Experimental and modelling evidence for structural crossover in supercritical CO$_2$

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Physics of supercritical state is understood to a much lesser degree compared to subcritical liquids. Carbon dioxide in particular has been intensely studied, yet little is known about the supercritical part of its phase diagram. Here, we combine neutron scattering experiments and molecular dynamics simulations and demonstrate the structural crossover at the Frenkel line. The crossover is seen at pressures as high as 14 times the critical pressure and is evidenced by changes of the main features of the structure factor and pair distribution functions.

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INTRODUCTION

Supercritical fluids have unique properties that have led to a rich variety of applications [1]. Rare gases, nitrogen, CO$_2$ and H$_2$O are among the most common supercritical fluids. CO$_2$ in particular is an important greenhouse gas of Earth’s atmosphere, and in its supercritical state is the main component (97%) in the atmosphere of Venus. Supercritical CO$_2$ is used in a great variety of applications (see, e.g., applications in solubility, synthesis and processing of polymers [2–4], dissolving and deposition in microdevices [5], green chemistry and solvation [6–12], green catalysis [9, 13–15], extraction [16], chemical reactions [17], green nanosynthesis [18] and sustainable development including carbon capture and storage [19]). It has been widely appreciated that improving fundamental knowledge of the supercritical state is important for the reliability, scale-up and widening of these applications (see, e.g., Refs [1] [7] [9] [12] [15] [17]).

Compared to subcritical liquids, the supercritical state is not well understood. Traditional understanding amounted to a general assertion that this state is physically homogeneous, with no qualitative changes taking place anywhere above the critical point [1]. The first challenge to this view was the Widom Line (WL). Close to the critical point, the WL characterises persisting near-critical anomalies such as the maximum in the heat capacity [20], which can be used to stratify different states in the supercritical region. A different subsequent proposal was based on the Frenkel line (FL) separating two distinct states in the supercritical state with liquid-like and gas-like dynamics. Differently from the WL, the FL extends to arbitrarily high pressures and temperatures (as long as chemical bonding is unaltered), is unrelated to the critical point and exists in systems with no boiling line or critical point [21–23]. The FL is also of practical importance because it corresponds to the solubility maxima in supercritical CO$_2$ [24].

Here, we combine neutron scattering experiments and molecular dynamics (MD) simulations and show evidence for the structural crossover of supercritical carbon dioxide at the Frenkel line. The crossover extends to pressure as high as 14 times the critical pressure and is evidenced by changes of the main features of the structure factor and pair distribution functions. The neutron scattering experiments evidencing a crossover at highly supercritical pressure are the first of its kind for CO$_2$.

METHODS

We recall that particle dynamics combine solid-like oscillations around quasi-equilibrium positions and diffusive jumps between different positions below the FL, the typical character of molecular motion in liquids [25]. Above the line, particle dynamics lose this oscillatory component and become purely diffusive. This gives a practical criterion to calculate the FL based on the
disappearance of minima of the velocity autocorrelation function (VAF) \[22\]. This criterion coincides with the thermodynamic criterion \(c_v = 2k_B\) corresponding to the disappearance of transverse-like excitations in a monatomic system \[26\]. Since structure and dynamics are related \[27\], the FL crossover was predicted to result in a crossover of the supercritical structure.

The experimental pressures were 500 and 590 bar. In MD simulations, we have additionally considered 1000 bar pressure. The FL in \(\text{CO}_2\) was previously calculated using the VAF criterion \[24\], giving us the following three states points of the predicted crossover: (500 bar, 297 K), (590 bar, 302 K), and (1000 bar, 339 K). We recall that the FL extends to arbitrarily high pressure and temperature above the critical point, but at low temperature it touches the boiling line at around \(0.8T_c\), where \(T_c\) is the critical temperature \[22\] (note that the system does not have cohesive liquid-like states at temperatures above approximately \(0.8T_c\) \[28\], hence crossing the boiling line at around \(0.8T_c\) and above can be viewed as a gas-gas transition \[22\].) The critical point of \(\text{CO}_2\) is \(73.9\) bar, 304.3 K), hence our state points correspond to near-critical temperatures and pressures well above critical. In this regard, we note that the supercritical state is often defined as the state at \(P > P_c\) and \(T > T_c\). This definition is loose, not least because an isotherm drawn on \((P, T)\) diagram above the critical point crosses the melting line, implying that the supercritical state can be found in the solid phase. As a result, one can meaningfully speak about near-critical part of the phase diagram only when discussing the location of the supercritical state on the phase diagram \[29\]. As far as our state points are concerned, they correspond to temperatures much higher than the melting temperature and pressures extending to 14 times the critical pressure where near-critical anomalies are non-existent \[29\].

Cylinder of carbon dioxide was obtained from BOC, CP grade, and used without further purification. The pressure of the cylinder was around 50 bar and a SITEC hand pump gas was used to raise the pressure. Capillaries were used to connect intensifier manifold system to the cell. The flat plate pressure cell was made from an alloy of Ti and Zr in the mole ratio 0.676:0.324, which contributes almost zero coherent scattering to the diffraction pattern \[30\]. The cell consisted of a flat section that was 12 mm thick and had four 6 mm diameter holes running through it, so the occupied gas space was 6 mm thick and the wall thickness was 3 mm either side. The container was placed at right angle to the neutron beam, which was approximately 30 mm x 30 mm in cross section. A bottom loading closed cycle helium refrigerator was used to control the temperature within \(\pm 1\) K, using He exchange gas at \(\sim 20\) mbar to provide temperature uniformity. The employed temperatures and pressures are shown in Table I, where the densities were calculated from the data available in the NIST database \[31\].

| \(T_{exp}\) (K) | \(P_{exp}\) (bar) | \(d\) (g/mL) | \(T_{exp}\) (K) | \(P_{exp}\) (bar) | \(d\) (g/mL) |
|----------------|------------------|-------------|----------------|------------------|-------------|
| 250            | 500              | 1.1676      | 590            | 1.1821           |
| 270            | 500              | 1.1131      | 590            | 1.1306           |
| 290            | 500              | 1.0573      | 590            | 1.0784           |
| 310            | 500              | 1.0003      | 590            | 1.0257           |
| 330            | 500              | 0.9426      | 590            | 0.9729           |
| 340            | 500              | 0.9137      | -              | -                |
| 350            | 500              | 0.8848      | 590            | 0.9204           |
| 360            | 500              | 0.8560      | -              | -                |
| 370            | 500              | 0.8276      | 590            | 0.8688           |
| 380            | 500              | 0.7996      | 590            | 0.8436           |
| 390            | 500              | 0.7722      | 590            | 0.8188           |

Total neutron scattering measurements were performed on the NIMROD diffractometer at the ISIS pulsed neutron source \[42\]. Absolute values of the differential cross sections were obtained from the raw scattering data by normalising the data to the scattering from a slab of vanadium of known thickness, and were further corrected for background and multiple scattering, container scattering and self-attenuation, using the Gudrun data analysis program \[33\]. Finally the data were put on absolute scale of barns per atom per sr by dividing by the number of atoms in the neutron beam \((1\) barn = \(10^{-28}\) m\(^2\)).

\[
F(Q) = \frac{1}{9} b_C^2 H_{CC}(Q) + \frac{4}{9} b_O^2 H_{OO}(Q) + \frac{4}{9} b_C b_O H_{CO}(Q)
\]

(1)

where \(b_\alpha\) is the neutron scattering length of atom \(\alpha\), and the partial structure factor \(H_{\alpha\beta}(Q)\) is the three-dimensional Fourier transform of the corresponding site-site radial distribution function:

\[
H_{\alpha\beta}(Q) = 4\pi\rho \int_0^\infty r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin Qr}{Qr} dr
\]

(2)

and \(\rho\) is the atomic number density. Note that the \(H_{OO}(Q)\) and \(H_{CO}(Q)\) terms include both the intra- and inter-molecular scattering. The results are shown in Fig. [1].

The molecular dynamics (MD) simulation package DL_POLY \[34\] was used to simulate a system of 30752 \(\text{CO}_2\) particles with periodic boundary conditions. The potential for \(\text{CO}_2\) is a rigid-body non-polarizable potential based on a quantum chemistry calculation, with the partial charges derived using the distributed multipole analysis method \[35\]. The electrostatic interactions were evaluated using the smooth particle mesh Ewald method in MD simulations. The potential was derived and tuned using a large suite of energies from \textit{ab initio}
FIG. 1. Weighted sum of the experimental weighted partial structure factors $F(Q)$ for CO$_2$ at 500 bar (top) and 590 bar (middle). The curves for higher temperatures have been shifted along the y-axis by 0.05 per set. Bottom: Position of the maximum of the first peak in the total (weighted sum) experimental structure factor as a function of temperature for CO$_2$ at 500 bar (blue) and 590 bar (red). The straight lines are visual guides.

density functional theory calculations of different molecular clusters and validated against various sets of experimental data including phonon dispersion curves and $PVT$ data. These data included solid, liquid and gas states, gas-liquid coexistence lines and extended to high-pressure and high-temperature conditions [35]. We also used another rigid-body non-polarizable potential developed by Zhang and Duan [36] and found the same results.

The MD systems were first equilibrated in the constant pressure and temperature ensemble for 500 ps. The data were subsequently collected from production runs in the constant energy and volume ensemble. In order to reduce noise and see the crossover clearly, data were averaged over 500,000 frames, involving production runs of further 500 ps. The simulated pressures were 500, 590, and 1000 bar with temperatures in the range 205-500 K including the temperature at the FL.

RESULTS AND DISCUSSION

Before analyzing the data, we recall that the FL corresponds to the qualitative change of particle dynamics: from combined solid-like oscillatory and diffusive dynamics below the line to purely diffusive gas-like dynamics above the line. Therefore, the supercritical structure is predicted to show the crossover between the liquid-like and gas-like structural correlations. This is predicted to be the case for functions characterizing the structure, such as pair distribution function (PDF) and structure factor (SF). In our analysis, we focus on meaningful features such as maxima positions of PDFs and SFs.

The experimental weighted sum of the partial structure factors are plotted in Fig. 1 for two pressures. We plot the first peaks position of SFs vs temperature in Fig. 1 and observe that it undergoes the crossover at temperatures close to 320 K and around 12% larger than the FL crossover temperature predicted from the VAF criterion mentioned earlier.

We have Fourier-transformed the SF to obtain the experimental PDF. As with previous experimental and modelling results on Ar [27], Ne [37], CH$_4$ [38], and especially on H$_2$O [39] pronounced changes of first peak position in the PDF with temperature are observed, indicating a well-defined crossover. The first PDF peak position divided by the position ($r_0$) at a reference temperature vs the cube root of the volume divided by the volume ($V_0$) at the same reference temperature is shown in Fig. 2. The reason we plot the peak position vs the cube root of volume is as follows: the first peak position corresponds to the first nearest-neighbour (fnn) distance. When a system is compressed or expanded, one expects the fnn distance and the system’s “length” ($V^{1/3}$) to be proportional to each other unless the system undergoes a structural change. In other words the system structure undergoes uniform compression. In a simple cubic
crystalline solid, the constant of proportionality is readily seen as unity; in other crystals it differs slightly, as it should do in liquids if structure does not undergo any qualitative changes. In gases, the fnn distance is largely determined by the size, geometry, and interaction of the constituent molecules (see, e.g., [41]) rather than the density. This linear relationship has been experimentally observed in molten group 1 elements [42, 43] and liquid CS₂ [44]. The fnn distance is most readily extracted from the partial C-C PDFs. The experimental data give the total PDF, but the peak corresponding to the fnn distance is not profoundly changed, therefore the total PDF gives a good approximation of the fnn distance. In Fig. 2, we observe a reduction in height, and corresponding broadening of peaks with increasing temperature as expected.

We now discuss the MD results. Examples of C-C PDFs from MD simulations are shown in Fig. 3. We observe a reduction in height, and corresponding broadening of peaks with increasing temperature as expected. Fig. 4 displays the radial positions of the first PDF peaks as a function of volume, as discussed above, which shows a crossover at densities near the FL. Because of the reduced noise and abundance of temperature points we can perform statistical analysis of the data to quantify the crossover. We see the same behaviour, including a much clearer crossover, for both pressures. In order to quantify the crossover, we fitted the data to two different types of function. The first was a single functional dependence over the entire range. In order to avoid the extrapolation errors associated with high order polynomials, the trial functions we used were quadratic, or log plus linear: $f(x) = a + bx + c\log(x)$, with $a$, $b$, and $c$ the fitting parameters. The second set of functions was linear below a certain crossover volume $V_c$, and either quadratic or log plus linear above that volume (i.e., a piecewise function): $f(x) = \Theta(V_c - V)[a + bx] + \Theta(V - V_c)[a + \beta x + \gamma \log(x)]$, with $\Theta[V]$ the Heaviside step function and $a$, $b$, $\beta$, $\gamma$, and $V_c$ the fitting parameters ($\alpha$ depends on the other parameters in order to ensure continuity of the function).

Generally speaking, adding more parameters to a fitting function improves the numerical quality of the fit. A priori, one can penalise having too many parameters - this prevents the extreme situation of a perfect fit acquired using a piecewise function with a number of subdomains equal to the number of data. The two closely related quantitative measures of goodness of fit with penalty terms for the number of parameters are the AIC (Akaike Information Criterion) [45] and BIC (Bayesian Information Criterion) [46]. Applied to our data, at both pressures and with the quadratic and log plus linear variants, the AIC and BIC were substantially lower than −10 below those for the single function, representing a decisive preference for two different functional dependences.
above and below a certain volume \( V_c \). This volume is shown in the vertical dotted line (Fig. 4) and corresponds at both pressures to a temperature close to 350 K, which is within 12-15\% of the predicted crossover value. Also plotted as insets in Fig. 4 are the residuals of the low-volume linear fits which show a sharp and sudden increase above the crossover volume, which would not be the case if we had simply interpolated a straight line between non-linear data.

Fig. 5 shows theoretical PDF peak heights. We note that the PDF peaks heights of a solid \( h \) are predicted \[25, 40\] to have a power-law relationship with temperature, resulting in the following relation: \( \log h \propto -\log T \) with \( h = g(r) - 1 \) at the peak. The same relation can be argued to apply to liquids below the FL where the solid-like oscillatory component of molecular motion is present \[27\]. The peak heights in Fig. 5 clearly show the crossover at the FL, with the observed crossover temperatures differing from the predicted ones by about 7-15\%. This is in agreement with the width of the FL crossover seen experimentally and modelling on the basis of structural and thermodynamic properties \[37, 47\].

Before concluding, we note that previous experiments detecting the structural crossover at the FL involved X-ray scattering in supercritical Ne \[37\] and the combination of X-ray with Raman scattering in supercritical CH\(_4\) \[38\]. Only one small-angle neutron scattering experiment had been used to study the FL in CO\(_2\) in the vicinity of the critical point only \[38\]. Our current neutron scattering experiment detecting the crossover at the FL at highly supercritical pressures is the first of its kind and importantly widens the range of techniques used to detect the FL. It will stimulate further neutron scattering experiments in important systems such as supercritical H\(_2\)O where a pronounced crossover at the FL was recently predicted on the basis of MD simulations \[39\].

In summary, our combined neutron scattering and molecular dynamics simulations study has detected the structural crossover in CO\(_2\) at pressures well above the critical pressure and temperatures well in excess of melting temperature. The crossover is seen in the main features of the SF and PDFs and corresponds to the predicted crossover at the FL. Apart from the fundamental importance of understanding the supercritical state, the FL corresponds to the solubility maxima of several solutes in supercritical CO\(_2\) \[24\] and is therefore of practical importance.

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