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Neutron-diffraction study of two organic liquids conducting under a low electric field

F. J. Mompeán
Instituto de Ciencias de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain

A. Chahid
The Studsvik Neutron Research Laboratory, S-611 82 Nyköping, Sweden

D. Martín
Isis Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kindgom

B. Ouladdiaf
Institute Laue-Langevin, Boîte Postale 156, F-38042 Grenoble Cedex 9, France

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A neutron-diffraction study of two organic liquids (carbon tetrachloride and deuterated nitrobenzene) under conditions in which they are weakly electrically conducting is reported. Experiments carried out with two different neutron incident energies do not reveal any significant changes in the measured structure factors with respect to the unperturbed liquids. The results are discussed in the light of the space and time scales probed in these experiments. [S1063-651X(98)05404-X]

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I. INTRODUCTION

Interest in the microscopic description of insulating and weakly conducting organic liquids subject to external electric fields has been prompted both by the progress in experimental and simulation techniques and by their immediate technological applications [1]. Particular emphasis has been placed on the description of the phenomenology leading to dielectric breakdown of liquid insulators at sufficiently high values of the applied field and the formulation of the corresponding microscopic models [2,3]. Below the breakdown threshold, the study of the electrohydrodynamical effects that couple the charge distributions to macroscopically observable magnitudes, such as changes in viscosity, has been the focus of experimental [4,5] and simulation [6] research leading to the formulation of microscopic pictures compatible with the experimental observations. The knowledge gained on both regimes of the liquids under electrical disturbance suggest an alteration of their structure and dynamics over a wide range of time and length scales. With the current availability of synchrotron radiation and neutron-scattering facilities, it is increasingly appealing to approach these problems from the complementary perspectives offered by photon scattering from the electronic distributions and neutron scattering from the spatial distribution of the nuclei in the sample. In this paper we address the problem experimentally by judging the sensitivity of the structure factors determined from neutron diffraction of two organic liquids (of a small number of atoms per molecule) to changes induced by the application of an external dc electric field in conditions in which the samples are weakly conducting. From a theoretical standpoint, the structure factors $S(\mathbf{Q})$ can be related to the initial Van Hove correlation function $G(\mathbf{r},0)$ and to the dynamical structure factor $S(\mathbf{Q},E)$ via the integral transforms

$$S(\mathbf{Q})=\int d^3r\ \exp(i\mathbf{Q}\mathbf{r})G(\mathbf{r},0)$$
$$=\int_{-\infty}^{\infty}dE\ \exp(-E/2k_BT)S(\mathbf{Q},E). \qquad (1)$$

In practice, in neutron scattering at a continuous (reactor) source, an approximation to $S(\mathbf{Q})$, which we shall denote by $F(\mathbf{Q})$, is derived from measurements of the single differential scattering cross section with neutrons of a fixed incident energy E_i (corresponding to a wavelength λ_i) [7]. These measurements are usually conducted at constant scattering angle 2θ and, in isotropic media, allocated to the elastic value of the neutron momentum transfer, $|\mathbf{Q}|=Q=(4\pi/\lambda_i)\sin(\theta)$. $F(Q)$ can be related to an integral over the energy transfer E of the total dynamic structure factor $S(Q,E)$ along curved paths determined by the accessible scattering angles and traversing a region of the wave-vector–energy transfer space (Q,E) determined as well by the neutron incident energy [8]. The relative weights of the (Q,E) points in that region are dictated by the instrument design characteristics. As a consequence, $F(Q)$ differs from $S(Q)$ in that the latter would require the realization of the integral of $S(Q,E)$ over the whole range of relevance to the dynamics of the sample along constant Q paths. In practical terms, this means that diffraction experiments carried out with different incident energies will probe the integrated dynamical response from the sample in different space and time scales. A very common choice of neutron incident energies in the range of tens of meV will probe the dynamics of the system on a time scale of the order of 10^{-12} s and on a length scale of 1–10 Å.

With the above restrictions, $F(Q)$ will be expected to be sensitive to any changes in the static correlations or to those changes in the dynamics rearranging the distribution on the

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explored region of the (Q,E) plane of the loci for collective and intramolecular modes. A second limitation inherent to the experimental technique is the macroscopic size of the portion of the sample explored by the neutron beam. This implies that contributions from localized changes in the liquid structure or dynamics would be weighted against those arising from unperturbed regions of the sample. Another source for concern is the intrinsic sensitivity of the technique chosen to probe our samples. To gain insight into this subject, we mention here that the observation of orientational correlations of polyatomic molecular fluids is a challenging goal as can be learned from model calculations of even simpler systems showing extreme types of intermolecular correlations. In addition, and bearing in mind the lack of contrast in the scattering cross sections between the perturbed and unperturbed molecules when the electric potential difference is applied, an empirical estimate renders our experimental approach sensitive only to changes affecting at least a few molecules in every hundred.

As far as we are aware, no similar experimental studies on simple molecular liquids have been reported in the literature and the many aspects involved in the response to the electrical perturbation of insulating liquids support our choice of an experimental line of approach.

II. EXPERIMENTAL DETAILS AND RESULTS

For our study we have chosen two liquids with different intermolecular potentials: carbon tetrachloride (CCl_4) and deuterated nitrobenzene ($C_6D_5NO_2$). The former constitutes an example of a nonpolar system exhibiting a high degree of isotropy in its intermolecular potential. The latter possesses a high dipolar moment per molecule, close to 4 D (1 D $\approx 3.3356 \times 10^{-30}$ C m), and can be obtained commercially with a high degree of chemical and isotopical purity (in relation to the fully substitution of H by D atoms). Its comparatively large and elongated molecular shape makes it a good candidate to exhibit, under electrical stress, anisotropic scattering patterns. Both liquids have been extensively studied macroscopically in connection to the electroviscous effect [4,5]. Nitrobenzene has been characterized by Kerr effect measurements as a liquid showing bipolar homocharge behavior following the application of 3-kV/mm electric potential differences [9]. Electrochemical studies in conjunction with electron-spin resonance measurements have led to a mechanism for ionic conduction following electrolytic dissociation of the liquid. In the case of CCl_4 a similar mechanism is not ruled out, but a more prominent role of the intrinsic impurities is to be expected [10].

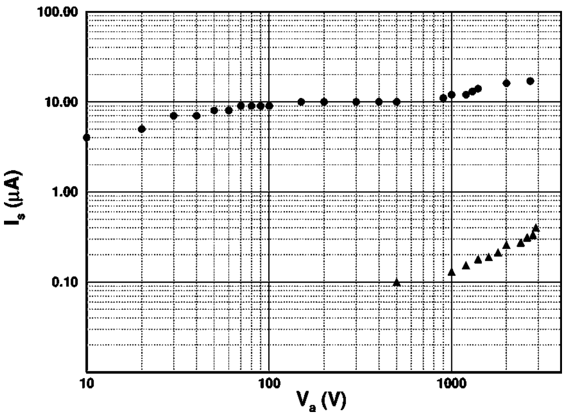

FIG. 1. Stabilization values of the current for the two liquids studied as a function of the applied potential difference. Triangles correspond to CCl_4 at $T = 291$ K and circles to $C_6D_5NO_2$ at $T = 281$ K.

Our experiments were carried out in a specially designed cell that consisted of two circular aluminum plates held a distance of 1 mm apart by a Teflon ring spacer that also provided for the containment of the liquid samples. The confronted area of the electrodes was $S = 28\ \text{cm}^2$. The container was cleansed thoroughly with the liquid to be used (CCl_4: Riedel, optical quality; $C_6D_5NO_2$: Aldrich, 99.9% isotopic purity in D) in the experiment and subsequently filled with the filtered sample. The ensemble was sealed with Teflon stoppers and placed into the neutron beam, taking special care to illuminate only the central part of the sample, far from the Teflon ring. Thermal stability (to within 1 K) was achieved by placing the sample container ensemble in a closed circuit refrigerator, thermal contact being ensured by a copper link between the refrigerator and the grounded electrode. The sample temperature was measured by means of a Pt resistance thermometer attached to the grounded electrode. For the measurements under weak conduction conditions, a dc potential difference was applied to the aluminum electrodes while the current conducted by the sample was monitored with a microamperimeter. The potential difference applied to the plates (V_a) was measured by an additional voltmeter. It was applied in a stepwise procedure: Following a small increase in V_a, we observed a rapid increase in the current followed by a decrease with a time constant of the order of minutes and final stabilization at a value I_s. Once the current had decayed to this stable value, the potential difference was increased again. The maximum value of V_a was dictated in the case of the nonpolar liquid CCl_4 by the design of our power supply and in the case of the polar liquid by a limit found in bench tests (tests of the experimental setup *without* neutron beam) for the absence of dielectric breakdown. Typical electrical response characteristic curves for the two liquids studied are shown on Fig. 1. Table I summarizes the experimental conditions related to the samples. Neutron measurements were performed for both samples at the SLAD diffractometer (using the 220 reflection from a Cu monochromator, $E_i = 67.61$ meV, $2° < 2\theta° < 125°$)

TABLE I. Summary of sample experimental conditions.

Liquid	Measurement temperature (K)	Melting temperature (K)	Maximum applied applied voltage V_a (V)	Current density at V_a, I_s/S (mA/cm^2)
CCl_4	291	250	3000	0.015
$C_6D_5NO_2$	285	279	2700	0.610

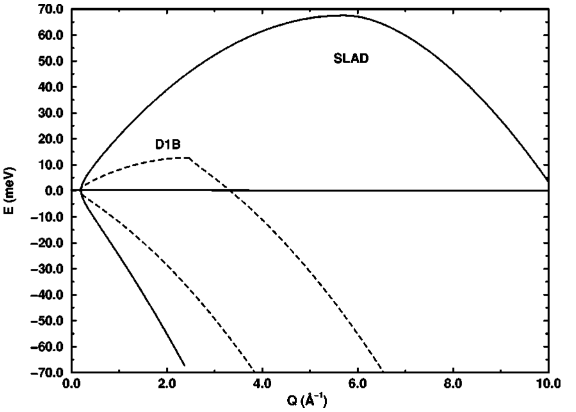

FIG. 2. Accessible regions of the momentum-energy transfers space (Q,E) on the SLAD (continuous line) and D1B (dashed line) instruments as determined by the neutron incident energies and maximum and minimum scattering angles.

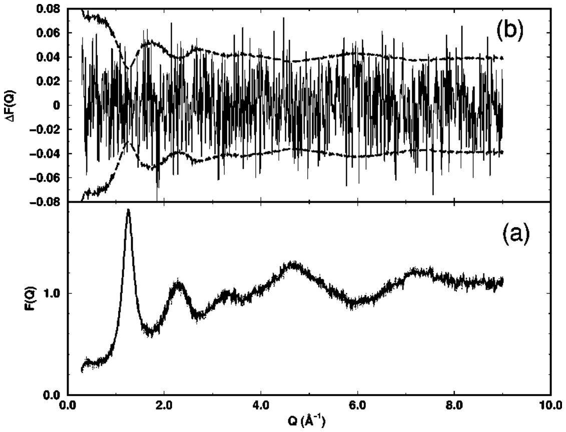

FIG. 3. (a) $F(Q)$ for CCl_4 at $T=$ 291 K as measured on the SLAD difractometer with a field (broken line) and without an electric field (continuous line). The sample orientation is at 45° with respect to incident neutron beam. (b) Difference in the measured structure factors (continuous line) and standard error band (defined by the two dashed lines) derived from counting statistics and error propagation.

of the Studsvik Neutron Research Laboratory and, for the polar liquid only, at the D1B diffractometer (using the 002 reflection from a pyrolitic graphite monochromator, $E_i = 12.8$ meV, $4° < 2\theta < 84°$) of the Institute Laue-Langevin. Figure 2 shows the regions of the (Q,E) plane sampled on both diffractometers.

The main features of our search for changes in $F(Q)$ upon application of the electric potential difference should be briefly discussed now: The sample size, reciprocal space search scheme, and real-space detector coverage are relevant to the interpretation of our results. In both instruments, the area exposed to the neutron was determined by a cadmium mask of rectangular shape (4 cm height × 2 cm width) and well centered with respect to the Teflon spacer. The normal to this area was always kept in the scattering plane. The SLAD diffractometer is equipped with position sensitive detectors built from three sets of long ^{3}He tubes. One set is placed in the scattering plane and the other two parallel to the first set but 3.5 cm respectively above and below the scattering plane. The distance to the detectors from the sample position is 1–1.1 m. The D1B diffractometer is equipped with a multiwire position-sensitive detector that extends 5 cm above and below the scattering plane at a distance of 1.525 m from the sample position. In these circumstances, on both instruments most of the scattering plane anisotropy would not be detected, although it is not easily conceived that, in the event of changes occurring in the sample upon application of the electric potential difference, the $F(Q)$ extracted from the solid angle covered by our detectors would not deviate from that observed in the absence of the electrical perturbation. On both instruments, short runs (10 min) were taken with the sample plane at 45° with respect to the incident neutron beam while gradually increasing the electric potential difference in order to look for changes with time $F(Q)$. The relatively high flux on the sample position (10^6 and 6×10^6 neutrons cm^{-2} s^{-1} on SLAD and D1B, respectively) allows for this kind of transient study, although with a limited signal-to-noise ratio in the case of liquid samples. These short runs were carefully compared for differences allowing for the experimental errors. We consistently failed to observe statistically significant changes in the single differential scattering cross sections during such short runs both in the nonpolar (CCl_4) and in the polar (deuterated nitrobenzene) liquid cases. Longer integration times (2 h on SLAD and 1 h on D1B) were used to explore the response at the maximum applied voltages, at different values of the angle defined by the normal to the electrodes and the incident beam covering a total range of 90° at both sides of the incident neutron beam in steps of 5°. Blank (zero applied potential difference), normalization, and background measurements were taken at these same orientations after the measurements with the application of the electric potential difference were completed. Figures 3–5 exemplify the measurements of the scattered intensities for CCl_4 at 291 K and nitrobenzene at 285 K under the electrical conditions summarized in Table I, the corresponding blank measurements, and their difference $\Delta F(Q) = F(Q)_{V=V_a} - F(Q)_{V=0}$. The magnitude $F(Q)$ shown in those figures has been obtained after vanadium normalization and background and absorption corrections. It should be noted that no ''inelasticity''

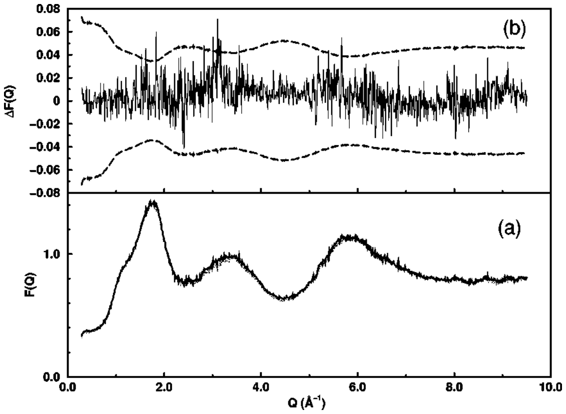

FIG. 4. (a) $F(Q)$ for $C_6D_5NO_2$ at $T=$ 285 K as measured on the SLAD difractometer with a field (broken line) and without an electric field (continuous line). The sample orientation is at 45° with respect to incident neutron beam. (b) Difference in the measured structure factors (continuous line) and standard error band (defined by the two dashed lines) derived from counting statistics and error propagation.

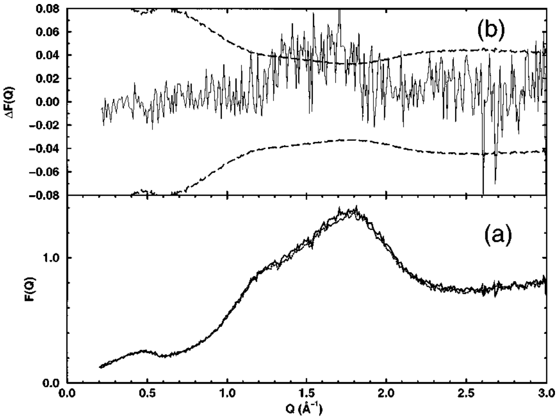

FIG. 5. (a) $F(Q)$ for $C_6D_5NO_2$ at $T = 285$ K as measured on the D1B diffractometer with a field (broken line) and without an electric field (continuous line). The sample orientation is at 45° with respect to incident neutron beam. (b) Difference in the measured structure factors (continuous line) and standard error band (defined by the two dashed lines) derived from counting statistics and error propagation.

corrections have been applied. Figures 3–5 correspond to the sample orientation at 45° with respect to the incident neutron beam. Similar results were obtained for other orientations. Together with $\Delta F(Q)$ we have included estimates of the standard error associated with a single data point of $F(Q)$ on each instrument. These estimations are based on neutron counting statistics and on error propagation through the data correction procedure. As can be appreciated from the figures, the greatest values of $\Delta F(Q)$ are found on the nitrobenzene measurements on D1B and are localized near $Q = 1.7$ Å^{-1} in the region of the first clear maximum in $F(Q)$. However, although a systematic trend in Q seems to exist, it cannot be considered as statistically meaningful with our experimental accuracy since there is substantial overlapping with the error band.

III. DISCUSSION

We briefly discuss now our results in the context set in the Introduction with respect to the limitations of our experimental approach. The absence of significant changes on $F(Q)$ upon application of the dc electric potential difference suggests the absence of significant structural changes in the liquids. Structural correlations can be loosely defined as those prescribed as static by the neutron probe in a given experiment and it is common knowledge that they are the most efficiently sampled ones in diffraction experiments on molecules composed of heavy atoms. For molecular liquids such as those studied here, a certain amount of inelastic scattering is always present as discussed in the Introduction. The response of the collective origin is expected in the region $E < 5$ meV (for CCl_4 see Ref. [11]) and the existence of low-lying vibrationally excited states (populated at room temperature) gives rise to intramolecular response around 20 meV [12]. In principle thus, these two contributions have been adequately sampled by the joint use of the two diffractometers. Any modifications in the dynamics of the bulk would have reflected in our restricted integrated measurements of $S(Q,E)$ with the possible exception of the translational and rotational diffusion quasielastic contributions. These latter contributions appear typically in a region centered at $E = 0$ and with characteristic widths of the order of 1 meV for $Q < 2$ Å^{-1} (for CCl_4 see Ref. [13]) and should be approached most conveniently by either cold neutron diffractometry [for integrated $F(Q)$ measurements] or preferably by time-of-flight neutron spectrometry to determine the $S(Q,E)$ in the low-Q region. This latter investigation is even more attractive since, unless we assume that the effect of the application of the external potential difference is localized in a thin boundary layer near the electrode plates, our present results are difficult to reconcile with the reported changes in the viscosities (up to 20%) [4,5]: For nitrobenzene an estimate of the thickness of this layer based on the Debye length computed from the dielectric permittivity ($\epsilon = 34.8\epsilon_0$), the diffusion coefficient ($D_T \approx 10^{-5}$ cm^2 s^{-1}), and the measured resistivity ($\rho \approx 10^{-8}$ Ω^{-1} m^{-1}) yields $\lambda_D = \sqrt{\epsilon D_T \rho} \approx 50\,000$ Å. This value lies in between those deduced by wall heat capacity measurements on quartz-nitrobencene interfaces (500–1300 Å) and from optical measurements on steel-nitrobencene interfaces (1–10 μm), in the absence of external electrical perturbations [14]. On the other hand, the existence of a boundary layer with a characteristic thickness of the order of λ_D can be verified by neutron reflectometry [15]. While no other experimental information is available, the absence of detectable changes in our experiments upon application of an external potential difference in our samples is consistent with a crude picture in which, for neutron-sample classical interaction times of the order of picoseconds and typical currents in the microampere range, only one unit charge carrier in every 10^{21} molecules is needed to account for the observed current intensity. The absence of changes in $F(Q)$ upon the application of the external potential difference would imply then that the phenomena taking place in the sample are below the sensitivity limits of our experiments.

IV. CONCLUSIONS

Our aim in this study was the search for differences in the scattering pattern that can be attributed to the effect of weak external electrical fields. The limitations of our experimental approach have been discussed. Although no statistically significant differences have been found in our experiments, the direct access (without the need to revert to electro-optical response tensors) provided by neutron diffraction to the initial Van Hove correlation function $G(\mathbf{r},0)$ makes this study attractive and worth reporting. In the light of the comparison of our results with data from the electroviscous effect, a further investigation of the translational (diffusion) and rotational degrees of freedom seems to be in order to complete the current picture as observed in the thermal and cold neutron accessible (Q,E) windows. Effects localized on a mesoscopic boundary layer cannot be ruled out. However, a very crude model accounting for the rate of charge transport in our experiments suggests that perturbations to the liquid are below the sensitivity threshold of the technique.

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