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2005 J. Phys.: Condens. Matter 17 S4105

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Orientalional diffusion of *n*-alkyl cyanides

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Received 20 July 2005, in final form 4 August 2005

Published 25 November 2005

Online at stacks.iop.org/JPhysCM/17/S4105

Abstract

Ultrafast optical Kerr effect spectroscopy has been used to study the temperature-dependent orientational dynamics of a series of nitriles with *n*-alkyl chains ranging from one to 11 carbons in length. In all cases the orientational diffusion is found to be described by a single-exponential decay. Analysis of the orientational correlation times using the Debye–Stokes–Einstein equation suggests that the molecules adopt extended configurations and reorient as rigid rods. The liquids with shorter alkyl chains undergo an apparent ordering transition as they are cooled.

1. Introduction

The determination of diffusion constants is a powerful means of gaining microscopic information about the structure and dynamics of liquids. Both translational and orientational diffusion constants are capable of providing detailed insights into microscopic properties such as local viscosity, molecular association, local structure, and even molecular structure. Here we present detailed studies of orientational diffusion in liquid *n*-alkyl cyanides.

Linear alkyl cyanides have been used widely in the study of dynamics in solution, due to the smooth variation of their physical properties with chain length [1–7]. Despite the ubiquity of these solvents, little is known regarding their microscopic structure in the liquid phase. Tools such as neutron scattering, x-ray scattering, and molecular dynamics simulation, which are commonly used to study such microscopic structure, have not been applied to *n*-alkyl cyanides to a significant extent. Indeed, while methyl cyanide (acetonitrile), ethyl cyanide (propionitrile) and propyl cyanide (butyronitrile) have been studied using x-ray scattering [8], to our knowledge no experiments have been performed to determine the liquid structure of any of the *n*-alkyl cyanides with longer alkane chains.

Linear alkanes are well known to display a relatively high degree of ordering in the liquid phase [9–11]. While short-chain alkanes show little ordering, as the chain length increases

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there is a tendency for molecules to adopt an extended conformation and to exhibit local parallel ordering, with some differences being observed between alkanes with odd and even numbers of carbon atoms [9–11]. As the chains grow longer still, the molecular conformations become less extended, and local ordering decreases [9–11].

Our goal here is to address these same microscopic structural issues in *n*-alkyl cyanides. These liquids are not subject to the hydrogen-bonding interactions that contribute to the structure of liquids such as straight-chain alcohols and straight-chain carboxylic acids. However, cyanide groups are highly polar, and so dipole–dipole interactions would be expected to contribute significantly to local structuring in *n*-alkyl cyanides. For short-chain alkyl cyanides these interactions would be expected to dominate the local structure, but as the alkyl chain lengthens the microscopic structure might be expected to approach that of *n*-alkanes.

Our technique for studying these issues is ultrafast optical Kerr effect (OKE) spectroscopy [12–15], which is the time-domain equivalent of Rayleigh-wing scattering. In this technique, a polarized, ultrafast laser pulse is incident on a transparent liquid composed of molecules with a polarizability anisotropy. The pump pulse creates a slight alignment of the molecules based upon their axis of maximum polarizability. This alignment in turn leads to a transient birefringence, which can be measured via the depolarization of a second, probe laser pulse that is polarized at 45° relative to the pump pulse. By measuring the time dependence of the transient birefringence it is possible to monitor the orientational diffusion of the molecules as the liquid returns to an isotropic orientational state. We present the results of OKE experiments on *n*-alkyl cyanides over a broad range of temperatures; these experiments have allowed us to develop a microscopic picture of the structure of these liquids and have revealed the possibility of an ordering transition in the alkyl cyanides with shorter alkyl chains at the lower end of their liquid temperature range.

2. Experiment

Our experimental apparatus and data collection procedure for optical heterodyne detected OKE spectroscopy [16] have been described in detail elsewhere [17]. Our results for methyl cyanide are taken from a previous publication [18]. Samples of all of the other *n*-alkyl cyanides (ethyl cyanide to undecyl cyanide) were used as received. A complete list of the liquids studied and relevant physical parameters is given in table 1. Each liquid was placed in a 2 mm path-length cuvette, which was subsequently capped and sealed with vacuum epoxy. The cell was mounted on the cold finger of a nitrogen-flow vacuum cryostat. A temperature probe was placed directly on the face of the cuvette, near the point where data were obtained, so that the temperature could be measured and maintained accurately at this position. Data were obtained for each liquid over a broad range of temperatures, and the temperature of each sample was allowed to equilibrate for at least 30 min before any data were collected. Typically, at least ten OKE decays were recorded for each liquid, half at a small positive heterodyne angle and half at the equivalent negative heterodyne angle. The data for each angle were averaged, and then the averaged data for the opposite angles were subtracted from one another to obtain the pure heterodyne contribution to the signal. The final data sets were then integrated with respect to time to obtain the collective orientational correlation function, $C_{\text{coll}}(\tau)$ [19]; the constant of integration was set by ensuring that the long-time decay was exponential, in good agreement with the unintegrated data. The integrated data were fitted to the sum of two exponentials using a nonlinear least-squares fitting routine [20]. The fits began at a time (typically on the order of 5 ps) great enough that the peak from the intermolecular response had decayed to a negligible value. Viscosities were obtained from [21].

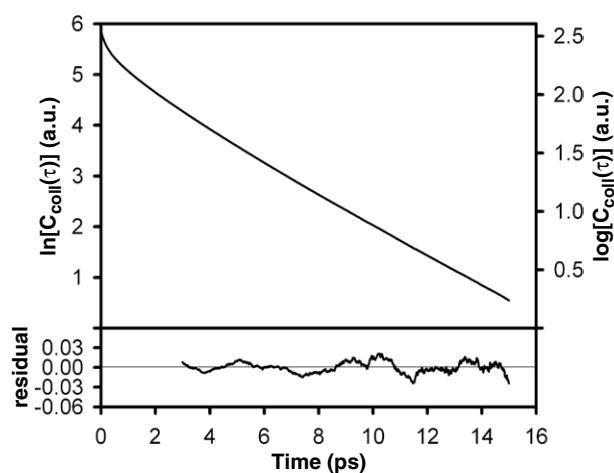


Figure 1. Collective orientational correlation function (solid line) and biexponential fit (dotted line) for butyl cyanide at 366.5 K. The lower panel shows the residual derived by subtracting the fit from the data.

Table 1. Melting points, boiling points, and slopes of Debye–Stokes–Einstein plots for the liquids studied here.

Liquid	T_m (K)	T_b (K)	Slope 1 (ns K cP ⁻¹)	Slope 2 (ns K cP ⁻¹)
Methyl cyanide	225	354	1.13(6)	
Ethyl cyanide	180	370	1.66(9)	0.81(8)
Propyl cyanide	161	388	2.1(1)	1.2(1)
Butyl cyanide	177	412	3.0(2)	1.6(2)
Pentyl cyanide	193	437	5.9(3)	2.8(3)
Hexyl cyanide	209	459	6.3(6)	
Heptyl cyanide	228	471	7.1(6)	4.4(4)
Octyl cyanide	239	497	8.9(8)	5.4(6)
Nonyl cyanide	255	517	12(1)	
Decyl cyanide		538	16(1)	
Undecyl cyanide		543	19(2)	

3. Results

Shown in figure 1 is the logarithm of a typical $C_{\text{coll}}(\tau)$ derived from an OKE decay, in this case for *n*-butyl cyanide at a temperature of 366.5 K, along with a fit to the sum of two exponentials. The quality of the fit is excellent, as can be seen from the flatness of the residual plot. The time constant of the more slowly decaying exponential, τ_1 , is 3.48 ps. The time constant of the other exponential, τ_2 , is 1.74 ps. The collective orientational correlation functions for this liquid at other temperatures, shown in figure 2, are fitted equally well by the sum of two exponentials. As would be expected, the time constants of these exponentials increase as the temperature is lowered. These results are representative of those observed for each liquid studied here; in every case the collective orientational correlation function is fitted well by the sum of two exponentials. The fit parameters for all of the liquids are summarized in tables 2 to 11.

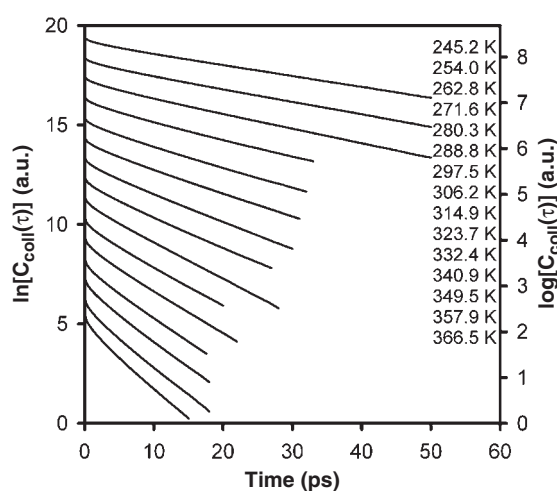


Figure 2. Collective orientational correlation functions for butyl cyanide as a function of temperature.

Table 2. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for ethyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
174.3	0.67(7)	45(2)	0.33(7)	15(6)
179.8	0.78(4)	33(2)	0.22(4)	11(3)
186.1	0.84(3)	21.6(7)	0.16(3)	5.6(9)
193.3	0.84(2)	16.9(3)	0.16(2)	4.3(4)
200.6	0.82(2)	14.3(3)	0.18(2)	4.5(4)
209.3	0.80(1)	11.6(2)	0.20(1)	4.3(3)
220.8	0.78(2)	10.3(2)	0.22(2)	3.9(4)
221.4	0.75(2)	10.4(2)	0.25(2)	4.4(5)
237.3	0.78(2)	7.2(1)	0.22(2)	2.8(2)
255.4	0.77(2)	5.1(1)	0.23(2)	2.0(2)
272.4	0.70(2)	4.05(7)	0.30(2)	2.0(2)
289.0	0.71(1)	3.16(5)	0.29(1)	1.6(1)
304.9	0.77(3)	2.48(8)	0.23(3)	1.1(2)
321.2	0.57(8)	2.24(3)	0.43(8)	1.4(1)
337.4	0.57(2)	1.90(7)	0.43(2)	1.2(2)
357.4	0.65(3)	1.49(6)	0.35(3)	0.9(2)

4. Discussion

Alkyl cyanides are composed of two portions with quite distinct properties. Although the cyanide groups do not hydrogen bond with one another, they are highly polar and interact relatively strongly with one another. The alkyl tails interact with one another through weak dispersion interactions, but as the chain length is increased these interactions become increasingly important in the liquid. The relative importance of these two types of interactions, as well as the cross interactions between the two moieties, is crucial in determining how the alkyl chain length influences the microscopic properties of the liquid.

We begin by considering the origin of the two exponentials used to fit the collective orientational correlation functions in these liquids. For a liquid composed of linear or

Table 3. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for propyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
175.7	0.83(11)	85(9)	0.17(11)	19(10)
182.4	0.83(7)	60(4)	0.17(7)	14(4)
196.4	0.81(5)	35(2)	0.19(5)	10(2)
209.5	0.83(4)	23(1)	0.17(4)	5(1)
219.6	0.81(3)	17.8(7)	0.19(3)	5.1(7)
242.1	0.73(4)	11.8(9)	0.27(4)	4.5(9)
258.1	0.59(3)	8.9(9)	0.41(3)	4.7(9)
273.9	0.77(2)	6.0(3)	0.23(2)	2.1(3)
289.2	0.76(2)	4.8(2)	0.24(2)	1.8(2)
296.7	0.71(2)	4.5(2)	0.29(2)	1.9(2)
313.3	0.71(2)	3.7(2)	0.29(2)	1.7(2)
330.0	0.71(2)	3.0(2)	0.29(2)	1.5(2)
346.0	0.70(2)	2.5(1)	0.30(2)	1.0(1)
362.0	0.62(1)	2.23(8)	0.38(1)	1.14(8)
368.0	0.68(1)	2.05(7)	0.32(1)	1.00(7)

Table 4. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for butyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
245.2	0.86(6)	18(1)	0.14(6)	4(1)
254.0	0.83(2)	16.0(3)	0.17(2)	4.4(4)
262.8	0.79(3)	13.7(6)	0.21(3)	4.5(6)
271.6	0.63(2)	12.8(8)	0.37(2)	5.7(8)
280.3	0.67(2)	10.4(7)	0.33(2)	5.0(7)
288.8	0.73(2)	8.8(4)	0.27(2)	3.8(4)
297.5	0.75(3)	7.4(5)	0.25(3)	3.4(5)
306.2	0.65(1)	7.0(2)	0.35(1)	3.6(3)
314.9	0.76(2)	5.5(2)	0.24(2)	1.8(6)
323.7	0.65(2)	5.5(3)	0.35(2)	2.8(5)
332.4	0.68(2)	4.8(2)	0.32(2)	2.1(2)
340.9	0.68(1)	4.3(2)	0.32(1)	1.9(2)
349.5	0.57(2)	4.1(3)	0.43(2)	2.1(3)
357.9	0.57(2)	3.8(2)	0.43(2)	1.9(2)
366.5	0.57(2)	3.5(3)	0.43(2)	2.0(3)

symmetric-top molecules, orientational diffusion is expected to result in a single-exponential decay in the OKE signal [22]. This is indeed what is generally observed in such liquids. However, a second, faster exponential decay is also commonly observed in these liquids [16, 18, 23–29], even though only a single orientational diffusion time should exist. We have previously performed detailed, temperature-dependent OKE studies of a number of linear and symmetric-top liquids, including methyl cyanide, to study the behaviour of this component of the relaxation (which is often called the intermediate decay in the OKE literature) [18]. We have found that the intermediate decay time in these liquids generally scales with viscosity over temperature, suggesting a hydrodynamic origin, and is a factor of three to six faster than the contribution from orientational diffusion [18]. The physical origin of the intermediate decay remains a topic of debate, but this relaxation component is a ubiquitous feature of the OKE decay in simple liquids.

Table 5. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for pentyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
231.5	0.77(7)	64(5)	0.23(7)	16(6)
253.3	0.66(4)	41(2)	0.34(4)	14(4)
271.1	0.76(3)	22.1(7)	0.24(3)	6(1)
288.9	0.78(2)	16.6(4)	0.22(2)	4.2(5)
297.3	0.65(6)	16(1)	0.35(6)	6(2)
305.7	0.64(4)	13.5(7)	0.36(4)	5(1)
314.1	0.70(2)	10.9(2)	0.30(2)	3.5(4)
323.8	0.73(3)	8.8(3)	0.27(3)	3.5(7)
341.3	0.73(3)	6.8(2)	0.27(3)	2.5(4)

Table 6. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for hexyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
262.4	0.76(14)	57(9)	0.24(14)	11(5)
271.3	0.80(11)	39(5)	0.20(11)	9(5)
280.2	0.70(6)	36(2)	0.30(6)	10(3)
289.2	0.65(4)	31(2)	0.35(4)	10(3)
297.4	0.75(7)	22(2)	0.25(7)	6(2)
305.8	0.74(6)	19(1)	0.26(6)	5(2)
314.3	0.75(6)	16(1)	0.25(6)	4(1)
322.9	0.73(8)	14(1)	0.27(8)	4(1)
331.5	0.75(7)	11.4(9)	0.25(7)	3(1)
340.0	0.73(6)	10.5(7)	0.27(6)	2.7(9)
348.4	0.70(6)	9.3(6)	0.30(6)	2.6(8)
356.9	0.68(6)	8.7(6)	0.32(6)	2.6(9)

Table 7. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for heptyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
249.3	0.87(10)	97(10)	0.13(10)	16(8)
254.7	0.84(10)	84(8)	0.16(10)	12(6)
272.0	0.83(15)	56(6)	0.17(15)	11(6)
280.4	0.79(6)	47(3)	0.21(6)	10(3)
289.3	0.72(6)	42(3)	0.28(6)	11(4)
296.6	0.73(4)	36(2)	0.27(4)	8(2)
304.2	0.75(9)	29(3)	0.25(9)	7(3)
311.6	0.77(10)	24(2)	0.23(10)	5(2)
319.3	0.74(7)	21(2)	0.26(7)	5(2)
326.8	0.73(6)	18(1)	0.27(6)	4(1)
341.7	0.72(5)	14.2(8)	0.28(5)	4(1)
349.0	0.70(7)	13(1)	0.30(7)	3(1)

The biexponential nature of all of the OKE decays presented here is highly reminiscent of the behaviour of linear and symmetric-top liquids, suggesting that τ_1 is the time constant for collective orientational diffusion and τ_2 is the time constant for the intermediate decay. Before making such an assignment, however, we must note that the OKE spectroscopy of the liquids

Table 8. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for octyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
243.2	0.83(16)	220(48)	0.17(16)	33(16)
250.8	0.82(12)	184(31)	0.18(12)	29(12)
266.6	0.74(12)	118(14)	0.26(12)	20(12)
278.1	0.72(12)	97(12)	0.28(12)	19(12)
289.3	0.76(8)	67(6)	0.24(8)	14(6)
304.1	0.74(5)	55(4)	0.26(5)	11(3)
321.5	0.79(5)	31(2)	0.21(5)	6(2)
337.3	0.71(3)	26.7(7)	0.29(3)	8(1)
352.1	0.73(4)	21(1)	0.27(4)	5(1)
367.1	0.72(5)	18(1)	0.28(5)	4(1)
382.0	0.66(3)	17.2(6)	0.34(3)	4.9(8)

Table 9. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for nonyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
297.1	0.78(9)	110(11)	0.22(9)	16(8)
311.0	0.68(8)	84(8)	0.32(8)	19(9)
314.0	0.73(11)	70(19)	0.27(11)	11(6)
319.7	0.72(10)	63(7)	0.28(10)	14(7)
322.7	0.74(5)	55(3)	0.26(5)	12(3)
331.3	0.71(9)	48(5)	0.29(9)	9(3)
341.6	0.72(8)	39(4)	0.28(8)	9(4)
348.5	0.73(11)	34(7)	0.27(11)	7(3)
350.1	0.71(4)	36(2)	0.29(4)	8(2)
358.6	0.76(8)	26(3)	0.24(8)	5(2)

Table 10. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for decyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
288.9	0.74(6)	191(13)	0.26(6)	30(10)
297.0	0.73(11)	152(19)	0.27(11)	26(10)
305.4	0.77(5)	112(6)	0.23(5)	16(4)
313.7	0.76(5)	92(5)	0.24(5)	17(4)
322.2	0.75(2)	74(2)	0.25(2)	15(2)
330.7	0.78(3)	61(2)	0.22(3)	11(2)
339.2	0.75(4)	51(2)	0.25(4)	9(2)
347.8	0.75(5)	45(2)	0.25(5)	8(2)
356.3	0.74(8)	39(5)	0.26(8)	7(3)
364.6	0.76(6)	32(2)	0.24(6)	7(2)

studied here has the potential to be considerably more complex than that of linear molecules or symmetric tops. While *n*-alkyl cyanides are roughly linear, the majority of the polarizability of these molecules is associated with the cyanide moieties, which are not collinear with the alkyl chains (except in the case of methyl cyanide). As a result, even if the molecules were to reorient as rigid rods, the diffusion tensor and the polarizability tensor do not share the same principal axis system, which could lead to decays that are described by as many as five exponentials [22].

Table 11. Normalized amplitudes and decay times for biexponential fits to $C_{\text{coll}}(\tau)$ for undecyl cyanide as a function of temperature.

T (K)	A_1	τ_1 (ps)	A_2	τ_2 (ps)
314.1	0.75(8)	140(12)	0.25(8)	23(10)
322.5	0.77(4)	106(5)	0.23(4)	18(4)
331.0	0.77(5)	87(5)	0.23(5)	13(4)
339.4	0.76(8)	71(7)	0.24(8)	12(5)
347.8	0.78(4)	59(3)	0.22(4)	10(2)
356.3	0.77(4)	46(2)	0.23(4)	7(1)
372.7	0.77(4)	36(1)	0.23(4)	7(1)

Given the conformational freedom of these molecules, the decays could be more complex still. There is no direct experimental evidence from previous studies that these molecules adopt a fully extended conformation in the liquid phase, although this is a reasonable hypothesis based upon analogies with straight chain alkanes and related molecules [9–11]. Even if the molecules are fully extended it is not clear that they would reorient in a rod-like manner. Given long enough alkyl chains, the local orientational dynamics of a cyanide group should differ from the overall orientational dynamics of its parent molecule, with the limiting case being a cyanide group at the end of a long polyethylene molecule. Based on these considerations, it is therefore possible that both τ_1 and τ_2 reflect diffusive orientational dynamics.

While there is no absolute means of determining from our OKE data whether τ_2 arises from orientational diffusion or is a manifestation of the intermediate decay, the relationship between τ_1 and τ_2 can give us a basis for favouring one of these two possibilities. When multiple exponentials appear in the collective orientational correlation function, individual exponentials generally cannot be assigned to diffusion about particular axes [22]. Nevertheless, the relationships among the time constants of these exponentials should be connected to the aspect ratio of the liquid molecules. Thus, if both exponentials arise from orientational diffusion, we would expect their relationship to be very different in going from ethyl cyanide to undecyl cyanide. On the other hand, we have found for liquids composed of linear molecules or symmetric tops that the collective orientational correlation time and the intermediate decay time generally scale with one another [18]. In figure 3 we plot τ_2 versus τ_1 for all of the OKE decays for all of the liquids studied here, as well as for methyl cyanide. Within the uncertainty of our measurements, all of these data fall on a single straight line, which strongly suggests that τ_2 does reflect the same intermediate decay as observed in liquids composed of simpler molecules.

While it is somewhat surprising that even long-chain alkyl cyanides should exhibit single-exponential orientational diffusion in OKE data, this behaviour has significant precedent in other types of molecules. For instance, single-exponential OKE decays have also been observed in liquids composed of disc-like molecules with single substituents that should break the symmetry of the diffusion tensor and lead to multiple exponentials in the OKE decays [23, 29, 30]. In addition, as mentioned above, the polarizability of the molecules studied here is highly localized on the cyanide groups. For the molecules with short alkyl chains, the OKE decays must reflect the orientational dynamics of the entire molecules. On the other hand, for longer alkyl chains the OKE decays may reflect only the cyanide orientational dynamics rather than the overall orientational dynamics of the molecules. The fact that similar behaviour is seen for all of the liquids studied here suggests that we are observing the dynamics of the entire molecules in all of the liquids studied here, but this argument on its own is not conclusive.

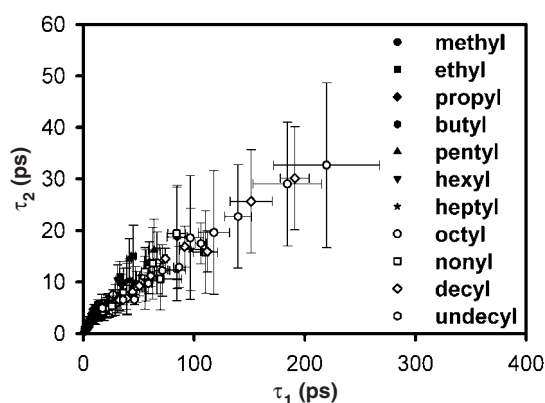


Figure 3. Plot of τ_2 versus τ_1 from all of the OKE decays reported previously for methyl cyanide and for all of those summarized here in tables 2–11.

Orientational diffusion of molecules in simple liquids generally follows the Debye–Stokes–Einstein (DSE) relation:

$$\tau \propto \frac{\eta V_H}{k_B T}, \quad (1)$$

where τ is the orientational correlation time, η is the viscosity, V_H is the hydrodynamic volume of the reorienting molecule, k_B is Boltzmann’s constant, and T is the temperature [31, 32]. There can be an additional factor in this equation to describe the tendency of the reorienting molecule to drag its neighbours with it, and there is also commonly a non-zero value offset that is often interpreted as the reorientational time at zero viscosity [32]. In addition, this equation is intended to describe the orientational diffusion of probe molecules that are large compared to the molecules of the surrounding solvent. Nevertheless, in OKE studies of pure liquids the orientational correlation time is generally found to scale linearly with η/T with a slope that is consistent with reasonable estimates of the hydrodynamic volume of the molecules. We have previously found this to be the case, for instance, in methyl cyanide [18].

Shown in figure 4 is the DSE plot for butyl cyanide; the behaviour in this plot is typical of what is seen for most of the liquids studied here. At high temperature (low η/T) the plot is linear, and at a lower temperature there is a transition to a second linear region with a different slope. The slopes of the DSE plots for these liquids in the higher-temperature (slope 1) and lower-temperature (slope 2) regions are listed in table 1. Some of the liquids show signs of having a third region with another slope, whereas the longest-chain liquids exhibit only a single slope. However, we should also note that for the longer-chain liquids we could not investigate a significant portion of the liquid temperature range due to limitations in the maximum temperature attainable in our cryostat. As shown in figure 5, for shorter-chain alkyl cyanides the value of η/T at which the transition occurs decreases linearly with chain length. As the chain length increases the transition value of η/T increases again, but this may actually reflect a different transition than seen for the shorter-chain liquids (see below).

Before considering the source of the change in slope in the DSE plots, we should first consider what can be learned about the microscopic structure of these liquids based upon our OKE data. In particular, we can assess different models of the molecular structure by comparing the slope of the DSE plots to the hydrodynamic volume corresponding to that structure. In one structural extreme the molecules would be completely collapsed, whereas

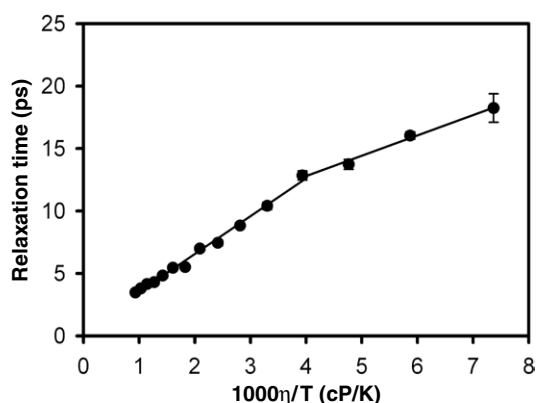


Figure 4. Debye–Stokes–Einstein plot for butyl cyanide.

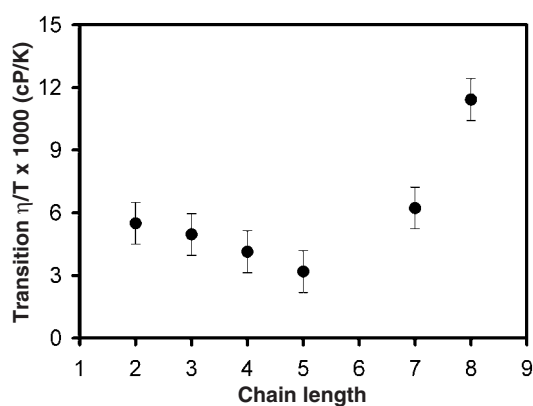


Figure 5. Value of η/T at the transition in slopes in the DSE plot for alkyl cyanides as a function of number of carbons in the alkyl chain.

in the other extreme they would be completely extended. In either of these extremes it is reasonable to believe that orientational diffusion would be described by a single exponential.

If the molecules are collapsed, then the hydrodynamic volume will be approximately equal to the volume per molecule. In figure 6 we plot the slopes from the DSE plots as a function of molecular volume. While there is clearly a correlation between the molecular volume and the DSE slope, the relationship is not a linear one. Using the molecular volume to approximate the hydrodynamic volume of a collapsed chain will work best for the molecules with longer alkyl chains, and so for the shorter chains the molecular volume is undoubtedly an underestimate of the hydrodynamic volume in a collapsed state. However, even taking this effect into account does not appear sufficient to linearize the data plotted in figure 6. We conclude that the alkyl chains are not fully collapsed, as would be expected.

To investigate the limit in which the molecules are fully extended, a molecular modelling program was employed to estimate the lengths of the molecules in this configuration [33]. The hydrodynamic volume was then estimated to be $\pi/6$ times the cube of this length. A plot of the DSE slope as a function of this hydrodynamic volume is shown in figure 7. It is clear that an extended structure is consistent with our OKE data. For the short-chain molecules, methyl cyanide to hexyl cyanide, slope 1 falls on a straight line on this plot. Similarly, slope 2 for

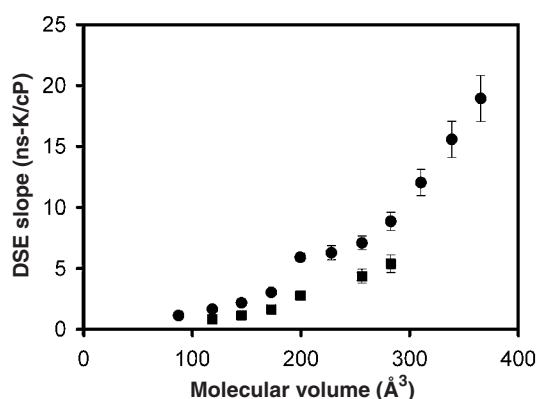


Figure 6. Slope of the DSE plots as a function of molecular volume for methyl cyanide and the liquids studied here. Circles denote slope 1 and squares slope 2.

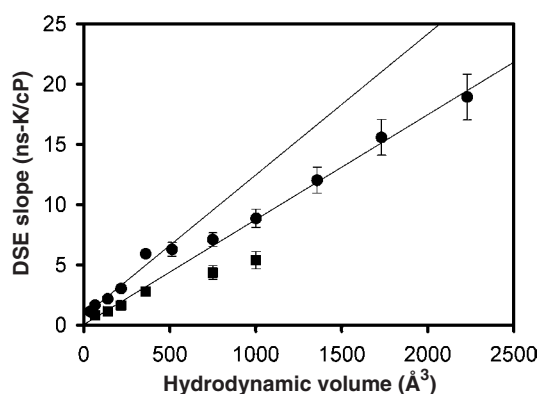


Figure 7. Slope of the DSE plots as a function of hydrodynamic volume assuming fully extended alkyl chains for methyl cyanide and the liquids studied here. Circles denote slope 1 and squares slope 2. The solid lines are linear least-squares fits.

ethyl cyanide to pentyl cyanide falls on a straight line along with slope 1 for heptyl cyanide to undecyl cyanide. The ratio between the slopes of these two linear fits is approximately 1.35. Slope 2 for heptyl and octyl cyanides does not fall on either of these lines.

The above results strongly suggest that the molecules of the alkyl cyanides studied here are extended in the liquid and that they reorient essentially as rigid rods. If the dynamics of the cyanide groups were to begin to decouple from those of the molecules as a whole with decreasing temperature, then the slope of the DSE plot would fall below that expected from the hydrodynamic volume calculated for an extended molecule. There is no sign of this happening even for the longest-chain liquids studied here. It is somewhat surprising that molecules with so much conformational flexibility would reorient in a rod-like manner, although this is not inconsistent with the results of previous OKE studies in which single-exponential decays have been observed for straight-chain alkanes [34–39].

The ability of the molecules to reorient in this manner may be indicative of the underlying intermolecular structure of the liquid, which we will now consider. Despite their molecular simplicity, linear alkanes and their derivatives can exhibit rich phase behaviour. For instance, many linear alkanes form plastic crystals and exhibit rotator phases [40–45]. This type of

behaviour is used to advantage, for instance, in the creation of Shpol'skii matrices for high-resolution spectroscopy at low temperature [46]. As another example, liquid alkanes and long-chain alcohols can exhibit surface freezing phenomena well above their bulk freezing points [47]. These phenomena are all manifestations of the propensity of linear alkanes and their derivatives to form aligned structures, even in the liquid phase. A tendency for local parallel alignment among the molecules in the liquids studied here would make the molecules tend to adopt extended conformations, and therefore could contribute to the apparent rod-like nature of their orientational diffusion.

We now consider the origin of the slope changes in the DSE plots observed in many of these liquids. The challenge is to explain why the slope decreases at lower temperatures, as most of the plausible mechanisms for a change in slope would tend to work in the opposite direction. For instance, it is possible that the change in slope reflects a decrease in the hydrodynamic volume of the molecules. However, this scenario is the opposite of what one would predict from the behaviour of *n*-alkanes and their monosubstituted derivatives [9–11]. Another possibility is that the boundary conditions for reorientation change as the temperature is lowered. However, this situation would require that the boundary condition change from stick at high temperature to slip at low temperature, which would not be expected. Furthermore, the magnitude of the difference in reorientation time due to such a change in boundary condition should be highly dependent on the aspect ratio of the molecules [48], yet the variation of both DSE slopes is a linear function of hydrodynamic volume.

One factor that needs to be kept in mind is that OKE experiments measure a collective orientational correlation time, τ_{coll} , rather than a single-molecule orientational correlation time, τ_{SM} . These two correlation times are related by

$$\tau_{\text{coll}} = \frac{g_2}{j_2} \tau_{\text{SM}}, \quad (2)$$

where g_2 and j_2 are, respectively, the static and dynamic pair orientational correlation parameters [32, 49]. The former parameter is a measure of the degree of parallel ordering in a liquid, with higher values corresponding to a greater degree of order. The latter parameter is generally assumed to be approximately unity in simple liquids. Another possible explanation for the decrease in the DSE slope at lower temperatures is therefore that there is a change in the intermolecular structure that leads to a decrease in g_2 . This idea seems counterintuitive at first, as the degree of parallel ordering of molecules would be expected to increase with decreasing temperature. At room temperature, g_2 for methyl cyanide is approximately 1.7 [18, 50], and this parameter takes on a similar value across the entire liquid temperature range of this substance. We would therefore expect g_2 to take on a similar value for slope 1 in ethyl cyanide to hexyl cyanide, based on the data in figure 7. If the change in slope is due to a change in g_2 , then this parameter must take on a value of approximately 1.25 in the slope 2 region of ethyl to pentyl cyanides and in the slope 1 region of heptyl to undecyl cyanides, reflecting a lower degree of parallel ordering. However, because the polarizability of these molecules is largely localized on the cyanide groups, it is the parallel ordering of these moieties that is of prime importance in determining the value of g_2 . Thus, it is possible that while the liquids as a whole become more ordered with decreasing temperature, the ordering among cyanide groups actually decreases.

Based on room-temperature x-ray scattering studies of methyl, ethyl and propyl cyanide, it has been suggested that dipole–dipole interactions are the dominant force in determining the structure of these liquids [8]. This idea is consistent with the relatively high value of g_2 found for methyl cyanide. We propose that dipole–dipole forces are also dominant in determining the structure of butyl, pentyl and hexyl cyanides at high temperature. However, we believe that interactions between the alkyl chains become increasingly important as the temperature is lowered, and that there is a transition point at which these interactions dominate the liquid

structure, leading to a decrease in the degree of parallel ordering of cyanide groups. The temperature at which the alkyl–alkyl interactions begin to dominate the liquid structure would be expected to increase with increasing chain length, as is observed. Furthermore, for long enough alkyl chains the interactions among cyanide groups may not be the dominant factor in determining the liquid structure at any temperature, which is again consistent with our observations. We should also note that the slope 2 data for heptyl and octyl cyanides may be indicative of yet another ordering transition.

5. Conclusions

We have presented detailed, temperature-dependent OKE studies of liquid *n*-alkyl cyanides. Based on the behaviour of the orientational diffusion in these liquids, we have been able to gain insights into their microscopic structure. The molecules of these liquids appear to adopt an extended conformation, and to reorient essentially in rod-like manner. Our data further point to the possibility of microscopic structural transitions in the alkyl cyanides with shorter chains. Decreases in the slope of DSE plots at low temperature lead us to propose that, while interactions among cyanide groups dominate the liquid structure at high temperatures, interactions between alkyl chains take on greater importance at reduced temperatures.

The microscopic structural transitions that we are proposing based on our data may not be full-fledged phase transitions. Although the proposed structural changes may in fact be subtle, they are reminiscent of the multiple phases that can be observed below the freezing point of many *n*-alkanes and their derivatives. We should note that there is also an analogy to the cyanobiphenyl class of liquid crystals, in which the cyanide group appears to play a key role in the phase behaviour of the molecules [51]. Alkyl cyanides are relatively unstudied compared to other monosubstituted linear alkanes, but it is clear from the results presented here that further temperature-dependent studies of these liquids with techniques such as calorimetry and x-ray or neutron scattering may be of great interest.

Acknowledgment

This work was supported by the National Science Foundation, grant CHE-0314020.

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