Supporting Information for:

On the Transition from Gaslike to Liquidlike Behaviour in Supercritical N₂

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Experimental and analysis methods

Raman spectroscopy

A diamond anvil cell (DAC) was equipped with diamonds having 1 mm culets and a stainless steel gasket, indented then drilled using a custom-constructed spark eroder. Liquid N₂ was loaded into the sample chamber by immersing the entire DAC in liquid N₂ then turning the pressure screws using long Allen keys to close the DAC. Pressure was measured using the ruby photoluminescence method, resulting in a typical error of ± 0.002 GPa. Pressure was measured both before and after the collection of the Raman spectra at each step to evaluate the total error in the pressure measurement. In all cases, error bars are too small to display. Data were collected on pressure decrease from 2.6 GPa at constant temperature. To calibrate the pressure measurement at ambient conditions.

Spectra of the intense Raman-active vibron at ca. 2330 cm⁻¹ were collected on a Renishaw InVia Raman spectrometer (633 nm laser excitation, 2800 lines per mm grating). The total instrumental linewidth was confirmed from the Raman spectrum of the unstressed diamond to be, at most, 1.3 cm⁻¹ HWHM. Each spectrum was fitted using a single Lorentzian peak in Magicplot Pro following subtraction of a linear background. The calibration of the Raman measurements was checked using the intense Raman-active vibration of diamond at 1332 cm⁻¹ at ambient conditions. Our data are in good agreement with those collected in previous studies in the pressure ranges in which they overlap, confirming the accuracy of this calibration.

Neutron diffraction

Time-of-flight neutron diffraction data were collected on the SANDALS instrument at the ISIS pulsed neutron source. The experiments utilized the TiZr high pressure cell, allowing pressures up to 3 kbar to be generated using a compressor and capstan pump. Pressure measurement was made using a transducer on the gas pipeline leading to the cell. Data were normalized and corrected using Gudrun to obtain the static structure factor S(Q). The equation of state (EOS) utilized to normalize the data was the Span-Wagner EOS (25) available on NIST REFPROP. Collection time was varied between 8 hours and 24 hours depending on the density of N₂ at each pressure studied.

Empirical potential structure refinement (EPSR)

Neutron diffraction data were analysed using the EPSR software package. At each pressure at which neutron diffraction data were collected a fitting routine was run using a box of 1000 N₂ molecules at the fixed density obtained from the Span-Wagner EOS. After allowing the potential energy to equilibrate the empirical potential was turned on and allowed to change in order to fit to the diffraction data. After this process was complete and the energy had stabilized again, the parameters output from EPSR were accumulated for 5000 iterations, keeping the previously obtained empirical potential fixed. Further details on the EPSR analysis method are available in ref. (27). A number of parameters are output by an EPSR simulation. In this work we used the total radial distribution function g(r), the running coordination number and the intramolecular radial distribution function d(r) (simply the distribution of N-N bond lengths). The function d(r) was fitted using a single Gaussian at each pressure studied.

Ab-initio molecular dynamics (MD) simulations

A series of Ab-Initio molecular dynamics (AIMD) simulations were performed using periodic boundary conditions in a cubic cell containing 108 molecules at densities ranging from 10 mol/l to 45 mol/l. Simulations used the CASTEP code (28) using ultrasoft pseudopotentials with an energy cut off of 490 eV, the PBE exchange-correlation functional and the TS semi-empirical dispersion correction (29). The ab-initio molecular dynamics simulations used a timestep of 1.0 fs and Nosé-Hoover thermostats (5 chains) in a constant NVT ensemble. Each simulation was equilibrated for 1 ps (1000 timesteps) then continued for a further 2000-6000 steps. The pressure for each simulation was obtained from the set density using the Span-Wagner EOS (25). Raman frequencies were obtained by calculating the Fourier transform of each individual molecular bondlength versus time followed by averaging of Fourier transforms over all molecules (Welch windowing and zero padding was used to calculate individual Fourier transforms). In the analysis the Raman frequencies produced using AIMD were normalized by subtraction of a small constant (32 cm⁻¹) to ensure the lowest density experimental and AIMD datapoints produced the same Raman shift as the underlying DFT framework resulted in a systematic overestimate of frequency.

The time averaged values of the electronic Hamiltonian are tabulated below, along with the corresponding calculated Raman frequency:

Density (mol/L)	Frequency (cm ⁻¹)	Time-averaged Electronic
		Hamiltonian (Hartrees)
10	2369.3	-2.192681
15	2369.7	-2.192695
20	2365.8	-2.192740
25	2364.7	-2.192727
30	2367.1	-2.192565
35	2369.1	-2.192256
40	2371.5	-2.191739
45	2372.6	-2.190979



Plots of various parameters in $S({m Q})$ and g(r) as a function of pressure





Figure S1. Plots of the position and width of the first peak in S(Q), position of the first and second peaks in g(r) and second shell co-ordination number as a function of pressure.



Figure S2. Plot of the N – N bond length obtained from the EPSR software, as a function of pressure.

Termination of Widom lines

Out of the Widom lines we studied using the fundamental EOS, those that persisted to the highest temperature were those for viscosity, density (compressibility) and thermal conductivity. In our judgement, by 195 K the variation in these parameters around the critical isochore was not sufficiently large in a narrow P,T range to justify plotting as part of a Widom line. Figure S3 shows plots of these parameters at 195 K.





Figure S3. Plots of density, thermal conductivity and viscosity as a function of pressure at 195 K obtained from the fundamental EOS.