Microscopic structures and dynamics of high- and low-density liquid trans-1,2-dichloroethylene


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We present a study of the dynamics and structural changes for trans-1,2-dichloroethylene between high- and low-density liquids using neutron-scattering techniques (diffraction, small-angle neutron scattering, and time of flight spectroscopy) and molecular-dynamics simulations. We show that changes in the short-range ordering of molecules goes along with a change in the molecular dynamics: both structure and dynamics of the high-density liquid are more cooperative than those of the low-density liquid. The microscopic mechanism underlying the cooperative motions in the high-density liquid has been found to be related to the backscattering of molecules due to a strong correlation of molecular ordering.

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Classical thermodynamics establishes the existence of one unique liquid state for any material, i.e., there is only a liquid phase characterized by its density given the thermodynamic coordinates pressure and temperature. Nevertheless, recent experimental results and molecular-dynamics (MD) simulations suggest that, even for one-component systems, several liquid phases can appear with an associated liquid-liquid phase transition (LLPT). A noticeable number of cases has been found for atomic liquids, the best-known example concerning liquid phosphorus, where the LLPT appears as a liquid-liquid critical point scenario, i.e., the liquid undergoes a first-order phase transition. The present study is aimed to determine if they are related to a singularity-free or a liquid-liquid critical point between a high-density liquid and a low-density liquid, that takes place when the isobaric heat capacity has a maximum, but no critical point or LLPT are observed at nonzero temperature.

An early work on trans-1,2-dichloroethylene ($T_{\text{melt}} = 223$ K) suggested the existence of a LLPT at $T_s = 247$ K $> T_{\text{melt}}$ based on a small jump in density (less than 0.06%) as well as in the compressibility and a clear discontinuity on the spin-lattice relaxation time $T_1$. The observed changes in $T_1$ were tentatively related to a lack of freedom of the molecular rotation in the HDL, not present in the LDL. The change in the dynamics of this substance between both liquids was thereafter also supported by discontinuities in the viscosity measurements and the slope of the rotational relaxation time and by the absorbance, frequency, and linewidth of several infrared vibrational spectroscopy bands. Concerning structural related magnitudes, subsequent measurements of the density as a function of the temperature did not find a jump at the expected LLPT but only a change in its slope. More recently, some of the authors of the present work have also undertaken calorimetric and nonlinear dielectric experiments. In that work a strong pretransitional anomaly of nonlinear dielectric effect was obtained, similar to the one observed in the isotropic phase of nematic liquid crystals, together with a maximum of $C_p$. Therefore, experimental results unambiguously show a clear change in the dynamics, together with a slight change in the structure, between HDL and LDL, that takes place when $C_p$ is in a maximum. However, those facts are not enough to unambiguously determine if they are related to a singularity-free or a liquid-liquid critical point scenario, i.e., the liquid undergoes a first-order phase transition. The present study is aimed to investigate the microscopic structural and dynamical differences between the HDL and LDL from the experimental point of view and from MD simulations.

Because the differences between the HDL and LDL in trans-1,2-dichloroethylene were related to a change from a nematic-like to an isotropic molecular ordering as temperature is raised, we have performed a series of small-angle neutron-scattering (SANS) measurements from 220 K to room temperature to ascertain whether there is formation of intermediate range nematic-like structures or clustering in the HDL. Experiments were performed on the KWS-2 diffractometer of the Jülich Centre for Neutron Science at the
The program QTIKWS
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tometer at the Institute Laue-Langevin
means of neutron-scattering experiments on the D4c diffrac-
ence of molecular clustering on length scales of about
the differences between both liquids are related to the emer-
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F
also observed in a series of temperature-dependent experi-
peak which reflects a change in the SRO. This change was
shape of the profile emerges between the first and second
of experiments performed on HDL water at high pressures22
and MD simulations on HDL silicon.23,24
The microscopic mechanisms giving rise to the changes in
the interference function $F(Q)$ have been investigated
through a series of MD simulations (Fig. 1). Those were
performed using the program AMBER8 (Refs. 25 and 26) with
a simulation box containing 3629 molecules and a time step
of 1 fs. The intermolecular and intramolecular interactions
for the trans-1,2-dichloroethylene molecule were described
using the General AMBER Force Field.25,26 The simulations
were carried out for the temperature range 200–350 K in the
NPT ensemble, therefore allowing the box size to change,
and the total time scale of each simulation run was 40–50
ns.27,28 As can be seen in Fig. 1, the agreement between
simulations and experiment is excellent. Note that not only
the shapes of the simulated $F(Q)$ closely resemble the ex-
perimental ones but also positions and intensities are equal
within the experimental error.
To emphasize quantitatively which are the SRO changes
between the HDL and LDL, we show in Fig. 2 the probab-
ility of finding two molecules with a determined relative ori-
entation for the HDL.17 The data exclude that
changes are also reflected in the relative position of two mol-
ecules and in the relative orientation of the planes defined by
the Cl–C–H bonds of two molecules. As proposed in the
frame of two order parameter theories,6–9 this liquid can
therefore not be simply characterized by its density but also
a parameter reflecting the SRO should account for the
changes occurring between the two liquids.
To ascertain the influence of the aforementioned structural
changes in the dynamics of the system, we have performed a
series of quasielastic neutron-scattering (QENS) experiments
for temperatures ranging from 220 to 300 K, conducted with

FIG. 1. (Color online) Total interference function of
trans-1,2-dichloroethylene for the LDL and the HDL, obtained (a)
by neutron-scattering experiments and (b) by molecular-dynamics
simulations, where an ab initio calculation of the molecular struc-
ture is also shown. Inset shows the macroscopic cross section for
low $Q$ values obtained by SANS experiments also for temperatures
above and below $T_c$. The microscopic short-
range order (SRO) concerning a length scale of the order of
a few molecular lengths ($l_{mol} \approx 4$ Å) has been analyzed by
means of neutron-scattering experiments on the D4c diffrac-
tometer at the Institute Laue-Langevin (ILL, Grenoble, France)18
using a wavelength of 0.5 Å and a deuterated sample. Data were corrected and normalized using the pro-
gram CORRECT (Ref. 19) and inelastic corrections were also
carried out (for details on data reduction see Ref. 20). The
obtained total interference function $F(Q)$ (Ref. 21) is shown in
Fig. 1 for two representative temperatures. A change in
the shape of the profile emerges between the first and second
peak which reflects a change in the SRO. This change was
also observed in a series of temperature-dependent experi-
ments on the D20 diffractometer (ILL) using a wavelength of
1.3 Å, giving better access to the low-$Q$ region. It should be
pointed out that similar changes have been found in the case
of experiments performed on HDL water at high pressures22
and MD simulations on HDL silicon.23,24

The microscopic mechanisms giving rise to the changes in
the interference function $F(Q)$ have been investigated

FIG. 2. (Color online) Short-range order for the HDL (left) and
the LDL (right), at 230 and 280 K, respectively. The $y$ axis is the
cosine of the angle $\alpha$ formed between the vectors defined by the
C–C double bonds of two neighbor molecules and the $x$ axis is the
number of molecules surrounding a central one. The $z$ axis repre-
sents the probability of finding two molecules at a distance deter-
mined by the MCN with a relative orientation defined by the $\alpha$
angle.
To have an insight of possible changes in the dynamics, a stretched exponential $\exp(-t/\tau)^\beta$ was fitted to the intermediate scattering function, obtaining a decrease in the exponent $\beta$ in the HDL, which is related to a broadening of the relaxation time distribution, i.e., an increase in the cooperativity of the molecular motion. A deeper analysis was performed through a careful fit of data to several models using a Bayesian approach with the program FABADA.31–33 In order to keep the number of physical parameters describing the data to a minimum, we performed the fits to the whole scattering function independent for this liquid.

We have shown that the microscopic ordering of the LDL data giving rise to a good quality fit and a radius of rotation $\delta R=2.12 \pm 0.07$ Å. Moreover, the obtained $A(Q)$ are almost independent of temperature for the LDL, which means that the length scale of the confined motion is roughly temperature independent for this liquid.

The need for an additional confined motion at low temperatures to describe the QENS spectra goes along with a backscattering effect observed in the simulations. We can therefore assert that a cooperative molecular motion is present for the HDL but not for the LDL, which agrees with other experimental results.15 The complex dynamics of the HDL agrees with a stronger molecular ordering present in this liquid, where on average there are many orthogonally oriented molecular pairs. This strong correlation is partially lost in the LDL, where molecular movements are due to noncoupled movements of diffusion and rotation.

We have shown that the microscopic ordering of
molecules and molecular dynamics are different between the HDL and the LDL. The changes in the dynamics are not due to temperature or density effects but due to changes in the SRO: for the HDL there are molecules perpendicularly oriented that are randomly oriented in the LDL. This accounts for the change in molecular dynamics from simple noncooperative motions in the LDL to cooperative motions for the HDL. However, if these effects are to be explained in the frame of a singularity-free scenario or a liquid-liquid critical point scenario associated to a first-order phase transition remains an open question.

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