PHYSICAL REVIEW E VOLUME 47, NUMBER 6 JUNE 1993

Connection between integrated intensities of depolarized-light-scattering spectra and mesoscopic order in liquids

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(Received 29 October 1992)

We have examined the temperature dependence of the integrated intensity of the broad spectral contribution to the depolarized light scattered from liquids in four different experiments analyzed by four different approaches. Although the quantitative results depend upon the method of analysis, in all cases the integrated intensity, which is an equilibrium property, diminishes rapidly with decreasing temperature. This rapid decrease can be understood if the broad spectral line is associated with dipole-induced dipole interactions, which are known to exhibit a cancellation effect and which, in turn, are dependent upon the structure of and degree of order in the liquid. Therefore the integrated intensity of the broad spectral line may be an experimentally determined indicator of the degree of order in liquids and supercooled liquids.

PACS number(s): 78.40.Dw, 64.70.Pf

INTRODUCTION

The depolarized light-scattering spectra of liquids and supercooled liquids have been extensively studied, but most of the attention has been focused on the frequency dependence rather than on the integrated intensity of the various spectral features. A recent suggestion [1,2] that a clue to the structural order of supercooled liquids might be found in the temperature dependence of the integrated intensities of the "broad" spectral features has led us to reexamine some relevant data on integrated intensities.

The suggestion that the integrated intensity of the "broad" spectral feature corresponds to an indicator of structural order is based on the supposition that this part of the spectrum arises from dipole-induced dipole (DID) interactions. The integrated intensity of a well-separated spectral feature is a *static* (equivalently, an equilibrium in contrast to a dynamical or transport) property described by an equal-time correlation function. The DID equal-time correlation function depends upon two- three- and four-body correlations and appears to be a sensitive measure of the equilibrium structure of the liquid on a length scale which is probably mesoscopic [1–4]. (By mesoscopic we mean any range between about 3 and 1000 molecular diameter.) This sensitivity to structure arises through the "cancellation effect," which is merely the fact that dipolar interactions cancel out if the dipoles are arranged sufficiently symmetrically about each other [3,4]. The DID equal-time correlation function, properly normalized to account for the number of dipoles, decreases as the number density (ρ) increases and as the temperature (T) decreases, presumably because the arrangement of molecules about each other becomes more symmetrical as one moves from high-temperature gas to low-temperature crystal [4]. However, the nontrivial aspect of this phenomenon is the associated observation that even throughout the liquid range, where density changes are not great and the apparent structure relatively invariant, the DID equal-time correlation function seems to decrease markedly with increase of density and decrease of temperature [1]; it is for this reason that it may be considered a sensitive measure of structural order, over and above the obvious order associated with increase of density.

Within a given phase, most thermodynamic or structural quantities change rather little with T and ρ unless the system approaches a second-order or other continuous critical point. However, the difference in entropy between the "disordered" liquid and the "ordered" crystal decreases markedly as the liquid is supercooled from the melting point (T_m) to the glass transition (T_g), often by 80% or more [5,6]. This high drainage of configurational entropy as the liquid is supercooled is suggestive of the continuous growth of order in the *apparently* disordered liquid [7–11]. Whereas the entropy is a macroscopic measure of ordering the DID equal-time correlation function may also be a measure of ordering, but on a smaller, mesoscopic length scale. Although a liquid appears amorphous as seen through short-range two-body correlations such as the pair distribution function, the additional three- and four-body correlations associated with the DID equal-time correlation function may be sensitive to more *complicated* [12–14] and longer-range order. Note that though we speak of a decrease in [S (liquid)-S(crystal)] of 80% as a dramatic change in a thermodynamic quantity (compared to, for example, the infinite-frequency shear modulus which changes very little) [15], the relaxation properties (such as viscosity) may change by 14 orders of magnitude over the same range. There are numerous relaxation or dynamical indicators of dramatic change occurring in liquids as they are cooled toward T_g, but the corresponding direct structural or equilibrium indicators are less in evidence [16].

Thus the rationale for studying the DID equal-time correlation function is that it is a structural quantity that may provide a means of studying mesoscopic ordering in supercooled liquids. The rationale for studying the integrated intensity of depolarized light scattering is that it may, in turn, be possible to associate it with the DID equal-time correlation function. The difficulty in determining DID equal-time correlation functions arises both from theoretical and experimental considerations. Integrated intensities are difficult to measure. Integrated intensities of individual spectral features are even more difficult to measure because one must be able to separate out the contributions from the different overlapping spectral features. And when the feature of primary interest is neither the sharpest nor the most intense, as is the case in many depolarized-light-scattering spectra for the feature associated with DID, the difficulty in determining the relevant intensity is enhanced even more. And there is the theoretical problem of assigning a specific spectral feature to the DID interactions, and only to the DID interactions.

We do not attempt to clarify all these problems. We do suggest, however, that the integrated intensity of the "broad" spectral feature observed in depolarized light scattered from molecular liquids and mixed atomic fluids appears to decrease markedly with decreasing T, a change sufficiently significant in an equilibrium quantity to suggest the existence of a cancellation effect. This significant decrease, when associated with a cancellation effect, in turn suggests that associating the broad feature with DID interactions is reasonable. There are also, of course, theoretical reasons to expect a significant DID contribution to the spectrum [3,4,17]. In particular, Cox and Madden [18], as well as Madden and Tildesley [19], have examined the separation of dynamic-light-scattering spectra into DID and rotational components and have stressed the importance of the cancellation effect on DID spectra, and Friedrich, Tarjus, and Kivelson [1] have shown that although fluctuations of various short-range interactions can contribute to the broad spectral features, they do not exhibit a cancellation effect. More recently, Madden *et al.* [20] have carried out simulations of light scattering (Raman) from ionic melts, but, though they identify a number of mechanisms, they do not attempt to study their contributions to the spectrum as a function of temperature.

Unfortunately, as explained above, although it should be possible in principle to separate out the DID contributions, it is not easy to do so. A clean experiment, impeccably analyzed, would enable us to identify and characterize the DID contributions, but to date this has not been a possible route. However, as the next best thing to do, we examine four independent sets of light-scattering measurements, for which the data have been analyzed on the basis of very different models and have been interpreted very differently, and we show that qualitatively they all lead to similar apparent cancellation effects. Thus this view of the spectra, though by no means established, appears to be rather robust even though each individual analysis can be subjected to well-founded criticism.

We want to make clear that when we associate the cancellation effect observed by means of the integrated intensity of the DID broad spectral feature with structural order in the liquid, we are merely specifying the "order" as the arrangement or arrangements that yield a particular value of the integrated intensity. The DID integrated intensity is a second-rank spherical harmonic probe of environmental symmetry; *bond-order* parameters corresponding to probes associated with higher-order spherical harmonics have also been investigated [13,21,22]. A complete set of such probes would give a full picture of the possibly complicated structure that sets in as a liquid is supercooled, a structure which may be based on the prevalence of icosahedra [13,14,21], and which some believe may grow continuously as a phase transition is approached [9,12]. At present, the only indicator of such order that appears to be measurable in a laboratory experiment is the DID correlation, obtained through depolarized light scattering. Consequently, we believe the depolarized-light-scattering spectrum and its connection to DID correlations to be worthy of serious attention.

DID CORRELATIONS

It is useful to outline the theory connecting DID interactions to depolarized light scattering. The DID correlation function for spherical top molecules can be written as [23]

$$C_{\mathrm{DID}}(t)=\alpha^4\left\langle \sum_{i,j,k,n} \frac{Y_2^m(\hat{\mathbf{r}}_{ij}(t))}{r_{ij}^3}\frac{Y_2^{-m}(\hat{\mathbf{r}}_{kn}(0))}{r_{kn}^3}\right\rangle ,$$

where r_{ij} and $\hat{\mathbf{r}}_{ij}$ are the modulus and the orientation, respectively, of the vector joining the ith and jth molecules, Y_2^m is a second-rank spherical harmonic, α is the molecular isotropic polarizability, and $\langle\ \rangle$ indicates an equilibrium ensemble average. Depolarized light can be scattered off these DID fluctuations. The corresponding light-scattering spectrum is the transform of $C_{\mathrm{DID}}(t)$, i.e., $\hat{C}_{\mathrm{DID}}(\omega)$. The integrated intensity $I_{\mathrm{VH}}(\mathrm{DID})$ of this DID spectrum is the integral of $\hat{C}_{\mathrm{DID}}(\omega)$ taken over all ω, and this is equal to the equal-time correlation function $C_{\mathrm{DID}}(0)$. It is $C_{\mathrm{DID}}(0)/\rho^2$, the integrated DID intensity per pair of scatterers, that we take as a measure of structural order in the liquid.

The DID contribution to the light-scattering spectrum arises because the local field polarizing a molecule consists of the applied laser field plus the field arising from the laser-induced dipole on a neighboring molecule [3,4,23]. The formula given above applies if the molecular polarizabilities are isotropic, but for nonspherical molecules this need not be the case, and the relative orientations of the molecules play a role; since the molecules are nearly randomly oriented, one might expect the effect of the three- and four-body correlations in $C_{\mathrm{DID}}(t)$ to be reduced. This has been discussed elsewhere [4]. Furthermore, there may be other contributions to the depolarized-light-scattering spectrum; in particular, the orientational fluctuations of the anisotropic polarizability can give rise to intense scattering. Although DID fluctuations may relax over a wide range of time scales, the orientational fluctuations are usually considerably slower than most of the DID fluctuations, and consequently the orientational spectral contributions tend to be concentrated at very low frequencies; it should thus be possible to carry out at least a partial separation of the DID from the orientational contributions. There are other fluctuations that lead to depolarized light scattering, for example, fluctuations in the degree of overlap between pairs of molecules; these fluctuations tend to be shorter ranged and faster than the DID fluctuations (and so possibly separable), and their integrated contributions to the spectrum rather small and devoid of a cancellation effect. On top of all the difficulties mentioned, it is possible that further complications arise through cross correlations between the various fluctuations.

ANALYSIS

Friedrich, Tarjus, and Kivelson [1] measured the integrated depolarized light intensity, I_{VH} (broad), scattered from liquid CCl_4 as a function of pressure and temperature (T). A sharp central peak, which could be due to a host of factors, was excluded from the integration. Clearly observed was a sharp decrease in the I_{VH} (broad) throughout the liquid regime as T decreased and pressure increased, i.e., as density (ρ) increased. Even above the freezing point, I_{VH} (broad) becomes too small to measure in the presence of the strong central peak (at least by the methods used by these researchers), but a loose extrapolation of the existing data suggests that I_{VH} (broad) becomes vanishingly small near the melting point. We do not ascribe special significance to this extrapolated limit, but merely to the fact that well above any putative glass transition, I_{VH} (broad) became negligibly small. We interpret this as suggesting that for tetrahedral molecules, which pack easily and crystallize readily, there is considerable order (not necessarily crystalline order) at relatively elevated temperatures, which may be one of the reasons that crystallization takes place readily.

Steffen *et al.* [24] measured the depolarized light scattering of liquids composed of the nonspherical orthoterphenyl (OTP) molecule. The dominant feature is a sharp central rotational line which is not of interest here and whose contributions to the integrated intensity must be removed. (In doing so, one implicitly assumes that this central line contains little DID character.) This central line is well characterized and its removal was carefully executed, but because it is so dominant, one cannot be sure that the removal leaves the broad component untainted. (This is true of all four sets of measurements summarized in this paper.) In addition, Steffen *et al.* found a "broad" line associated with a fast process. The whole experimental spectrum was deconvoluted from the instrumental function and fitted to two Lorentzians, one for the slow (rotational) process and one for the additional fast process. The assumption of Lorentzian shapes is adequate to describe the data, although its theoretical justification is dubious. Steffen *et al.* found that the integrated intensity of the broad line divided by ρ^2, i.e., I_{VH} (broad)$/\rho^2$, decreased by a phenomenal factor of 25 over the temperature range 400–240 K, i.e., from normal liquid to supercooled liquid near the glass transition T_g. Kivelson *et al.* [2] interpreted the broad line as DID in origin and argued that the decrease was an indication of the cancellation effect and of an increase in structural order. A loose extrapolation [2,24] to T's below T_g suggests vanishingly small values of I_{VH} (broad) near $T_0 \approx 200$ K, a temperature at which, when fitted by a Vogel-Fulcher function, the viscosity diverges. We do not ascribe special significance to this extrapolated limit, but we point out that the supercooled liquid has a high degree of structural order as measured by DID correlations, and that order seems to be increasing appreciably as $T \rightarrow T_0$. We also note that above the melting point the structural order for OTP is much lower than that for CCl_4, a phenomenon that is perhaps connected with the reason why methane freezes readily and OTP supercools readily. In this connection we note that extreme cancellation in DID correlations is readily achieved by the local packing of spheres (i.e., on a nearest-neighbor scale), but such cancellation is possible for nonspherical molecules only on a longer scale, i.e., on a mesoscopic scale.

Kivelson [25], using data provided by Chappell and Kivelson [26], examined the depolarized spectrum of triphenyl phosphite (TPP) in some detail, focusing on the shear-wave side peaks. The spectrum can reasonably be treated as the superposition of two spectra, both dominated by an intense, sharp central rotational line; one of these superposed spectra has a "broad feature" and the other may have a weak broad feature, but its most singular characteristic is two very weak shear-wave side peaks readily identified by the characteristic linear k dependence of the frequency shifts. The simplest generalized hydrodynamic analysis of these spectra introduces three collective variables: the orientation density D, the momentum density $\mathbf{p}$, and the stress tensor σ. In this model, it is the interaction of $\mathbf{p}$ and σ that gives rise to both the broad features and the shear waves, and the coupling between these two variables and the orientational density D is small; thus in this model the broad features and, in particular, the spectral shear waves are observed only to the extent that fluctuations in σ are observed directly. In contrast, the rotational line arises through the fluctuations of D. By examining the relative intensities of the rotational lines and the side peaks, as well as other features associated with the side peaks, the relative contributions to the spectrum of the D and σ fluctuations can be determined. If, as expected [2], the intensity of the D contributions change little with T, one then has a measure of the dependence of the σ component upon T. The integrated intensity of this spectral component decreases by a factor of 7 over the range of T's covered (87 to -35 °C), a range in which viscosity increases several hundredfold. This decrease suggests a cancellation effect, and so one might argue that the σ fluctuation has a large DID component. Note that this conclusion is similar to that obtained for OTP; the lesser decrease here may be correlated with the smaller temperature range, since the measurements reported are at T's well above T_g. But noteworthy is the fact that the approaches used in analyzing the two problems, though model dependent, are very different.

Finally, we turn to the recent measurements of Li *et al.* [27] on $[\mathrm{Ca(NO_3)_2}]_{0.4}$-$[\mathrm{KNO_3}]_{0.6}$. These authors measured the depolarized-light-scattering spectra out to several thousand GHz, neglecting the very low-frequency spikes (of about 0.1-GHz linewidth) which could be due to leakage of the polarized scattering, including that due to concentration fluctuations (the leakage of Brillouin lines is clearly discerned). They argue that the spectra are mainly due to DID scattering. Broadly speaking, from some low frequency of about $\omega_0 = 1$ GHz to an experimental cutoff frequency of about $\omega_c \leq 10^4$ GHz, the spectrum appears to be roughly linear in $\omega^{-\lambda}$, where λ varies from about $\lambda = 1$ at high temperatures to about $\lambda = 0.3$ near T_g; near ω_c, the spectra at all T's are very similar, presumably because at such high frequencies the spectra are dominated by molecular processes which are not very temperature dependent. If we assume that the relevant relative integrated intensities can be obtained by integrating $(\omega_c/\omega)^\lambda$ from a low-frequency ω_0 to the high-frequency cutoff $\omega_c \gg \omega_0$, then we find that the ratio of the integrated intensity at the lowest T to that at the highest T is about $\frac{1}{7}$. Again this is a very marked decrease, though less than reported for OTP; in this connection it should be noted that although the particles here are quasispherical, there are several different sized spheres, the variation in size resulting in lower environmental symmetry [28] and thwarted crystallization.

Friedrich and co-workers [1,29] made a thorough study of the contributions of Raman and "short-range" interactions to the depolarized-light-scattering spectrum measured by means of interferometric experiments. These high-frequency, molecular contributions presumably give rise to a broad spectral background which does not exhibit a cancellation effect and should not vary much with temperature and pressure. For tetrahedral molecules, the systems studied by Friedrich and co-workers, the overall contribution of these high-frequency molecular processes to the integrated intensity was estimated to be no more than 15% of the DID contributions; if these broad background contributions are not explicitly treated, the apparent DID cancellation effect should be *less* than the actual effect. In the final analysis of Friedrich and co-workers, this background spectral contribution to the integrated intensity was not subtracted out. For the other, more complicated systems discussed above, no theoretical estimate of the contributions from the Raman and short-range high-frequency molecular processes has been carried out. In the analysis of OTP by Steffen *et al.* the contributions from these molecular processes were assumed to be incorporated into the broad background baseline, which was explicitly separated out in obtaining a DID-integrated intensity, while in the analysis of TPP by Chappell and Kivelson this was not done; this may account for the greater apparent cancellation effect observed in the OTP data. In our use of the data of Li *et al.* some (but not much) recognition of these molecular processes was given by cutting the integration at a high frequency ω_c, where the experimental data ended. Overall it would appear that appropriate treatment of the molecular processes would be necessary for a quantitative analysis of the DID integrated intensity, but that at a qualitative level they can be ignored.

COMMENTS

From the discussion above, we see that, loosely speaking, the integrated intensity of the broad features (but not the very broad ones) of the depolarized-light-scattering spectra measured over the liquid–supercooled-liquid range exhibit a marked (order of magnitude) decrease with decreasing T and increasing pressure. This qualitative result seems to be quite robust, quite independent of the model used for analysis of the data. If associated with the equal-time DID correlation function, this integrated intensity can be interpreted as a measure of structural order, which increases as T is lowered even though the short-range indicators of structure suggest an amorphous random structure. Presumably the marked decrease in intensity as T decreases and ρ increases can be explained in terms of the cancellation effect. Although this analysis and interpretation of the spectra has not been established beyond reasonable doubt, it has been sufficiently justified, we believe, to warrant attention.

The DID correlation function (and hence the integrated intensity) depends on two-, three-, and four-body correlations and is presumably quite long range (mesoscopic). This might be the case if one is to explain the apparently nearly complete DID cancellation (very small integrated intensity of the broad line) observed at lower temperatures for liquids composed of unsymmetrical molecules such as TPP and OTP; even with crystalline order, one would not expect appreciable DID cancellation from near neighbors, which suggests that the DID correlation function must depend upon all correlations over a rather large range. On the other hand, in liquids composed of spherical molecules (such as $\mathrm{CCl_4}$), the short-range ordering is high, and the DID correlations cancel out so easily, even at T's above the melting point, that they are not useful indicators of the mesoscopic ordering. For atomic systems (such as argon or Lennard-Jones spheres), the changes in DID properties that occur throughout the liquid regime are quite unspectacular; see the discussion in Ref. [1].

One might expect to get similar or complementary structural information from any measured quantity that depends on many-body correlations, although it seems that in order to yield significant information the relevant interactions must be quite long range [30]. So, for example, the shear modulus, which depends upon two-, three-, and four-body correlations varies little as T is lowered through the supercooled liquid range, presumably because the correlations between intramolecular forces are very short range.

There is some expectation that as the temperature of a supercooled liquid is lowered, a true, continuous (not a regular first-order) transition to an ideal glass at a temperature T_0 below T_g is approached [7–12]. T_0 is roughly the temperature at which the viscosity extrapolated to T's below T_g diverges, i.e., the Vogel-Fulcher temperature. T_0 is also roughly the temperature at which the extrapolated value of the excess entropy of the liquid above that of the crystal vanishes, i.e., the temperature at which the configurational entropy of the liquid becomes very small. If there is such a transition there should be, associated with the order, a correlation length that diverges continuously as T is lowered toward T_0. And one might then expect some indicator of ordered fluctuations to increase (or decrease) as the correlation length increases. Thus one might speculate that the DID correlation function decreases as the correlation length associated with structural order increases; this is being checked via computer simulations [30]. (See Refs. [21] and [22] for a similar check, not on the DID function but on a bond-order parameter.) One must keep in mind that although the DID function may indeed decrease as a function of increasing structural correlation length, there may be other indicators of structural order that are more closely tied to the increasing correlation length and to the putative transition; however, for OTP, it appears that the tie-in between both the decrease in entropy and the increase in viscosity as T is lowered toward T_g is well tracked by the decrease in the DID function [2].

ACKNOWLEDGMENTS

We wish to thank both the NSF and the CNRS for their support of this research. We would also like to thank Professor Steven Kivelson and Sidney Nagel, and Dr. Jay Variyar, for their useful comments.

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