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Frenkel Line in Nitrogen Terminates at the Triple Point

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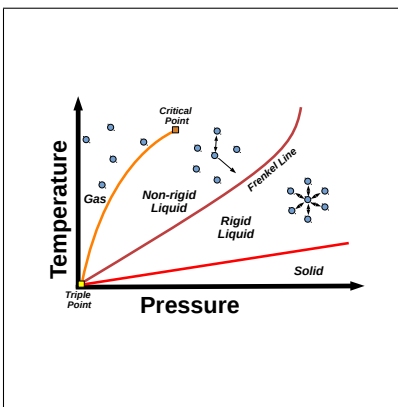
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Abstract

Recent studies on supercritical nitrogen revealed clear changes in structural markers and dynamical properties when the coordination number approaches its maximum value. The line in PV space where these changes occur is referred to as the Frenkel line. Here we qualitatively reproduce such changes in the supercritical regime using the popular “Optimized Potential for Liquid Simulation” (OPLS) classical forcefield for molecular dynamics. Unfortunately, at 160 K OPLS nitrogen predicts sublimation rather than producing a liquid phase, so we developed our own forcefield to achieve quantitative agreement with experimental data. We confirm the asymptotic behaviour of the coordination number on crossing the Frenkel line, and note an associated change in the diffusion constant, consistent with the non-rigid to rigid liquid-like character of the ‘transition’. The simulations allow us to track the Frenkel line to subcritical temperatures, and demonstrate that it terminates at the triple point. This establishes the experimentally measurable changes which could unequivocally determine the Frenkel line in other systems.

Graphical TOC Entry



Keywords

nitrogen, supercritical, molecular dynamics, liquids, high pressure

Introduction

For the past decade an intense debate has brought together the supercritical fluid and high pressure communities. This was ignited by the postulate that a previously unconsidered crossover ‘transition’ exists in supercritical fluids. This transition occurs along what has been called a Frenkel line¹ in (P,T) space. It divides the supercritical fluid state into two distinct regions: a non-rigid so-called gas-like one and a rigid liquid-like one. The two regions are claimed to differ in a number of crucial properties, among them: the ability of the fluid to sustain shear waves; the existence of medium-range order and a relatively close packed and repulsion-dominated structure of the liquid-like state; an abrupt change in diffusivity when crossing from one region to the other; there is also a maximum in solubility of other chemical species. This proposed maximum in the ability to solvate other chemicals has increased even further the scrutiny of the Frenkel line, as supercritical fluids are a core industrial-interest² due to their wide-spread use as potent solvents.

A point of contention has long been the positioning of the Frenkel line with respect to the critical point of a given system, and hence its relation to Widom lines. Widom lines are defined by extrema in thermodynamic properties, represent continuations of the gas-liquid transition (boiling) line into the supercritical regime. The P-T path of a Widom line depends on which thermodynamic property is considered, so for instance heat capacity and compressibility yield different lines. In one of the earliest analytic studies, Brazhkin and Rhyzov³ showed that for a Van der Waals fluid the Widom lines merge into the phase line at $T < 1.07T_C$ (critical temperature) and $P < 1.25P_C$ (critical pressure). By contrast the Frenkel line lies on the liquid-like side of critical point. The Frenkel line has been shown to continue to high temperature and pressure, but little attention has been paid to its low temperature behaviour. Evidently, any line on the phase diagram must terminate at $P=0$, on the gas-liquid coexistence line, or on the melt curve.

On the theoretical front, since the proposal of the Frenkel line almost 10 years ago, multiple studies attempted to provide a meaningful characterization and clearly indicate

which properties of the fluid change when crossing it. As the Frenkel line does not describe a thermodynamic transition but rather a crossover, it is generally dynamic properties that have to be determined rather than thermodynamic ones. Brazhkin et al.⁴ identified changes in mean-square displacement and velocity auto-correlation function in Lennard-Jones and SSp fluid models. Using the same criteria, Yang et al.⁵ identified the Frenkel line and related it to the solubility maxima observed in CO₂, CH₄ and H₂O.

Computationally, the search for the Frenkel line is impeded by a lack of transferable classical forcefields for most simple molecules, the vast majority of which have been fitted solely against ambient data. Despite this, Ghosh and Khrishnamurthy⁶ have successfully identified it in bulk and confined argon (Lennard-Jones type potential) and highlighted an Arrhenius to super-Arrhenius change in diffusivity upon its crossing. Working also on argon, Yoon et al.⁷ proposed a geometrical and topological characterization of the Frenkel line and reported percolation of solid-like structures above the densities of the Frenkel line. In another attempt to identify structural markers of the Frenkel line, Bolmatov et al.⁸ have found an onset of mid-range order in molecular dynamics on CO₂ (Buckingham model). In the opposite camp, Bryk et al.⁹ argued against the existence of the ‘Frenkel line’ based on simulations of supercritical neon that found several parameters associated with the rigid liquid-like state (medium-range order, high frequency oscillations) appear before meeting the Frenkel line.

Experimental measurements of the Frenkel line have used very varied characteristics, often hard to reconcile and bring to agreement. Smith et al.¹⁰ reported a turning point in the Raman frequency upon crossing the Frenkel line in CH₄, and a similar change in ethane was later reported by Proctor et al.¹¹ Structural investigations using X-rays in Diamond Anvil Cells by Bolmatov et al.¹² identified the line in neon and provided the first structural evidence for it. This was later reinforced by Prescher et al.¹³ also working on supercritical neon, who showcased the onset of medium-range order and a plateau of the coordination number as a function of pressure once the Frenkel line is crossed. Most recently, Proctor

et al.¹⁴ have provided the first structural study of the Frenkel line in nitrogen at 300 K using neutron diffraction, avoiding the criticism leveled at previous X-ray studies about inherent X-ray cut-off problems. The study confirmed that the coordination number is clearly pressure-dependent before the Frenkel line is crossed, and pressure-independent on the rigid liquid-like side. A recent investigation by Pruteanu et al.¹⁵ was able to trace again the same clear marker of the Frenkel line, the coordination number, in nitrogen at 160 K, in a region where Widom lines are also present. The study provided the first evidence of temperature-dependence of the Frenkel line, and showed that the Frenkel line does not terminate at the critical point and therefore is not a Widom Line.

In the present study we use computer simulations to reproduce qualitatively and quantitatively the reported change in coordination number in nitrogen when crossing the Frenkel line. We relate this to changes in other properties readily computable from molecular dynamics, indicative of the crossover. Stronger emphasis is placed upon quantities that are, in principle, measurable in experimental settings (such as diffusion constants), informing future measurements that will settle the debate on the existence, and character of the Frenkel line. Simulation can also unambiguously relate structural changes to the dynamical properties of a given material. To this end, we present a new, machine-learned classical forcefield for molecular dynamics that achieves better quantitative agreement with high pressure experimental data than currently available potentials for nitrogen.

Methods

Existing Forcefield Model

The GROMACS (GRONingen MACHine for Chemical Simulations) software package¹⁶ was employed for simulations of pure molecular nitrogen using the built-in "Optimized potential for liquid simulation" OPLS-AA forcefield.¹⁷ Each OPLS-AA molecule comprises of 2 N atoms, atom type NR ('aromatic' nitrogen), with a rigid 1.11Å intramolecular bond and a

10 Å cut-off for the Van der Waals interactions. Cubic simulation cells containing 2400 N₂ molecules were used. A 50 ps NVT equilibration using the Berendsen thermostat¹⁸ at the desired temperatures (300/500 K) was followed by a 300 ps NPT equilibration using the Parrinello-Rahman barostat¹⁹ at each desired pressure. Equilibration was followed by 1 ns production runs for all P-T choices considered.

New Machine Learning Interatomic Potential

A new machine learning (ML) forcefield was developed to accurately describe the potential energy surface (PES) of supercritical nitrogen at a range of pressures and temperatures. The LAMMPS package²⁰ was used to perform molecular dynamics simulations employing this newly-developed forcefield.

The ML forcefield is used with LAMMPS to perform both NVT and NPT simulations using a Nose-Hoover thermostat. The nitrogen molecules were modeled as rigid rotors by applying the SHAKE algorithm²¹ as implemented in LAMMPS. The intramolecular bond lengths were fixed at 1.1014 Å to match underlying model.²² Every simulation was first equilibrated for 300 ps followed by a 2 ns production run.

ML Model Details

In our new model, the total energy of the system is expressed as a sum of local energy contributions. The local atom environment is described using Gaussian Type Orbitals descriptors^{23,24} which capture up to three-body interactions between individual atoms, without requiring an expensive double loop over neighbouring atoms.

The mapping between descriptors and the total energy of the system is achieved using the Bayesian Linear Regression approach. Polynomial basis functions up to the order of two are used to fully capture a 4-dimensional PES of two rigid interacting N₂ molecules.

The training database development and model training are accomplished using an iterative process. In the first iteration a MD with the Lennard-Jones potential (LJ) was used to

generate an initial set of reference configurations. The LJ energies and forces are discarded and the total energy of the system is recalculated using an analytical five-site potential which in turn was parameterised based on high-level quantum chemical computations.²² Next, the ML model is trained using the initial set of configurations and then replaces the LJ potential in the next iteration. In the following iterations more configurations are included which are sampled from MD NVT trajectories every 1 ps at different density-temperature conditions: temperatures between 100 - 1300 K and the simulation box length between 6.1 - 15 Å.

Frenkel Line: Definition and Identification

The Frenkel line is related to structural and dynamic quantities, rather than discontinuities in derivatives of the free energy. In this work, we identify it with several features in the coordination and the diffusion arising from the inability of a typical molecule to escape from its current set of neighbours.

We do not use the turning point in Raman frequency: it is observable experimentally, but difficult to calculate. Furthermore, for non-diatomic molecules there may be more than one Raman-active frequency, so it is impossible to generalise.

Coordination Number

The coordination number is simply the number of nearest neighbours each molecule has. At low density, in a gas phase, this will be simply proportional to the density. At high density, it will tend to a value in the range 10-14 above which there is insufficient room around a molecule for additional neighbours. The Frenkel Line can be associated with the changeover between these two regimes. This simple concept requires a heuristic approach to define what constitutes a “neighbour”. The most common approaches involve counting all molecules within a chosen radius as “neighbours”. Two options exist to define this radius: a fixed value or as the first minimum in the radial distribution function $g(r)$.

Diffusion Constant

The diffusion constant in a liquid, measured in MD from the mean squared displacement of the molecule $\langle[\mathbf{r}(0) - \mathbf{r}(t)]^2\rangle/t$, relies on the concept of the molecule performing a random walk. The Frenkel line can be associated with the point where diffusion is dominated by thermally activated single-molecule escape from a cage of neighbours, while in the lower density liquid we can imagine mean free paths in excess of the intermolecular distance and large-scale rearrangements involving many molecules. In MD we can detect the Frenkel line from a transition from a low diffusion constant “caged” liquid to a rapidly diffusing free liquid.

Shear Waves

A final definition of the Frenkel line comes from the ability of the liquid to support transverse waves. Again, the idea is that any lateral motion of a molecule will encounter a restoring force from a full shell of neighbours.

Results

Lennard-Jones (OPLS-AA) Forcefield

The density along various paths (in P-T) space according to the Lennard-Jones model are shown in Fig.1 alongside the equivalent experimental densities (from Proctor et al.¹⁴ and Pruteanu et al.¹⁵) as calculated from the NIST REFPROP equation of state for nitrogen.²⁵ Unfortunately the OPLS-AA forcefield fails to produce a liquid state at 160 K (Fig.2 left panel – full analysis presented in the supporting information), so a direct quantitative comparison to experimental parameters is not possible. To maintain coherence with the experimental results, the coordination number for the first neighbouring shell was taken as the number of neighbours at the distance of the first minimum in the pair distribution functions ($g(r)$'s).

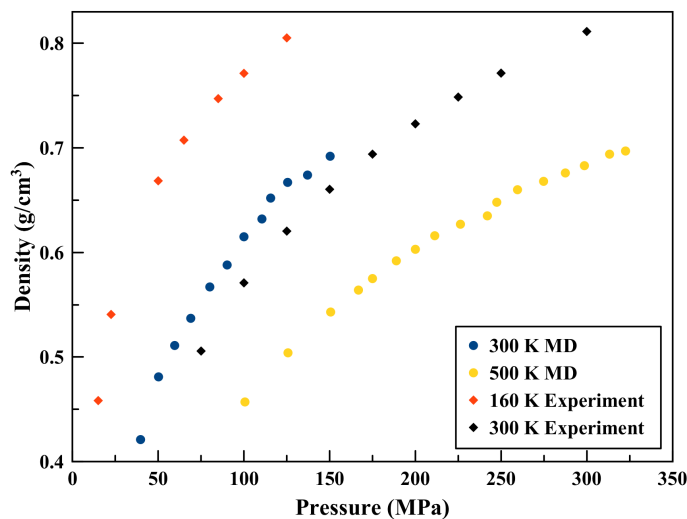


Figure 1: Isothermal paths followed in the present study compared with those used in experimental measurements on supercritical nitrogen by Proctor et al.¹⁴ and Pruteanu et al.¹⁵ The critical point of nitrogen is at 126K, 3.4MPa.

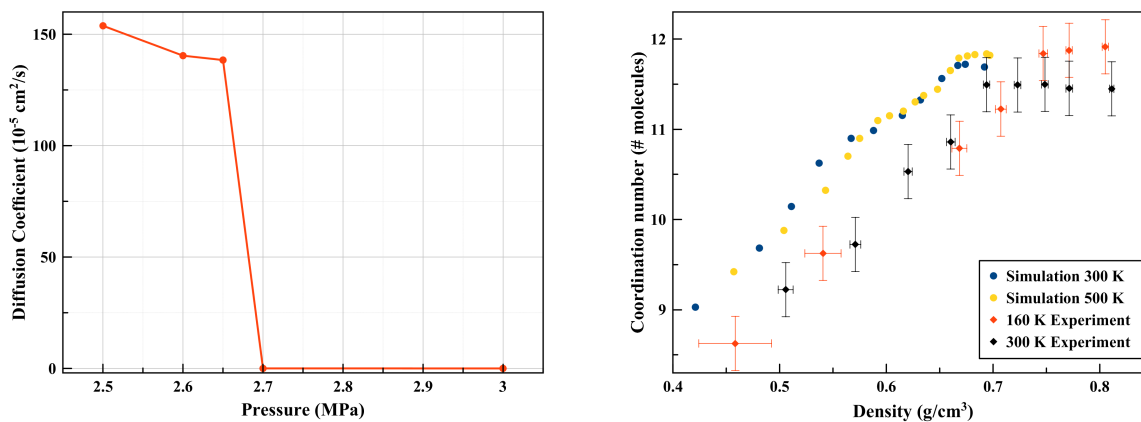


Figure 2: (Left) Diffusion constant for the OPLS-AA forcefield at 160 K, for the last 500 ps of the simulation. The constant changes by >4 orders of magnitude between 2.65 MPa ($139 \times 10^{-5} \text{cm}^2/\text{s}$) and 2.7 MPa ($0.0051 \times 10^{-5} \text{cm}^2/\text{s}$). The latter value is characteristic of solid phases where little to no diffusion occurs. These simulations at 160K reveal that the OPLS-AA potential predicts sublimation, making it inappropriate for the present study. (Right) Variation of the coordination number with density for OPLS-AA molecular dynamics simulations compared to available experimental data. The crossing of the Frenkel line is evident as the coordination number changes from being strongly density-dependent to almost constant.

In the supercritical regime, we notice a 5-7% discrepancy in the densities at 300K between

OPLS-AA simulation and experimental data. Although this difference reduces gradually with increasing pressure, at the highest investigated pressure point (150 MPa) it is still 4.6% denser than the experimental data at the same pressure. This difference translates to a shift of the entire coordination number-pressure curve to lower pressures (see supporting information) for the same choice of temperature. Despite this pressure offset, the qualitative shape of the curves are similar, displaying a strongly pressure-dependent coordination number up to a certain pressure and a very weakly pressure-dependent one afterwards.

A similar picture emerges when the coordination number is plotted against the density (Fig.2 right panel). Simulations at both temperatures show that once a certain density is achieved (and its corresponding packing fraction/coordination for nearest neighbours) the fluid changes from a non-rigid to a rigid state. This appears to confirm the statement by Pruteanu et al.¹⁵ that the Frenkel line is primarily density-driven. The exact P-T path is only relevant insofar as allowing one to reach the necessary density required by the fluid to enter the rigid liquid state.

Qualitatively, even for diatomic molecules which are more complex than the noble gases previously considered (argon and neon), Lennard-Jones type potentials are capable of producing the Frenkel line. Quantitative disagreement arises from the potential being fundamentally inadequate to describe nitrogen.

New Forcefield from Machine Learning

The isothermal equations of state of the newly-developed ML forcefield at several temperatures (including the same conditions as the measurements of the Frenkel line in nitrogen^{14,15}) are presented in Fig.3 left panel alongside the experimentally determined EoS used by the respective authors. A very good agreement between the model and experiment is readily noticeable for both temperatures, further reinforced by the comparison between selected radial distribution functions produced by the model and those measured by neutron scattering at 300 K (Fig.3 right panel).

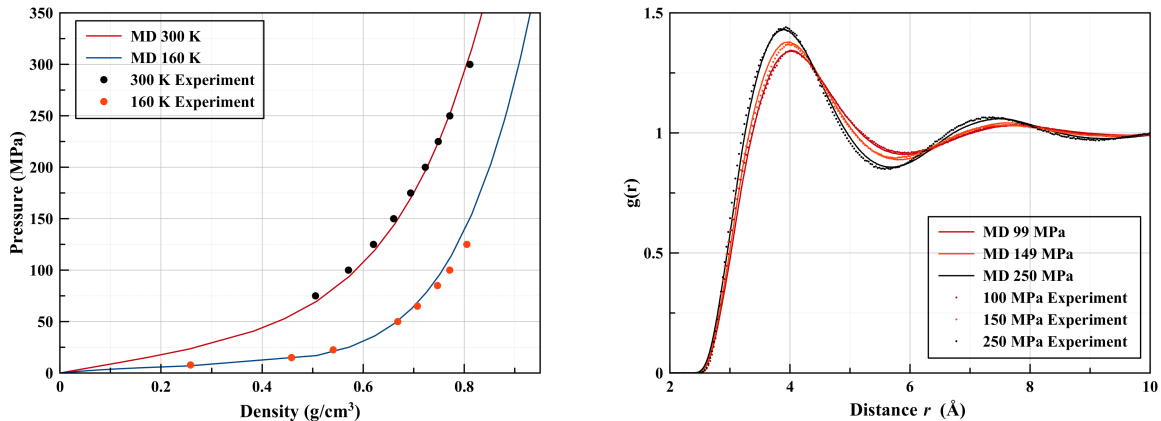


Figure 3: (Left) Equation of state for newly-developed machine learning potential compared with NIST EoS reference²⁵ at the pressures where the experimental RDFs were measured. (Right) A comparison of experimental and MD radial distribution functions for supercritical nitrogen at 300 K using the ML potential.

Despite the generally good agreement between our new model and reported equation of state and radial distribution functions, a few remarks are necessary. A close inspection of Fig.3 reveals slightly different trends of the equations of state. At 160 K, as pressure increases we notice a growing disagreement between the experimentally determined densities and those of our model (the model is denser). At 300 K we notice that for lower pressures the model is again denser than experimentally reported, but for higher pressures it appears less dense than measured. The radial distribution functions reveal similar trends, with the first minimum being generally at larger distances in the model than reported experimentally. Comparison with Fig.1 demonstrates the significant improvement over OPLS-AA nevertheless.

Experimental studies of supercritical nitrogen determined the coordination number by integration up to the first minimum in the $g(r)$ following the first peak. A change of slope in the evolution of the coordination number of nitrogen against pressure/density was used to identify the Frenkel line. The same criterion was used to analyse the MD in present study. In Fig.4 (left panel) the coordination number of the first neighbouring shell is depicted as a function of pressure along with the experimentally-reported values. The simulation data is noticeably smoother than the experimental data, however the crossover to a fully-

coordinated liquid can be identified for both sets at similar pressures. The discrepancies between the MD and experimental values are due to the differences in the EoS's and radial distribution functions to be integrated produced by the two respective methods (Fig.3).

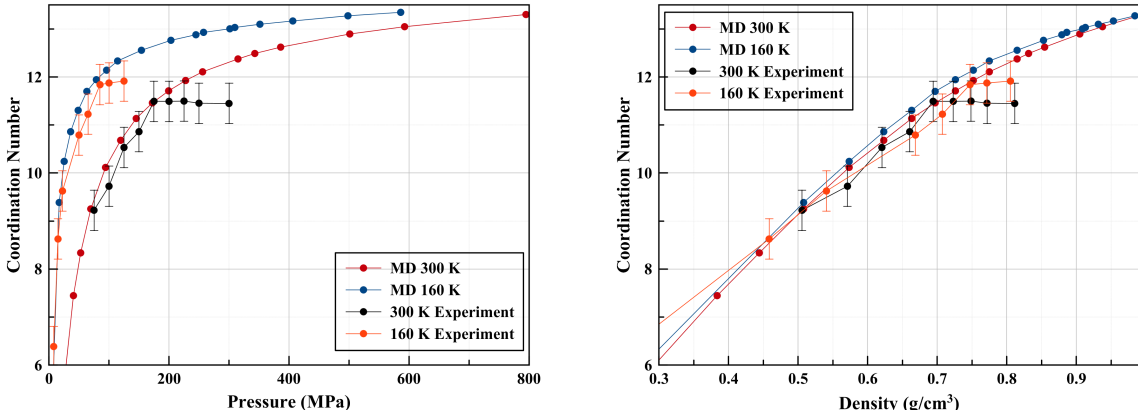


Figure 4: Results from ML MD simulations compared with experimental data reported by Proctor et al.¹⁴ and Pruteanu et al.¹⁵ (Left) Coordination number as a function of pressure. (Right) Coordination numbers as a function of density.

Fig.4 right panel shows the coordination number at 160 K and 300 K against density, again indicating that the Frenkel line is close to an isochore.

Frenkel Line Using the New Forcefield

The motivation for exploring sub-critical temperatures is two-fold:

- As most of the available experimental data about the Frenkel line is restricted to the supercritical regime, a validation exercise was necessary to ensure our model does not produce unphysical situations in more regular phases of matter.
- There is still an ongoing debate about the exact path of the Frenkel line into the sub-critical region, and hereby by employing the same criteria of identification as for the supercritical regime we can ensure a coherent investigation of this conundrum.

The isotherms followed in the present study are shown below, in Fig.5, along the melting

curve and vapour curve as curated by NIST,²⁶ and the experimental paths followed by Proctor et al.¹⁴ and Pruteanu et al.¹⁵ for neutron measurements of the Frenkel line.

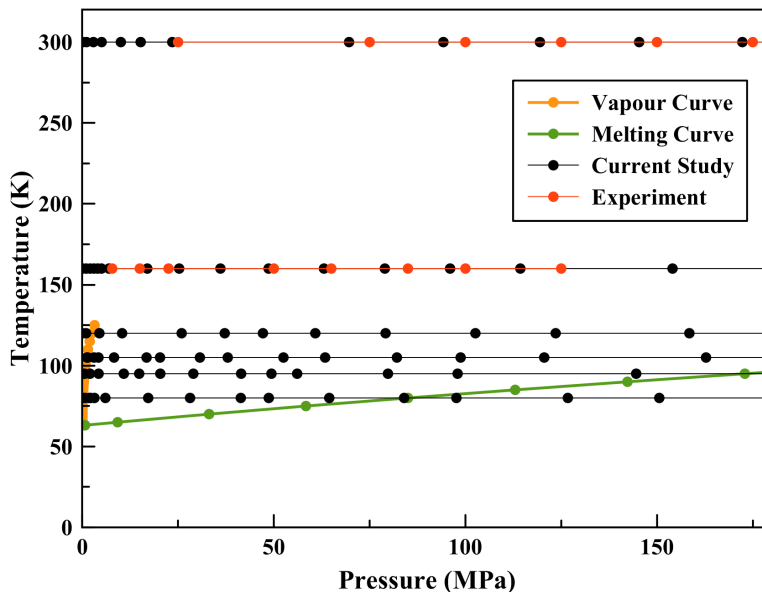


Figure 5: Isotherms followed in the present study along the vapour and melting curves of nitrogen curated by NIST²⁶ and the experimental path used by Proctor et al.¹⁴ and Pruteanu et al.¹⁵ to identify the Frenkel line in supercritical N_2 using neutron scattering.

In a similar fashion to the OPLS-AA model presented in the previous section, changes in the evolution of the coordination number (Fig.4) are evident as the Frenkel line is crossed, suggesting a change in the structure as well as the dynamics of nitrogen accompanying the crossing of the line.

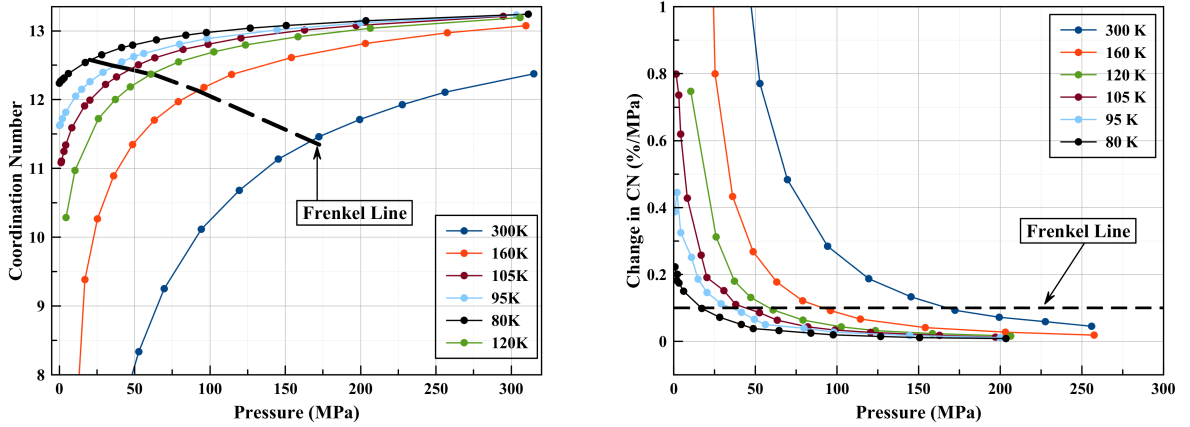


Figure 6: (Left) Coordination number of nitrogen from ML potential MD as a function of pressure. (Right) Percentage change in the coordination number of N_2 with increasing pressure.

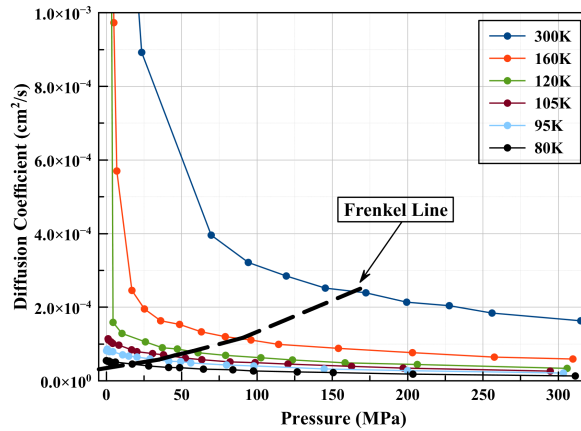


Figure 7: Diffusion coefficient from ML potential MD as a function of pressure and Frenkel line as determined from the coordination number equation below.

Both the coordination number and diffusion constant change in tandem, and in both cases two ‘regimes’ can be easily identified: a lower pressure one where the coordination number increases and diffusion constant decreases abruptly with increasing pressure, and a higher pressure regime where minimal changes occur in both, even for very large pressure differences.

As the phenomenon of interest is a crossover and not a thermodynamic phase transition, all changes are continuous. There is no hard criterion to select the pressure of the regime

change, and in the absence of any sort of analytical expression for the pressure evolution of the coordination number and diffusion coefficient with pressure the exact ‘location’ of the pressure at which the crossover occurs is somewhat subjective. We have chosen as the Frenkel pressures on each isotherm the points in Fig.6 where the coordination number obeys the following criterion:

$$\frac{P_{TP}}{C_N} \times \frac{dC_N}{dP} < 10^{-5} \quad (1)$$

where P_{TP} is the triple point pressure. Unfortunately, we have not been able to find a similar analytic criterion for the diffusion constant due to the noise in the data at low temperatures.

The application of this criterion leads to the points presented in Fig.8 for the position of the line on the P-T phase diagram of nitrogen. It is consistent with the criteria used by Cockrell et al.²⁷ Our data was plotted along with the vapour curve and the melting line of nitrogen as curated by NIST.²⁶

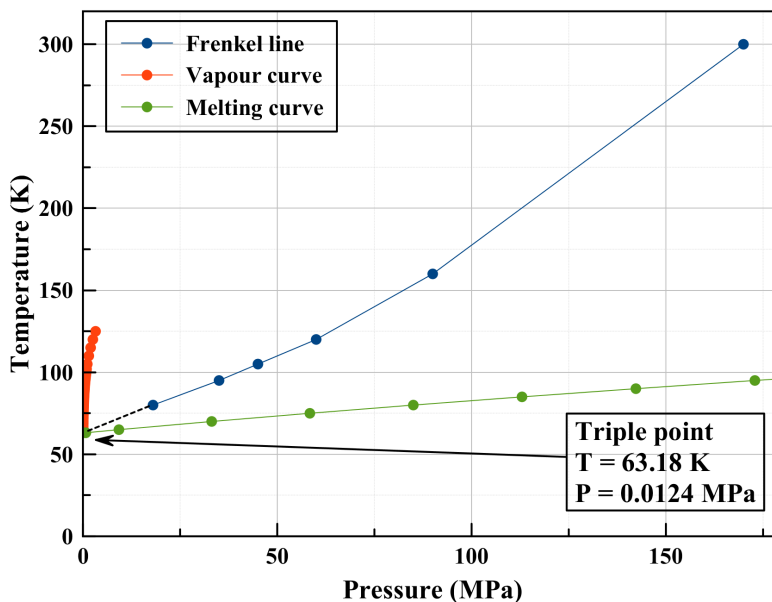


Figure 8: Current line as identified using correlated changes in coordination number and diffusion constant of nitrogen. The vapour and melting curves are depicted according to data from NIST.²⁶

Encouraged by the good agreement with experiments in the supercritical regime, the present study aimed to identify in a consistent manner (deploying the same criteria) the position of the Frenkel line in the subcritical regime using the ML model. The surprising outcome is that the Frenkel line appears to terminate at the triple point.

Discussion and Conclusions

In the present study we aimed to extend the experimental data for the Frenkel line into the subcritical regime by means of molecular dynamics simulation.

The widely-used OPLS-AA forcefield for nitrogen is a Lennard-Jones model, and the Lennard-Jones potential is already known to exhibit a Frenkel line. It gives a qualitative picture of the changes, and exhibits a Frenkel line extending below the critical temperature. Yet it is far from giving quantitative agreement, rendering it of little practical use for comparison with and extension of the experimental data.

Hoping for quantitative agreement, a machine-learned classical forcefield was developed. Simulations performed with this new forcefield did achieve quantitative agreement with the experimental findings. This suggested our new potential would be capable of correctly identifying the location of the Frenkel line of nitrogen in both the subcritical and supercritical regions, making it of great practical importance due to the predicted solubility changes of a substance when crossing this line.

It is notable that the extrapolation of the coordination number-based Frenkel line to zero pressure does not give a zero coordination. This demonstrates that in the “non-rigid” region nitrogen is still a liquid held together by chemical interactions (presumably van der Waals type). This means that the subcritical Frenkel line lies on the high-pressure side of the liquid-gas phase line, and leads us to avoid using the previously-coined term “gas-like liquid”.

Following the subcritical Frenkel line to its end, it was found that the Frenkel line termi-

nates at the triple point. This means that along any subcritical isotherm, the gas condenses first to a free-flowing, non-close-packed liquid, and only subsequently to a rigid liquid with medium-range order. The low diffusion, asymptotic coordination and shear-wave properties are related via the microscopic behaviour. They arise from a situation where each atom is fully surrounded by a cage of neighbours (saturated coordination), such that any displacement encounters a restoring force (shear wave support) and diffusion proceeds by a thermally-activated process of escaping from the cage (Arrhenius-like slow diffusion).

These results have been demonstrated for nitrogen, and it will be of future interest to see if they also hold for other materials.

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Supporting Information: OPLS-AA Pair Distribution Functions; OPLS-AA Coordination Numbers; State of the OPLS-AA Forcefield at 160 K; Machine Learning Interatomic Potential for Nitrogen; Pair Distribution Functions for ML Model; Correlated Changes in Diffusion Constant and Coordination Number

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