) = H(Q) - \omega(Q), \quad (1)$$

where $H(Q)$ is the total structure function as obtained from a scattering experiment, ρ is the number density of scattering units, and the magnitude of the scattering vector $Q = 4\pi \sin \theta / \lambda$, with 2θ the angle of scatter and λ the neutron wavelength.

This method has been applied with success in cases involving small rigid molecules,¹ for which $\omega(Q)$ can be calculated easily. Approximate methods,² however, are employed in the calculation of $\omega(Q)$ for chain molecules, which can exist in any of many available conformations. Despite these approximations, Eq. (1) has been used to yield estimates for $h(Q)$ of chain–molecule liquids.^{3,4}

In contrast to the above procedure of analysis, no reference to an intramolecular model is necessary if the technique of hydrogen/deuterium isotopic substitution is used in neutron diffraction experiments. This type of study was performed on liquid hydrogen chloride⁵ and on aqueous solutions of tetramethylammonium chloride,⁶ from which the hydrogen–hydrogen (HH) intermolecular pair correlation functions $g_{HH}^{inter}(r)$ were obtained. This method is related to the ideas of Stein⁷ and others,⁸ which have been used for over a decade in the study of polymer conformations in the melt from small-angle neutron scattering experiments.

We have determined $g_{HH}^{inter}(r)$ for *n*-decane (C₁₀H₂₂) and *n*-eicosane (C₂₀H₄₂) from neutron diffraction isotopic substitution experiments, without recourse to intramolecular struc-

ture models. The results are shown to be in good agreement with molecular dynamics simulations on tridecane (C₁₃H₂₈). The intermolecular structure of such a chain–molecule liquid is also calculable by way of theories of polymer structure and thermodynamics,⁹ which are presently being developed to treat realistic melts. The experimental results of the sort presented here are expected to contribute, together with simulations, to the development of these theories.

THEORY

Consider a chain–molecule liquid, with a total number of chains N_c contained in a volume V , with Z monomers per chain, and each monomer unit being made up of one carbon and m_H hydrogens. The effects introduced by the presence of CH₃ instead of CH₂ groups on the ends of each chain are taken into account by defining m_H as the average number of hydrogens per monomer ($m_H = 2.2$ and 2.1 for C₁₀ and C₂₀, respectively). The scattering cross section of a purely hydrogenated sample, in units of barns per steradian, is given by

$$\left(\frac{d\sigma}{d\Omega} \right)_H = ZN_c \{ b_c^2 [1 + \omega_{CC,p}(Q) + \rho_m h_{CC,p}(Q)] + m_H b_H^2 [1 + \omega_{HH,p}(Q) + m_H \rho_m h_{HH,p}(Q)] + 2b_C b_H m_H [\omega_{CH,p}(Q) + \rho_m h_{CH,p}(Q)] \}, \quad (2)$$

where b_i is the neutron scattering length of element i , and $\rho_m = N_c Z / V$ is the monomer density. The intramolecular C–C structure function is defined as

$$\omega_{CC,p}(Q) = \frac{(Z-1)}{V} \int \omega_{CC,p}(r) e^{iQ \cdot r} dr \quad (3)$$

and the intermolecular structure function is given by

$$h_{CC,p}(Q) = \int h_{CC,p}(r) e^{iQ \cdot r} dr \quad (4)$$

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with $h(\mathbf{r}) \equiv g(\mathbf{r}) - 1$ and $g(\mathbf{r})$ the pair correlation function. The other structure functions have similar forms. The suffix p is used to refer to a pure sample, as opposed to the H/D mixture (see below). The expressions above, written in vector notation, are sufficient for our purposes. Extension to the corresponding azimuthally averaged expressions, which are slightly more complex, is straightforward. In the remaining

part of this paper the vector notation is dropped, ignoring orientational correlations which are small.^{10,11}

The expression for the scattering cross section of a totally deuterated sample, $(d\sigma/d\Omega)_D$, is as given by Eq. (2), except for a change from H to D in all relevant suffixes. The scattering cross section of a mixture sample, $(d\sigma/d\Omega)_m$, with a fraction X_H of chains fully hydrogenated and a fraction X_D of chains fully deuterated ($X_H + X_D = 1$) is given by

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_m = & ZN_c \{ b_c^2 [1 + \omega_{CC,m}(Q) + \rho_m h_{CC,m}(Q)] + m_H X_H b_H^2 [1 + \omega_{HH,m}(Q) + m_H X_H \rho_m h_{HH,m}(Q)] + m_H X_D b_D^2 \\ & \times [1 + \omega_{DD,m}(Q) + m_H X_D \rho_m h_{DD,m}(Q)] + 2m_H X_H b_C b_H [\omega_{CH,m}(Q) + \rho_m h_{CH,m}(Q)] + 2m_H X_D b_C b_D \\ & \times [\omega_{CD,m}(Q) + \rho_m h_{CD,m}(Q)] + 2b_H b_D X_H X_D m_H^2 \rho_m h_{HD,m}(Q) \}, \end{aligned} \quad (5)$$

where the suffix m is used to refer to a mixture sample.

We proceed by forming the following difference:

$$\begin{aligned} \Delta = & X_H \left(\frac{d\sigma}{d\Omega} \right)_H + X_D \left(\frac{d\sigma}{d\Omega} \right)_D - \left(\frac{d\sigma}{d\Omega} \right)_m \\ = & \Delta_{CC} + \Delta_{HH} + \Delta_{DD} + \Delta_{CH} + \Delta_{CD} + \Delta_{HD}. \end{aligned} \quad (6)$$

If deuteration does not affect the structure of the liquid, then the only terms that contribute to the difference are

$$\begin{aligned} \Delta = & [\Delta_{HH} + \Delta_{DD} + \Delta_{HD}]_{\text{inter}} \\ = & \rho_m ZN_c m_H^2 X_D X_H (b_H - b_D)^2 h_{HH}(Q). \end{aligned} \quad (7)$$

Equation (7) shows that Δ would yield only the intermolecular HH structure function of the chain fluid. All the intramolecular terms, as well as the single atom scattering terms, which contain significant distortion from nuclear recoil effects, cancel in the process of calculating Δ . This result is strictly valid only when the effects of isotopes on the structure are small,¹² and when all the samples are run at the same molecular number density. These two conditions were satisfied in our experiments, within the likely error of extracting the structure factor from the experimental data. The other pair correlation functions, CC and CH, cannot be obtained in isolation from a simple linear combination of the differential cross sections. The linear combinations proposed earlier¹³ yield total C-C and C-H structure functions which are coupled to the H-H intramolecular structure function. These are not discussed further.

EXPERIMENTAL PROCEDURE

Experiments were carried out on two short-chain linear alkanes, *n*-decane ($C_{10}H_{22}$, $\rho_a = 0.0989$ atoms \AA^{-3} , $T = 295$ K) and *n*-eicosane ($C_{20}H_{42}$, $\rho_a = 0.1042$ atoms \AA^{-3} , $T = 323$ K). Three samples were measured for each alkane: a light sample (sample H; 100% H), a heavy sample (sample D; $98.5 \pm 1.0\%$ D), and a mixture (sample *m*; 50% of sample H and 50% of sample D). The samples, 1 mm thick, were contained in flat plate cells, 1 mm wall thickness, made out of $Ti_{0.676}Zr_{0.324}$ alloy, a material which has zero coherent neu-

tron scattering.¹⁴ The samples corresponding to the same alkane were run on the same container. Measurements were also made on empty containers, a vanadium slab (3.5 mm thick) and of the background.

The experiments were carried out on the SANDALS instrument at the ISIS spallation neutron source, Rutherford Appleton Laboratory, U.K. Neutron diffraction at spallation sources is carried out in an energy dispersive mode, in which a broad distribution of wavelengths is incident on the sample, and diffraction data are collected as a function of time of flight. Of the incident spectrum, only a portion of the wavelengths were used ($0.06 \leq \lambda \leq 3.5$ Å). The data were separated into eight groups ($7^\circ \leq 2\theta \leq 20^\circ$), and data from each group was corrected for background, multiple scattering, absorption, and empty can contributions as described in the ATLAS manual.¹⁵ Time of flight was converted to Q , and the intensity scale was normalized to absolute units (barn atom⁻¹ sterad⁻¹), $d\sigma/d\Omega$, using the vanadium spectra.

These corrections resulted in differential scattering cross sections, which are a sum of the "self" and "distinct" scattering cross sections. Figure 1 shows the differential cross sections of the three eicosane samples, for one of the detector groups. The self or single atom scattering cross section should be equal to $\sigma_s/4\pi$, which is the value expected from a collection of uncorrelated atoms of the same composition as the sample, where σ_s is the total scattering cross section per average atom. The scattering cross sections in Fig. 1 should approach the uncorrelated atom value at high Q , but they do not quite do so, because of inelasticity effects, which are large for the *m* and H samples (for eicosane D, *m* and H samples $\sigma_s/4\pi = 0.59, 2.57$, and 4.55 barn atom⁻¹, respectively). The self and inelasticity contributions constitute a smoothly and slowly varying background on which the more rapidly varying distinct scattering oscillates.

Corrections for self-scattering and inelasticity, $d\sigma/d\Omega_{\text{self}}$, were estimated by fitting^{13,16} a second-order Chebyshev polynomial in $\ln[E(\lambda)]$ space to the data from the H and D samples, where $E(\lambda)$ is the neutron energy. The differential cross sections for the mixture samples exhibit a

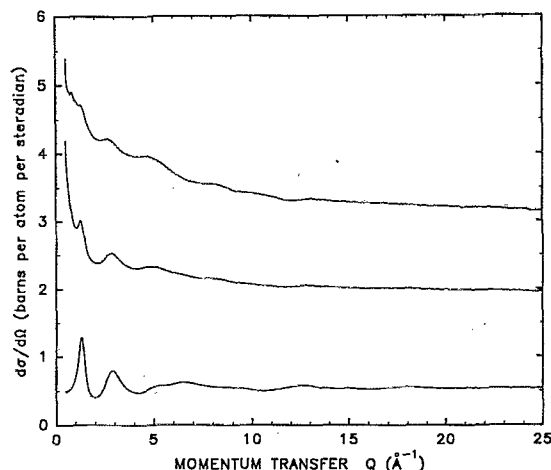


FIG. 1. Example of total differential cross sections for the three eicosane samples for one of the detector groups. Magnitude decreases with H fraction.

large rise at low Q (Fig. 1), which is the small-angle scattering due to intramolecular contributions, and therefore the fitting procedure cannot be used to estimate the self-scattering contributions. It has been shown⁵ that since self-scattering is an incoherent effect then it is reasonable to assume that

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{self},m} = X_H \left(\frac{d\sigma}{d\Omega}\right)_{\text{self},H} + X_D \left(\frac{d\sigma}{d\Omega}\right)_{\text{self},D} \quad (8)$$

If Eq. (8) were correct, then the difference Δ [Eq. (6)] would show no inelasticity effects; this is not the case in practice, in either the present or previous studies.^{5,6,17,18} However, it is important to realize that inelasticity effects are small for the intermolecular structure factors, and affect the self and intramolecular terms more strongly.^{5,17} To minimize the effects of these residual inelasticity effects, the differential cross sections for the H, D, and m samples were individually corrected, and then used to calculate Δ [Eq. (6)]. Equation (8) was used to compute the self-scattering and inelasticity correction for the mixture sample. The $d\sigma/d\Omega_{\text{self}}$ were subtracted from the differential cross sections to obtain the structurally significant part of the scattering $(d\sigma/d\Omega)_{\text{COH}}$.

ANALYSIS AND RESULTS

For each of the eight detector groups $h_{HH}(Q)$ [Eqs. (6) and (7)] was computed, using the set of $(d\sigma/d\Omega)_{\text{COH}}$ which had been corrected for self-scattering and inelasticity effects. The estimates of $h_{HH}(Q)$ from all the groups were subsequently merged into one dataset, spanning the range $0.3 \leq Q \leq 35.0 \text{ \AA}^{-1}$.

The merged datasets were affected by a substantial amount of noise. The structure functions $h_{HH}(Q)$ were smoothed¹⁹ in the region $5.0 \leq Q \leq 35.0 \text{ \AA}^{-1}$. We found that smoothing in this range had no effect on $g_{HH}^{\text{inter}}(r)$, apart from reducing noise. A window function was applied in the region $8.0 \leq Q \leq 35.0 \text{ \AA}^{-1}$ to ensure a smooth function termination.

In addition, the $h_{HH}(Q)$ were extrapolated from $Q=0.3 \text{ \AA}^{-1}$ to $Q=0.0 \text{ \AA}^{-1}$ as follows (for the experimental data $Q_{\text{min}}=0.3 \text{ \AA}^{-1}$). The $Q=0$ limits [$\rho_a h_{HH}(0)=-30.11$ and -60.12 for decane and eicosane, respectively] were evaluated from

$$\rho_a h_{HH}(0) = \rho_a k_B T \kappa_T - (Z m_H - 1) \frac{(m_H + 1)}{m_H}, \quad (9)$$

where ρ_a is the atomic density, k_B is Boltzmann's constant, and κ_T is the isothermal compressibility ($10.95 \times 10^{-11} \text{ dyn}^{-1} \text{ cm}^2$ for decane and $8.5 \times 10^{-11} \text{ dyn}^{-1} \text{ cm}^2$ for eicosane²⁰). The first term in Eq. (9) has values of 0.44 and 0.40, while the second term has values of -30.55 and -60.52 , for decane and eicosane, respectively. The values of $h_{HH}(Q)$ in the range $0.0 < Q < 0.3 \text{ \AA}^{-1}$ were evaluated in two different ways. First, a linear variation of $h_{HH}(Q)$ was assumed. Second, the molecules were assumed to be random coils, and Debye functions² were used in the estimate of $h_{HH}(Q)$. The radii of gyration of the molecules (4.5 \AA for C_{10} and 7.4 \AA for C_{20}) were determined by small-angle neutron scattering (SANS). For alkanes, the extrapolation based on the Debye model is more physically valid²¹ than the linear extrapolation, yet the $g_{HH}^{\text{inter}}(r)$ were independent of the method of extrapolation, and were only dependent on the intercept value $h_{HH}(Q=0)$. The structure functions $h_{HH}(Q)$, modified as indicated, were then Fourier transformed yielding initial estimates of $g_{HH}^{\text{inter}}(r)$. The unphysical structure in $g_{HH}^{\text{inter}}(r)$ was removed by setting this function to zero in the range $r < 1.7 \text{ \AA}$, and the resulting function was Fourier transformed back to Q space. This manipulation amounted to a background correction on $h_{HH}(Q)$.

Essentially identical results were obtained via the technique of minimum noise (MIN) reconstruction,²² which was also used in the calculation of the Fourier transforms. This method is designed to find a distribution which is consistent with the data and as smooth as possible. It is related to maximum entropy methods, except that the function minimized is not the entropy but a smoothness criterion. The $h_{HH}(Q)$ functions, which resulted from the merging procedure described above, were modified as before, i.e., extrapolation to $Q=0 \text{ \AA}^{-1}$, and background correction by removal of the unphysical structure in $g_{HH}^{\text{inter}}(r)$. Figures 2 and 3 show the $\rho_a h_{HH}(Q)$ functions which resulted from the MIN fits to the input data. These figures also show the residuals from the fits, and demonstrate that the MIN procedure was successful in stripping the noise from the input data. Figure 4 shows the corresponding $g_{HH}^{\text{inter}}(r)$ functions. The results of molecular dynamics simulations¹¹ on tridecane (see below) are also shown for comparison.

DISCUSSION

The radial distribution functions in Fig. 3 show broad features centered at ≈ 2.5 , ≈ 5 , and $\approx 7 \text{ \AA}$. These features can be interpreted as the first and successive shells of neighbors of the intermolecular HH structure of the chain fluid.

The position of the first feature in $g_{HH}^{\text{inter}}(r)$, centered at $\approx 2.5 \text{ \AA}$, is in agreement with x-ray scattering results of polyethylene fibers (85% crystallinity), which indicate that the

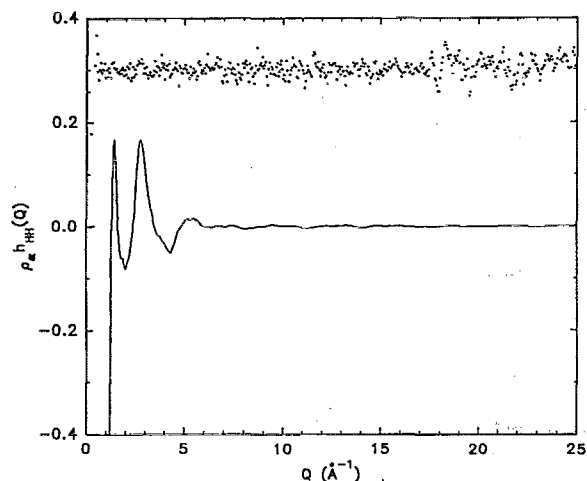


FIG. 2. Partial intermolecular structure function for H atoms in $C_{10}H_{22}$. Solid line—fitted function obtained from the MIN fits; dots—residual from the fit to the corrected data.

shortest H–H intermolecular distance in the crystal part is ≈ 2.3 Å (assuming $r_{CH}=1.0$ Å and angle $H\hat{C}H=106^\circ$). In addition, $g_{HH}^{inter}(r)$ for other materials (HI ,¹³ H_2S ,¹⁶ H_2O ¹⁷) show a shoulder or a peak at $r \approx 2.5$ Å, and a null value for this function in the range $0.0 < r \leq 2.0$ Å, in agreement with the present results.

Moreover, the distance at which the density reaches the bulk density, i.e., $g(r)$ tends to unity, is about 15 Å for eicosane and 10 Å for decane. This is a correlation hole due to the screening of the intermolecular correlations by intramolecular correlations, which occurs over a distance essentially given by the average end-to-end length of a single chain.²³ For typical chain models the end-to-end distance is approximately 2.5 times the radius of gyration, and the above values for decane and eicosane, at which $g(r) \rightarrow 1$, are slightly more than twice their respective radii of gyration as

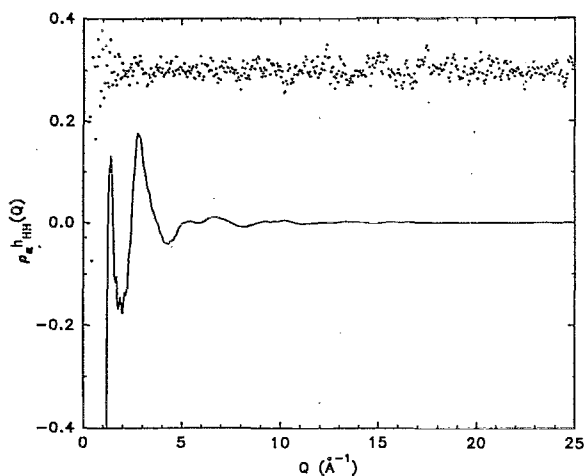


FIG. 3. Partial intermolecular structure function for H atoms in $C_{20}H_{42}$. Solid line—fitted function obtained from the MIN fits; dots—residual from the fit to the corrected data.

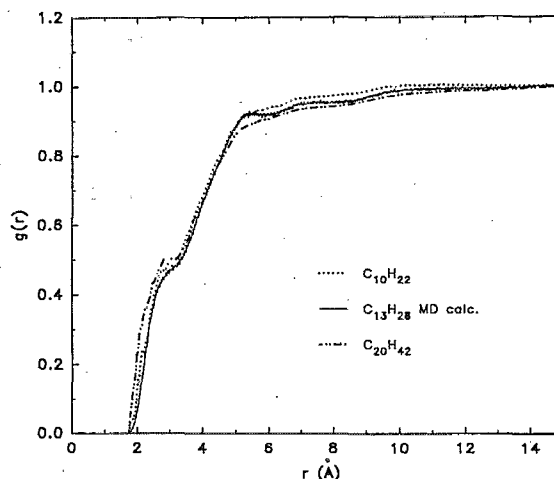


FIG. 4. Intermolecular H–H pair correlation functions for decane and eicosane as obtained from experiment, and compared with molecular dynamics simulation results for tridecane.

independently determined by SANS. This effect has also been observed in intermolecular C–C correlations.³ For comparison, in the case of small molecules^{13,16,17} which are unaffected by such screening, $g_{HH}^{inter}(r)$ exceeds the bulk density in the range 3 to 5 Å. Although the correlation hole effect was already present in our data prior to extrapolation of $h_{HH}(Q)$ to $Q=0$ Å^{−1}, the effect of the extrapolation was to increase the size of the correlation hole depending on the value of the intercept. The method of extrapolation had little bearing on its effects. Consequently, little would have been gained by extending data collection further into the small-angle region.

Figure 4 also shows molecular dynamics simulation results¹¹ for tridecane ($C_{13}H_{28}$). An explicit atom model was used in the simulations. All the features in the experimental results are reproduced in the simulation results, with the largest differences around the shoulder at ≈ 2.5 Å. The simulation results tend to unity at a distance intermediate between the experimental curves, as expected.

It is considerably more demanding to conduct computer simulations and integral equation calculations on polymers using models which include hydrogen atoms explicitly, than to use the united atom model²⁴ in which, e.g., CH_2 and CH_3 groups are treated as single sites. It has been shown that differences between explicit and united atom models, in terms of pair correlation functions, can be substantial,¹¹ even for C–C correlations. We have shown that neutron scattering studies on isotopically substituted samples can provide a useful test of simulation and theoretical results.

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- ¹ L. Blum and A. H. Narten, *Adv. Chem. Phys.* **34**, 203 (1976); A. H. Narten, *Acta Chim. Acad. Sci. Hung.* **121**, 173 (1986).
- ² P. J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley, New York, 1969).
- ³ A. H. Narten, A. Habenschuss, K. G. Honnell, J. D. McCoy, J. G. Curro, and K. S. Schweizer, *J. Chem. Soc. Faraday Trans.* **88**, 1 (1992).
- ⁴ T. W. N. Bieze, A. C. Barnes, C. J. M. Huige, J. E. Enderby, and J. C. Leyte, *J. Phys. Chem.* (in press).
- ⁵ A. K. Soper and P. A. Egelstaff, *Mol. Phys.* **42**, 399 (1981).
- ⁶ A. K. Soper, J. Turner, and J. L. Finney, *Mol. Phys.* **77**, 431 (1992).
- ⁷ G. Hadziioannou and R. S. Stein, *Macromolecules* **17**, 567 (1984); G. D. Wignall, R. W. Hendricks, W. C. Koehler, J. S. Lin, M. P. Wai, E. L. Thomas, and R. S. Stein, *Polymer* **22**, 886 (1981).
- ⁸ E. W. Fischer, M. Stamm, M. Dettenmaier, and P. Herschenroeder, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **20**, 219 (1979); C. E. Williams *et al.*, *J. Polym. Sci., Polym. Lett. Ed.* **17**, 379 (1979); A. Z. Akcasu, G. C. Summerfield, S. N. Jahshan, C. C. Han, C. Y. Kim, and H. Yu, *J. Polym. Sci.* **18**, 865 (1980).
- ⁹ K. S. Schweizer and J. G. Curro, *Phys. Rev. Lett.* **58**, 246 (1987); J. G. Curro and K. S. Schweizer, *J. Chem. Phys.* **87**, 1842 (1987); K. F. Freed and A. I. Pesci, *ibid.* **87**, 7342 (1987).
- ¹⁰ M. Vacatello, G. Avitabile, P. Corradini, and A. Tuzi, *J. Chem. Phys.* **73**, 548 (1980).
- ¹¹ The calculated g_{HH}^{inter} (HH) function in Fig. 4 is not published, but was obtained in molecular dynamics simulations described in G. D. Smith and D. Y. Yoon, *J. Chem. Phys.* **100**, 649 (1994). See also D. Y. Yoon, G. D. Smith, and T. Matsuda, *ibid.* **98**, 10037 (1993).
- ¹² J. D. Londono, A. H. Narten, G. D. Wignall, K. G. Honnell, E. T. Hsieh, T. W. Johnson, and F. S. Bates, *Macromolecules* **27**, 2864 (1994).
- ¹³ C. Andreani, V. Merlo, M. A. Ricci, and A. K. Soper, *Mol. Phys.* **73**, 407 (1991).
- ¹⁴ S. S. Sidhu, L. Heaton, D. D. Zaubersis, and F. P. Campos, *J. Appl. Phys.* **27**, 1040 (1956).
- ¹⁵ A. K. Soper, W. S. Howells, and A. C. Hannon, *ATLAS—Analysis of Time-of-Flight Diffraction Data from Liquid and Amorphous Samples*, Rutherford Appleton Laboratory Report RAL 89-046 (1989).
- ¹⁶ C. Andreani, M. Nardone, F. P. Ricci, and A. K. Soper, *Phys. Rev. A* **46**, 4709 (1992).
- ¹⁷ A. K. Soper, *Chem. Phys.* **88**, 187 (1984).
- ¹⁸ J. Turner, A. K. Soper, and J. L. Finney, *Mol. Phys.* **77**, 411 (1992).
- ¹⁹ W. H. Press *et al.*, *Numerical Recipes*, 1st ed. (Cambridge, New York, 1986).
- ²⁰ Compressibility values estimated from data in *CRC Handbook of Chemistry and Physics*, 74th ed., edited by D. R. Lide (Chemical Rubber, Boca Raton, 1993).
- ²¹ M. Dettenmaier, *J. Chem. Phys.* **68**, 2319 (1978).
- ²² A. K. Soper, in *Neutron Scattering Data Analysis 1990*, edited by M. W. Johnson, IOP Conf. Ser. No. 107 (IOP, Bristol, 1990), pp. 57–67.
- ²³ P.-G. de Gennes, *J. Phys. (Paris)* **31**, 235 (1970).
- ²⁴ R. H. Boyd, *Macromolecules* **22**, 2477 (1989).