Structural Markers of the Frenkel Line in the Proximity of Widom Lines

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Abstract

We have performed a neutron scattering experiment on supercritical fluid nitrogen at 160 K (1.27 T_C) over a wide pressure range (7.8 MPa / 0.260 g/ml to 125 MPa / 0.805 g/ml). This has enabled us to study the process by which nitrogen changes from a fluid that exhibits gas-like behaviour to one that exhibits rigid liquid-like behaviour at a temperature close to, but above, the critical temperature by crossing the Widom lines

followed by the Frenkel line on pressure (density) increase. We find that the Frenkel line transition is indicated by a transition to a regime of rigid liquid-like behaviour in which the coordination number remains constant within error, in agreement with our previous work at 300 K. The Frenkel line transition takes place at approximately the same density at 160 K and 300 K. The data do not conclusively show an additional transition at the location of the known Widom lines. We find that behaviour remains gas-like until the Frenkel line is crossed and our data support the hypothesis that the Widom line transitions are density increase-driven.

Introduction

Nearly a decade ago, a new dividing line was proposed between the basic states of matter on the pressure-temperature and pressure-density phase diagram: The Frenkel line.[1] The line was proposed to begin in the subcritical region on the liquid side of the vapour pressure curve at $\approx 0.7 T_C$ (critical temperature), dividing the liquid state into the rigid liquid and non-rigid liquid regions, then cross the critical isotherm at significantly higher pressure than the critical pressure (P_C), and extend to arbitrarily high P,T in the supercritical region. It was proposed that the line would divide the supercritical region into regions exhibiting liquid-like and gas-like behaviour and, as a corollary, that in the region of the phase diagram bounded by the Frenkel line, the vapour pressure curve, and the critical temperature, the sample exhibits gas-like behaviour in many respects. The part of the vapour pressure curve close to the critical point is now understood as a first order transition between the non-rigid liquid state and the gas state. For non-rigid liquid behaviour to be exhibited, there must be a net attractive potential between particles at some separation and the temperature must be sufficiently low for this to be a significant effect. However, to observe rigid liquid behaviour all that is necessary is the application of sufficient pressure. Indeed, the rigid liquid behaviour has been observed in simulations of systems where the potential between particles is entirely repulsive.[2]

Figure 1 shows the vapour pressure curve and melting curve of the fluid studied in the present work (nitrogen) on the P,T phase diagram illustrating the points above. The rationale for studying nitrogen is fourfold: it is the simplest and most fundamental diatomic molecule, more so than hydrogen which is exceptional due to the presence of quantum effects up to much higher temperatures; it is amenable to a wide range of experimental investigations as the naturally occurring isotope scatters neutrons reasonably strongly and it also has a Raman spectrum; due to the position of T_C relative to 300 K, crucial parts of the phase diagram from the critical point up to temperatures at which the Widom lines are no longer present are experimentally accessible; and lastly, studies of the properties of pure supercritical nitrogen can serve as control data for future studies of non-reacting supercritical fluid mixtures. At present the experimental study of the Frenkel line and associated phenomena in supercritical fluid mixtures is entirely *terra incognita*.

Estimating the P,T path of the Frenkel line in nitrogen is challenging as no molecular dynamics simulation studies tracking the Frenkel line position on the phase diagram are available to our knowledge. In the quasi-harmonic (Grüneisen) approximation (as defined in ref.[3]) far from the critical point, the Frenkel line corresponds to $C_V = 3k_B$. This is the heat capacity resulting from the rotational and translational degrees of freedom of the nitrogen molecule, plus a contribution from longitudinal sound waves (assuming adequate thermal energy to excite all modes up to the Debye frequency), but after the loss of all rigidity (i.e. no shear waves can propagate). In the temperature range shown in figure 1, there is not adequate thermal energy available to excite the intra-molecular vibrational mode (this was checked by referring to the heat capacity on NIST[4,5] in the low density limit). The quasi-harmonic approximation resulting in the $C_V = 3k_B$ criterion has been shown to work well for soft-sphere fluids[6] and be quite adequate for predicting C_V for a range of fluids over a wide P,T range[3]). However, as the critical point is approached the $C_V = 3k_B$ criterion can no longer be used due to the existence of a broad maximum in C_V in the vicinity of the critical point (as noted previously in ref.[7]). Our estimate of the Frenkel line position

(figure 1) therefore takes into account the trend in C_V alongside our coordination number (CN)-based determination of the Frenkel line position at 300 K in previous work,[8] and at 160 K in the present work.

The proposal of the Frenkel line , at first sight, raises some issues as in this case a sample subjected to a pressure increase at constant $T > T_C$ undergoes two separate transitions away from gas-like properties: the Widom line(s) followed by the Frenkel line at higher pressure. The Widom lines are the thermodynamic continuation of the vapour pressure curve: all properties that change discontinuously when the vapour pressure curve is crossed undergo a narrow (in P,T space) but continuous transition when a path close to the critical isochore is crossed at $T > T_C$. For instance, the inset to figure 1 shows the Widom line transition in C_P and the (barely visible) Widom line transition in C_V at 160 K. All Widom lines begin (by definition) at the critical point and, upon P,T increase gradually diverge from each other and fade out. This divergence is observed in the experimental data[5,9] and is expected theoretically.[10–14] Nonetheless, the fact remains that upon a P,T path such as that shown in figure 1 (isothermal pressure increase at 160 K) the sample has already undergone one transition from the gas state into a region on the phase diagram in which its properties are, to some extent, less gas-like, before the Frenkel line is reached.

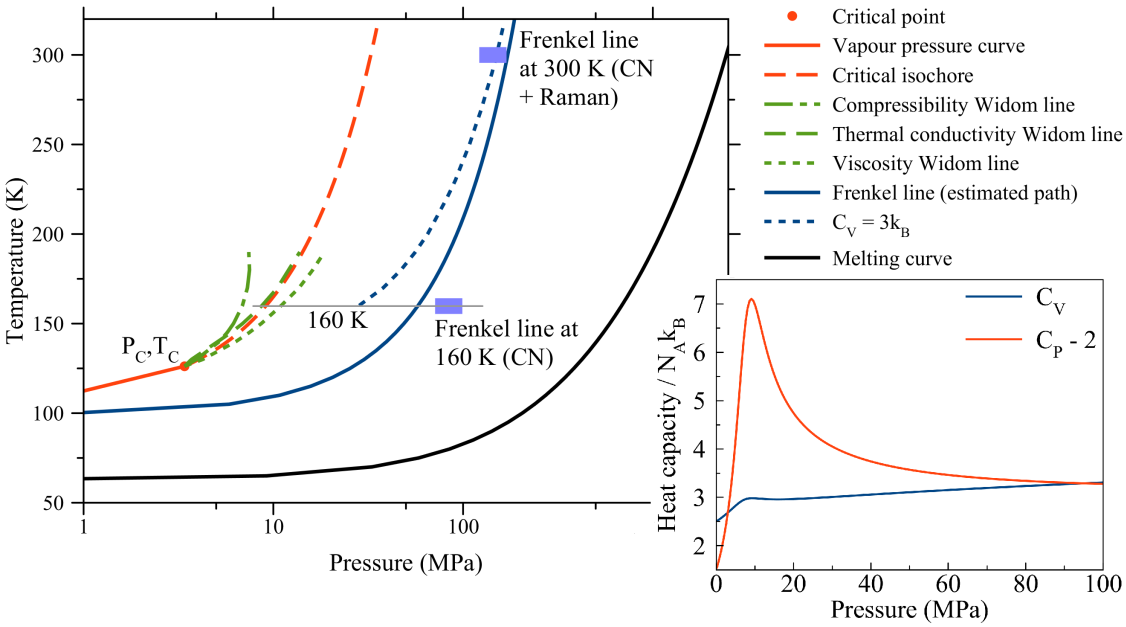

Figure 1: The phase diagram of fluid nitrogen. Vapour pressure curve, critical isochore and $C_V = 3k_B$ are obtained from NIST REFPROP, Widom lines are obtained from NIST REFPROP following analysis in ref.,[9] melting curve from ref.,[15] Frenkel line position at 300 K from ref.[8] The grey line indicates the 160 K isotherm studied in the present work, from which the Frenkel line position at 160 K was obtained. Inset: Trend in dimensionless heat capacities upon pressure increase at 160 K.

However, the existence of the Frenkel line has been confirmed experimentally in several studies,[16] using (for instance) Raman spectroscopy,[17] X-ray[18] and neutron[8] diffraction . The phonon theory of liquid thermodynamics[19] that underpins the Frenkel line has been verified in other ways;[20,21] in particular through its use to model the heat capacity of liquids over a wide P,T range.[3] However, there are several important aspects of the Frenkel line that have yet to be studied experimentally so the present study examines two areas in which further work is required.

Firstly, the Frenkel line has not been studied at temperatures at which the Widom lines are also present. A number of studies have examined the Frenkel line at temperatures where the Widom lines either barely exist or do not exist, so the Frenkel line is the only candidate for a transition from gas-like to liquid-like behaviour. Two studies[22,23] have examined the Frenkel line in the subcritical temperature region, confirming that it crosses the critical

isotherm at P>P_C, but to date no experimental study to our knowledge has convincingly measured both the Widom and Frenkel lines in a single comparative study.

Secondly, to date most studies have measured the Frenkel line at a single PVT point. Only two studies have attempted to track the path of the Frenkel line on the P,T / ρ,T phase diagram. Cockrell et al.[23] tracked the Frenkel line in subcritical H_2O over a wide pressure range but narrow temperature range. Smith et al.[17] tracked the Frenkel line over a wide supercritical P,T range in CH_4 but the study was hindered by the inadequate accuracy of pressure measurement in the diamond anvil cell above 300 K. Here, we present a neutron scattering study of supercritical fluid N_2 upon isothermal pressure increase at 160 K (1.3T_C). Our study covers a wide pressure range in which both the Widom lines and the Frenkel line are crossed. We previously studied fluid N_2 using this method at 300 K, so are able to characterize the line using the same criterion over a temperature range from 1.27T_C - 2.38T_C, a significantly larger temperature range in both relative and absolute terms than in our earlier work on CH_4.[17]

Methods

Samples of pure nitrogen were loaded into null-scattering TiZr high pressure cans inside a closed-cycle refrigerator held at 160K and operating with 100 mbar He as thermal transport fluid. Time-of-flight diffraction patterns were collected on the SANDALS instrument at the ISIS Neutron Spallation Source, Rutherford Appleton Laboratory, Harwell, UK. The pressure of each run was obtained using a two-stage intensifier and determined by use of a transducer attached to the gas pipeline feeding the cell. Background measurements of the empty can along with vanadium measurements were taken to normalize the data in the GudrunN program, from which the S(Q) was obtained. Collection times varied between 8 and 12 hours depending on the sample density (lower densities require longer collection times for the same level of statistics and confidence). Such long collection times are needed due

to the design of the high-pressure TiZr cell, whose integrity is maintained by locating the sample within 6 parallel cylindrical pores of 1.6mm diameter, resulting in an in-beam sample volume of only 0.28cc. The diffraction patterns have been measured up to 50 A^{-1}, with a 0.05 A^{-1} spacing. No inelasticity corrections have been applied.

Empirical Potential Structure Refinement[24] was performed on the data to extract the radial distribution functions and running coordination numbers. At each pressure point, a box containing 1000 N_2 molecules was built. The fitting routine was run for several hundred Monte-Carlo cycles until the fit stabilized and no further changes could be observed. Once this was achieved, 5000 configurations were accumulated maintaining the same empirical potential. The experimental structure factors, final EPSR fits, extracted pair distribution functions and running coordination numbers are available in the Supplementary Information (SI).

Results

Our results are summarized in figures 2 - 3. In figure 2 we show selected radial distribution functions obtained from our S(Q) data using EPSR and, obtained from these g(r) data, the radius of the first coordination shell as a function of pressure. The latter was determined as the distance at which the first minimum in the g(r) occurs, following the first maximum which corresponds to the first coordination shell.

At the lowest pressure point (7.8 MPa), the lower quality of the pattern (Si, first figure) is indicative of a gas-like system having low density and so having a reduced number of neutron-sample collisions within a given time frame when compared to higher density (where the probability of a collision increases quickly), and a better sampled pattern would require a significantly longer collection time. This fact is evidenced by the large uncertainties associated with this pressure. The associated radial distribution function is shown mostly for qualitative comparison with higher density points.

In figure 3a we plot the evolution of the coordination number with increasing pressure at 160 K and, for comparison, the data from our previous study at 300 K.[8] Finally, in figure 3b the same data are plotted as a function of density. The densities have been calculated from pressure using the fundamental equation of state for N_2,[5] available via NIST REFPROP.

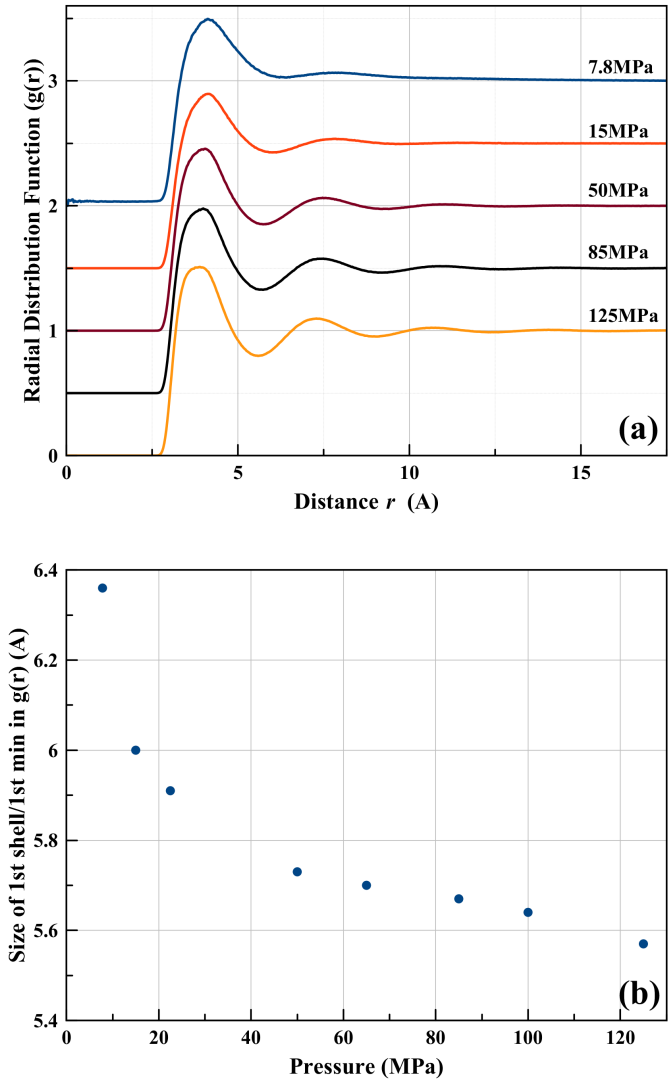

Figure 2: (a) Selected intermolecular Pair Distribution Functions (g(r)'s) on isothermal compression at 160 K. (b) Size of the first neighbour shell (distance at which first minimum in g(r) occurs) for Nitrogen at 160 K.

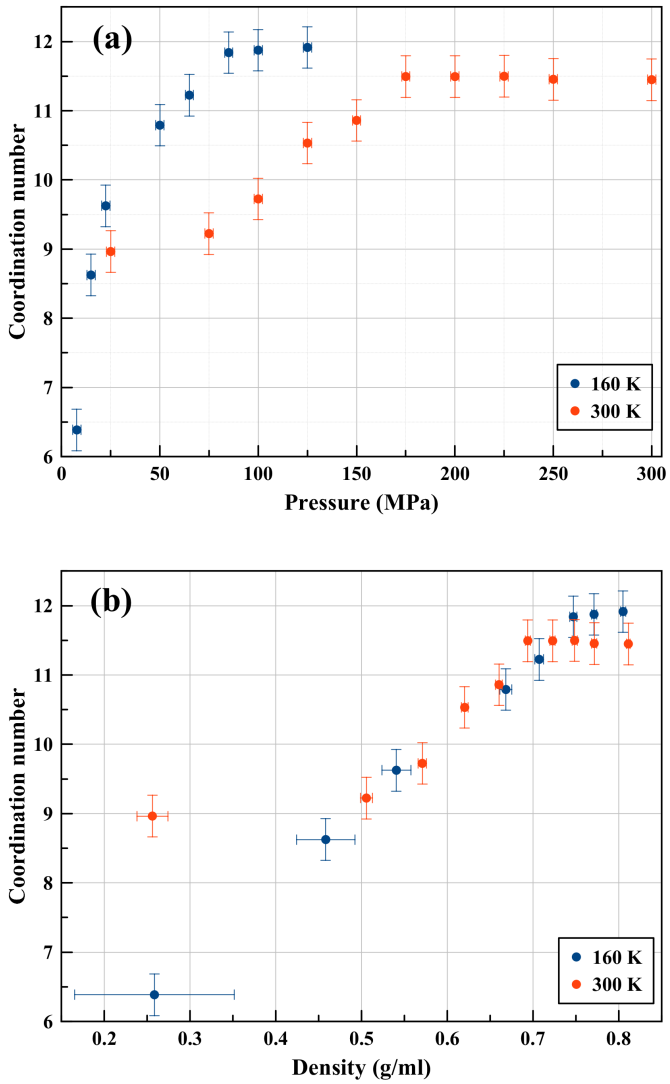

Figure 3: (a) Evolution of the coordination number with pressure for 160 and 300K. (b) Evolution of the coordination number with density for 160 and 300K. Crossovers are readily apparent when crossing the Frenkel line at both temperatures.

Discussion and Conclusions

The results obtained offer an insight into the fundamentally different nature of the Widom line and Frenkel line transitions in the supercritical state. The Frenkel line transition is similar to that observed in our previous work at 300 K. It is a transition to rigid liquid-like behaviour which is characterized by a constant coordination number, so further density

increase in this state must take place by other means. Possible mechanisms and the resulting local topologies of the rigid fluid have been proposed by Yoon et al.[6,25] Our analysis (given in the supplementary information) of the part of the $g(r)$ function resulting from the N - N bond allows us to conclude that any change in N - N bond length occurring along the P,T path followed is very small, which allows us to rule this out as the cause of the density increase in the rigid-liquid region. We therefore conclude that the significant density increase upon compression in the rigid-liquid region (shown in figure 3b) is due to compression of the first coordination shell as shown in figure 2b.

As stated in the introduction, very little work has been done to date tracking the evolution of the Frenkel line position on increasing temperature. Our findings in this work along with those from our recent study of the Frenkel line in N_2 at 300 K[8] allows us to make such a comparison over a large range in absolute temperature. At 300 K, the Frenkel line (as indicated by a constant coordination number) is crossed at 150 MPa. Here, at 160 K, the Frenkel line as indicated by the coordination number is crossed at 85 MPa. Whilst this is a lower pressure than at 300 K (see figure 1) it is at the same density within experimental error, 0.7 - 0.75 g/ml. This contrasts with the path of the Frenkel line according to the heat capacity criterion (the $C_V = 3k_B$ line on figure 1) which trends to slightly higher density upon temperature increase. The Frenkel line has been plotted on the density-temperature phase diagram using the velocity autocorrelation function and heat capacity criteria for a variety of real fluids ([9] and refs. therein), as well as for the model Lennard-Jones fluid[26] and exhibits a weak trend towards increasing density upon temperature increase in all cases. The discrepancy between these data and the findings of the present study warrants further experimental and theoretical investigation.

The pressure-temperature path taken in our study crosses that of several Widom lines between 5 - 15 MPa. The effect of the Widom lines at this temperature on important experimentally observable properties such as the density, C_P and the Joule-Thomson coefficient can be plotted out using the output from the fundamental equation of state,[5] and is significant.

What is less clear is whether crossing the Widom lines has any effect on the coordination number trend observed. Arguably, there is a crossover in the trend of coordination number increase (figure 3a) at ca. 15 MPa, which co-incides roughly with the Widom lines, but unfortunately there are an inadequate number of data points to be certain. Regardless of whether a crossover that co-incides with the Widom lines is observed, the behaviour remains gas-like (significant increase in coordination number upon pressure increase) until the Frenkel line is reached. Our data indicate that it is reasonable to describe the Widom lines as a gas-gas transition.

In addition, our data support (but do not prove) the hypothesis that many Widom-line phenomena are caused by the significant, but continuous, increase in density over a narrow pressure range when the density-Widom line is crossed at a density close to the critical isochore. When we plot the coordination number as a function of density instead of pressure (figure 3b) the Widom-line transition(s) essentially disappear whilst the Frenkel-line transition remains. This is expected for simple fluids similar to the Lennard-Jones fluid[27,28] and confirms the fundamentally different nature of the Frenkel line and Widom lines.

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Supporting Information: Analysis of the N≡N triple bond from the intramolecular neutron PDFs; (Attached archive) Experimental Structure factors for N_2 at 160 K - SANDALS Instrument, ISIS, RAL, UK; text files containing the raw total scattering signal (mint01), EPSR extracted pair distribution functions and associated uncertainties (g01) and EPSR extracted coordination numbers (z01) for all pressures described in the present study

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