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1 Crossover from “gas-like” to “liquid-like”  
2 molecular diffusion in a simple supercritical  
3 fluid

4 Umbertoluca Ranieri<sup>1,2</sup>, Ferdinando Formisano<sup>3,4\*</sup>, Federico  
5 A. Gorelli<sup>5,6,7\*</sup>, Mario Santoro<sup>5,6</sup>, Michael Marek  
6 Koza<sup>4</sup>, Alessio De Francesco<sup>3,4</sup> and Livia E. Bove<sup>1,8,9</sup>

7 <sup>1</sup>Dipartimento di Fisica, Università di Roma La Sapienza, Roma, Italy.

8 <sup>2</sup>Centre for Science at Extreme Conditions and School of Physics and  
9 Astronomy, University of Edinburgh, EH9 3FD Edinburgh, UK.

10 <sup>3</sup>CNR-IOM & INSIDE@ILL c/o Operative Group in Grenoble (OGG),  
11 Grenoble Cedex 9, France.

12 <sup>4</sup>Institut Laue-Langevin, Grenoble Cedex 9, France.

13 <sup>5</sup>Consiglio Nazionale delle Ricerche, Istituto Nazionale di Ottica,  
14 CNR-INO, Via Nello Carrara 1, Sesto Fiorentino (FI), 50019, Italy.

15 <sup>6</sup>European Laboratory for Nonlinear Spectroscopy, LENS, Via Nello  
16 Carrara 1, Sesto Fiorentino (FI), 50019, Italy.

17 <sup>7</sup>Center for High Pressure Science and Technology Advanced Research  
18 (HPSTAR), 1690 Cailun Road, Shanghai, 201203, China.

19 <sup>8</sup>Laboratory of Quantum Magnetism, Institute of Physics, École  
20 Polytechnique Fédérale de Lausanne, Lausanne, CH-1015, Switzerland.

21 <sup>9</sup>Institut de Minéralogie, de Physique des Matériaux et de  
22 Cosmochimie, Sorbonne Université, UMR CNRS 7590, Paris, France.

23 \*Corresponding author(s). E-mail(s): [formisan@ill.fr](mailto:formisan@ill.fr);  
24 [gorelli@lens.unifi.it](mailto:gorelli@lens.unifi.it);

25 Contributing authors: [umbertoluca.ranieri@uniroma1.it](mailto:umbertoluca.ranieri@uniroma1.it);  
26 [santoro@lens.unifi.it](mailto:santoro@lens.unifi.it); [koza@ill.fr](mailto:koza@ill.fr); [defrance@ill.fr](mailto:defrance@ill.fr);  
27 [liviaeleonora.bove@uniroma1.it](mailto:liviaeleonora.bove@uniroma1.it);

28 **Abstract**

29 According to textbooks, no physical observable can be discerned allowing  
30 to distinguish a liquid from a gas beyond the critical point. Here we report

31 quasi-elastic neutron scattering measurements of the molecular self diffu-  
32 sion in supercritical fluid methane as a function of pressure along the 200  
33 K isotherm (corresponding to 1.05 times the critical temperature) where  
34 we observe a clear crossover in the dynamic structure factor from a gas-  
35 like Gaussian to a liquid-like Lorentzian signal. The crossover is progres-  
36 sive and takes place upon compression at about the Widom line intercept.  
37 Concurrently, a sharp change in the pressure dependence of the molecu-  
38 lar self-diffusion coefficient takes place. At considerably higher pressures,  
39 we find that the same liquid-like jump diffusion mechanism can fit the  
40 experimental data on both sides of the Frenkel line, marking the change  
41 from a non-rigid to a rigid fluid. The observation of a gas-like to liquid-  
42 like dynamical crossover in supercritical methane could have planet-wide  
43 implications, and possible industrial applications in green chemistry.

44 **Keywords:** supercritical fluids, neutron scattering, molecular diffusion, high  
45 pressure

46 Matter can be pushed to temperatures and pressures above those of its criti-  
47 cal point, in a state, called supercritical fluid (SCF), where we are unable to  
48 distinguish whether the system is a liquid or a gas. As a result, supercritical  
49 fluids possess an intimate hybrid nature: they are said to have the capabil-  
50 ity to effuse “like a gas” but to dissolve materials “like a liquid”. This makes  
51 them used in the most disparate industrial processes, such as pharmaceutical  
52 and cosmetics processing, extracting essential oils, dissolving waste material,  
53 brewing or decaffeinating coffee beans without leaving toxic residues. In par-  
54 ticular, near the critical point, small changes in pressure or temperature result  
55 in large changes in density, allowing many properties of a supercritical fluid to  
56 be “fine-tuned” in such processes [1–6].

57 Understanding the physical behaviour of supercritical fluids is not only  
58 important for industrial applications but also to gain a much better knowledge  
59 of what goes on deep inside giant planets like Jupiter, Saturn, Uranus or  
60 Neptune. As we delve into their atmosphere, we may indeed encounter simple  
61 matter in the supercritical fluid state [7, 8]. This will determine not only their  
62 thermal properties, and in particular the way heat is stored and flows around  
63 planets, but also the anomalous solubility of other volatiles in their atmosphere  
64 [9, 10], as well as other surprising phenomena such as the separation of Uranus  
65 atmosphere from its interior, recently suggested by the anomalously low heat  
66 flow measurements from the Voyager spacecraft [11]. Considering the number  
67 of exoplanets and super-Earths that are being discovered, many of them larger  
68 and with more extreme environments than found in our own solar system,  
69 the possibility for supercritical fluids to be found in planetary environments is  
70 only set to increase. Furthermore, SCFs with gas-like viscosity as well as melt-  
71 like wetting and element-carrying capability are an ideal agent for chemical  
72 transport at subduction zones and could play a role as life-sustaining solvents  
73 on other worlds [12, 13].

74 Above the critical temperature, no increase in pressure can liquefy the sys-  
75 tem and when the pressure is greatly increased, a supercritical fluid of much  
76 higher density, close to the one of a solid, is produced. The significant changes  
77 in density observed close to the critical point are expected to correlate with  
78 changes in other properties of the fluid. The question scientists have long  
79 debated is: may a region of the pressure-temperature ( $P$ - $T$ ) plane and a phys-  
80 ical observable be discerned allowing to unambiguously distinguish between a  
81 gas-like and liquid-like behaviour in the supercritical fluid?

82 Two different scenarios have been recently put forward as an answer to this  
83 question. The first one indicates the Widom line, i.e. the line emanating from  
84 the critical point which represents the maxima/minima in certain thermophys-  
85 ical properties, as the line separating a gas-like behaviour from a liquid-like  
86 behaviour in the SCF. A crossover in the anomalous dispersion (i.e. the dif-  
87 ference between the unrelaxed and relaxed value) of the simulated THz sound  
88 velocity [14–16], the observation of a pseudo-boiling phenomenon [17] and of  
89 droplet formation [18], and a change in density fluctuations correlations [19–  
90 21] have been reported to occur when crossing the Widom line. The second  
91 scenario rather envisages the Frenkel line, i.e. the line along which the struc-  
92 tural relaxation time equals the shortest period of transverse oscillations of the  
93 particles (atoms or molecules) within the system [22–26], as the line separating  
94 a solid-like (rigid) diffusive behaviour of the fluid from a gas-like (non-rigid)  
95 one. At high pressures above the Frenkel line, with the exception that the  
96 particles occasionally hop from one position to another, dense SCFs somehow  
97 behave like solids. They can sustain transverse acoustic excitations and show  
98 a velocity autocorrelation function which monotonically decays to zero.

99 Here we report a quasi-elastic neutron scattering (QENS) study of super-  
100 critical methane as a function of pressure at a constant temperature of 200  
101 K (just above the critical temperature of 190.55 K), providing a direct mea-  
102 surement of the molecular diffusion in the system. We find that the measured  
103 self-dynamic structure factor, i.e. the space and time Fourier transform of  
104 the self pair correlation function [27], shows a clear change from a Gaussian  
105 lineshape, describing the molecular diffusion in a gas, to a Lorentzian line-  
106 shape, describing the molecular diffusion in a liquid. **The change is completed**  
107 **when pressure crosses the Widom line along the 200 K isotherm and no fur-**  
108 **ther changes are observed at higher pressures, for example when crossing the**  
109 **Frenkel line.** The molecular diffusion coefficient has been determined over a  
110 range of densities covering almost three orders of magnitude and compared to  
111 both (non-ideal) gas and dense-fluid theoretical descriptions. Its variation as a  
112 function of pressure shows a clearcut slowing down when crossing the Widom  
113 line, reminiscent of the change in the fluid compressibility. The observation  
114 of this crossover in supercritical methane could have planet-wide implica-  
115 tions, in particular due to the ubiquitous presence of methane in our solar  
116 system. **The existence of a non-homogeneous supercritical state in gas, like**  
117 **methane, constituting gas-giants, will indeed determine if a boundary between**  
118 **the planet’s interior and its atmosphere can be defined. This would impact**

119 planetary properties such as the thermal conductivity and other heat-related  
 120 physical phenomena like storm activity, as well as mass diffusion related prop-  
 121 erties like the ionic conductivities and consequent generation of anomalous  
 122 magnetic fields [28–30].

## 123 Experiments

124 Figure 1 reports the temperature-pressure phase diagram of methane. The  
 125 critical point is at  $T_C=190.55$  K and  $P_C= 46$  bar. Data at seventeen pressures  
 126 between 8.5 and 2450 bar were acquired for this study along the 200 K isotherm  
 127 ( $1.05 T_C$ ), six below and eleven above  $P_C$ . The used high-pressure setup is  
 128 described in the Methods section. The pressure range corresponds to a huge  
 129 density variation, from  $0.00868$  g cm<sup>-3</sup> at 8.5 bar to  $0.47101$  g cm<sup>-3</sup> at 2450 bar  
 130 (5000% of the initial value). The first value is only an order of magnitude higher  
 131 than the density of gas methane at ambient pressure ( $0.00097$  g cm<sup>-3</sup> at 200 K).  
 132 The second value is comparable to the density of liquid methane (for example,  
 133  $0.4389$  g cm<sup>-3</sup> at ambient pressure and 100 K). Density values used throughout  
 134 this paper are taken from the equation of state of the online National Institute  
 135 of Standards and Technology (NIST) Reference Fluid Thermodynamic and  
 136 Transport Properties Database, which uses ref. [31].

137 The pressure dependence of the density along the 200 K isotherm is also  
 138 reported in Fig. 1 (upper panel). The intercepts of the Widom line and of the  
 139 Frenkel line with the 200 K isotherm are at 59 and 670 bar, respectively [24, 31].  
 140 The criterion chosen to locate the Frenkel line in ref. [24] is the disappearance  
 141 of the first minimum of the calculated velocity autocorrelation function.  
 142 Figure 1 anticipates the main result of this study: We observe a crossover in  
 143 the lineshape of the experimental spectra (proportional to the self-dynamic  
 144 structure factor of the system) from Gaussian to Lorentzian upon pressure  
 145 increase, which is completed above the Widom line intercept.

146 Figure 2 depicts examples of QENS spectra of the sample, plotted as a  
 147 function of the energy transfer  $E$ , for a few selected  $P$  and  $Q$  values,  $Q$  being  
 148 the modulus of the wavevector transfer. It is well-known that because of the  
 149 very large incoherent neutron scattering cross section of <sup>1</sup>H, the QENS signal  
 150 from CH<sub>4</sub> is dominated by the *self* (single-particle) dynamics of the molecules.  
 151 In particular, the *translational* self-dynamic structure factor was measured in  
 152 the present study. The (quasi-elastic) signal monotonically gets broader either  
 153 with decreasing pressure at constant  $Q$  (see Supplementary Fig. 1) or with  
 154 increasing  $Q$  at constant  $P$  (see below), as expected in case of translational  
 155 motion. As can be seen in Fig. 2, spectra are best fitted by a Gaussian function  
 156 at low pressures and by a Lorentzian function at high pressures. The Gaussian-  
 157 to-Lorentzian transition is progressive. Gaussian fits were preferred for the  
 158 data at pressures up to 51.5 bar and Lorentzian fits were preferred at and  
 159 above 67.5 bar. More details about the extraction of spectra from the raw data  
 160 and about the fitting of the spectra are given in the Methods section.

## 161 Data analysis

162 In dilute fluids, the frequency of the collisions between particles is low and  
 163 the particles experience a ballistic motion between two collisions. As a con-  
 164 sequence, a velocity and a trajectory can be defined and the mean square  
 165 displacement (MSD) of the particle displays a  $t^2$  time dependence. This  
 166 behaviour translates, when switching to the experimental domain  $(Q, \omega)$ , into  
 167 the free-particles (ideal gas) expression for the self-dynamic structure factor  
 168  $S_{\text{self}}(Q, \omega)$  given by [27]:

$$S_{\text{self}}(Q, \omega) = \left( \frac{m}{2\pi k_B T Q^2} \right)^{1/2} \exp \left( -\frac{m\omega^2}{2k_B T Q^2} \right), \quad (1)$$

169 which is a Gaussian function of the frequency  $\omega$  ( $\omega = E/\hbar$ ) centered at  $\omega=0$ ,  
 170 whose width increases linearly with  $Q$ . Here,  $m$  is the mass of the particle  
 171 and  $k_B$  the Boltzmann constant.  $2k_B T/m$  gives the mean square velocity of  
 172 the diffusing particles. The self-diffusion coefficient  $D$  is given by the kinetic  
 173 Chapman-Enskog theory for a dilute fluid composed of hard spheres and can  
 174 be approximated for the non-dilute hard-sphere fluid by [32–34]:

$$D = \frac{1.01896}{g(\sigma)} \frac{3}{8n\sigma^2} \left( \frac{k_B T}{\pi m} \right)^{1/2}, \quad (2)$$

175 with the numerical factor 1.01896 being a result of using the ninth Enskog  
 176 approximation,  $g(r)$  being the radial distribution function,  $\sigma$  the spheres diam-  
 177 eter, and  $n$  the number density. Eq. 2 is almost exact in the low-density limit  
 178 while its applicability at higher densities has been thoroughly tested in molec-  
 179 ular dynamics calculations [33]. For the range over which Gaussian fits were  
 180 employed in the present study, i.e. for a packing fraction  $\zeta = \pi n \sigma^3 / 6$  up to  
 181 about 0.1, Eq. 2 is accurate within 10% compared to recent computational val-  
 182 ues for hard spheres [35, 36]. **On the other hand, there is extensive literature**  
 183 **[37, 38] showing that the hard-sphere model correctly reproduces the experi-**  
 184 **mental diffusion coefficient of methane at such modest pressures, provided**  
 185 **that the equivalent hard-sphere diameter is a free fitting parameter.** It follows  
 186 that the free-particles expression of Eq. 1 can be extended at higher densities  
 187 using Eq. 2 and the Gaussian  $S_{\text{self}}(Q, \omega)$  writes now as:

$$S_{\text{self}}(Q, \omega) = \left( \frac{\ln(2)}{\pi \Gamma_G^2(Q)} \right)^{1/2} \exp \left( -\frac{\ln(2)\omega^2}{\Gamma_G^2(Q)} \right), \quad (3)$$

$$\text{where } \Gamma_G(Q) = KQ. \quad (4)$$

188 The values of the half width at half maximum  $\Gamma_G(Q)$  obtained from the  
 189 Gaussian fits of our spectra display a clear linear trend with  $Q$ , as shown in Fig.  
 190 3a, where the data are reported together with their linear fit. From the values  
 191 of the fitted slope  $K$ , reported in Extended Data Figure 1 at each investigated  
 192 pressure, we obtained  $D$  in the gas-like regime using  $K = \frac{8}{3} \frac{(2\pi \ln(2))^{1/2}}{1.01896} n\sigma^2 g(\sigma) D$   
 193 **as obtained by comparing Eqs. 1 to 4**,  $g(\sigma) = \frac{1-\zeta}{(1-\zeta)^3}$  as given by the widely

194 employed Carnahan–Starling equation of state [39], and  $\sigma=3.61 \text{ \AA}$  as given  
 195 for methane at 200 K by NMR measurements of  $D$  [38]. The self-diffusion  
 196 coefficient is plotted in Fig. 4 as a function of pressure.

197 When the density further increases and becomes comparable to the one of  
 198 a liquid, the collision frequency also strongly increases and the particles expe-  
 199 rience several multiple uncorrelated collisions during the typical experimental  
 200 timescales, giving rise to a random Brownian motion characterized by a linear,  
 201 and not anymore quadratic, time dependence for the MSD [40, 41]. As a con-  
 202 sequence the self-dynamic structure factor has a Lorentzian shape centered at  
 203  $\omega=0$ , i.e.:

$$S_{\text{self}}(Q, \omega) = \frac{1}{\pi} \frac{\Gamma_L(Q)}{\omega^2 + \Gamma_L^2(Q)}, \quad (5)$$

204 which is the model customarily used to analyze QENS data on bulk liquid  
 205 samples. Typically, the half width at half maximum  $\Gamma_L(Q)$  is observed to be  
 206 proportional to  $Q^2$  at small  $Q$  (as expected for Fickian diffusion) and to lie  
 207 below that expectation at high  $Q$ , i.e., when one is probing shorter distances  
 208 and the microscopic details of the motion become relevant. It is often correctly  
 209 described by the formula:

$$\Gamma_L(Q) = \frac{DQ^2}{1 + \tau DQ^2}. \quad (6)$$

210 Eqs. 5 and 6 were previously employed in many QENS studies, including  
 211 studies of liquid methane [42], supercritical methane at liquid densities [43],  
 212 and high-pressure interfacial methane [44], as well as studies of other dense  
 213 fluids such as for example liquid water over wide ranges of temperature and  
 214 pressure [45, 46]. Eq. 6 is known to be associated to the jump-like nature of  
 215 the translational motion in dense systems, typically because of the presence of  
 216 a cage effect, and  $\tau$  represents the time spent by the diffusing particle at quasi-  
 217 equilibrium sites between rapid jumps [47]. Figure 3b reports the half width  
 218 of the Lorentzian fits of our spectra as a function of  $Q$  at each investigated  
 219 pressure as well as its best fits using Eq. 6, from which we extracted values of  
 220  $\tau$  and  $D$  in the liquid-like regime, reported in Fig. 4.

## 221 Results

222 As can be seen in Fig. 4,  $\tau$  shows a 20% decrease with increasing pressure  
 223 attaining a minimum at around the Frenkel line intercept (670 bar) followed  
 224 by a small 10% increase above that pressure. However, the estimation of the  
 225 residence time  $\tau$  is dominated by the high- $Q$  values of  $\Gamma_L(Q)$ ; its uncertainty  
 226 can be significant for different reasons, such as a high background. Figure 4  
 227 also plots the obtained self-diffusion coefficient  $D$  as a function of pressure and  
 228 values range from  $1481.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at 8.5 bar to  $6.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at 2450 bar.  
 229 At our highest pressure, the value of  $D$  is close to the typical values of liquid  
 230 methane (for example,  $3.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at 1.5 bar and 102 K [42]). In Fig. 4,  
 231 the diffusion coefficient is compared with NMR data of methane at the same

232 temperature of 200 K [48] and with a literature computational (molecular  
 233 dynamics) prediction for hard spheres [36]. The hard-sphere prediction [36]  
 234 reproduces the trend of the measured diffusion coefficient fairly well over the  
 235 entire pressure range, and this for a  $P$ -independent value of the sphere diameter  
 236  $\sigma$  of 3.61 Å. This is at variance with our earlier QENS work on methane [43],  
 237 where we reached the (much higher) freezing pressure of 1.4 GPa at 300 K and  
 238 observed failure of the hard-sphere model.

239 The largest relative deviations between our data and the hard-sphere pre-  
 240 diction are for the intermediate pressure range (40-80 bar), and this is likely  
 241 to be associated to the existence of a pressure regime where both the Gaus-  
 242 sian and Lorentzian modelling of the dynamic structure factor are not fully  
 243 justified **yet representing the only models, though approximate, presently avail-**  
 244 **able to describe the diffusive dynamics.** Consistently, this is also the pressure  
 245 range where the fits of the wavevector transfer dependence of the Gaussian  
 246 and Lorentzian half widths are less satisfactory. It can be also noticed that the  
 247 Gaussian and Lorentzian fits to our spectra are of comparable quality at about  
 248 40-50 bar and none of them perfectly reproduces the lineshape of the experi-  
 249 mental spectra (see Fig. 2). However, while the Gaussian fits provide reasonable  
 250 values for  $D$ , the Lorentzian fits provide unreasonably small values compared to  
 251 the literature experimental values [48] and to the hard-sphere predictions [36]  
 252 at all pressures below 67.5 bar. For example, at 51.5 bar, Lorentzian fits provide  
 253  $D=50.7\times 10^{-9}\text{m}^2\text{s}^{-1}$ , to be compared with  $89.4\times 10^{-9}\text{m}^2\text{s}^{-1}$  for the Gaussian  
 254 fits. This clearly indicates that the Gaussian description is more appropri-  
 255 ate than the Lorentzian one up to 51.5 bar. Above 51.5 bar, the situation is  
 256 reversed, with **i)** the Gaussian fits providing unreasonably small diffusion coef-  
 257 ficient values (for example at 67.5 bar,  $36.0\times 10^{-9}\text{m}^2\text{s}^{-1}$  for the Lorentzian  
 258 and  $23.5\times 10^{-9}\text{m}^2\text{s}^{-1}$  for the Gaussian fits) and **ii)** the Lorentzian fits clearly  
 259 describing the measured spectra **much better** (see Fig. 2). **To further support**  
 260 **our choice of employing Gaussian fits up to 51.5 bar and Lorentzian fits at**  
 261 **and above 67.5 bar, the likeliness of the obtained diffusion coefficient is bet-**  
 262 **ter quantified in the Supplementary Information (Supplementary Note 1 and**  
 263 **Figs. 2,3), where we also report the results of a Bayesian analysis [49] of the**  
 264 **experimental spectra (Supplementary Note 2 and Figs. 4–9).**

265 Finally, we calculated the product of the self-diffusion coefficient  $D$  with the  
 266 shear viscosity  $\eta$  (see Extended Data Figure 2), using the literature estimation  
 267 of  $\eta$  **given by the NIST Reference Fluid Thermodynamic and Transport Prop-**  
 268 **erties Database, which uses ref. [50].** The Stokes–Einstein–Sutherland (SES)  
 269 relation, which is commonly used in the literature of atomic and molecular liq-  
 270 uids, predicts a constant product  $D\eta$  along isotherms. In our case, the product  
 271 clearly shows two regimes along the 200 K isotherm: **while** below the pressure  
 272 of intercept with the Widom line,  $D\eta$  decreases with increasing pressure and  
 273 the **SES** relation is violated, above that pressure,  $D\eta$  is constant with pressure  
 274 and the **SES** relation holds. Experimental literature data showed that  $D\eta$  is  
 275 constant within the experimental uncertainties in compressed liquid methane  
 276 along the low-temperature isotherms 110, 140 and 160 K [38], as reported for



example in our previous work [43] (Supplementary Figure 5), but significantly increases with pressure in very dense supercritical methane along the room-temperature isotherm [43]. On the other hand, the SES relation is typically not expected to hold at low pressures below twice the critical density. It is a well-known result of isomorph theory [51], experiments of various simple fluids, and simulations of hard spheres and of the Lennard-Jones system [35, 36] that the product  $D\eta$  cannot be constant over isotherms in the gas phase.

## Final comments

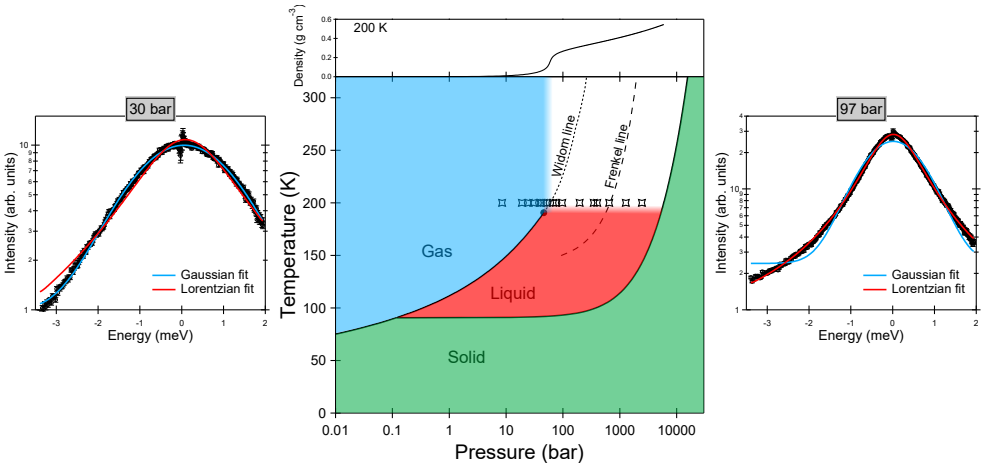
The fundamental problem of distinguishing between a gas-like and a liquid-like region in the phase diagram of simple supercritical fluids has fed a high-pitched debate in the literature [14–26]. In the present measurements, we establish the existence of a crossover in the self-dynamic structure factor of SCF methane measured by QENS along the 200 K isotherm. The change from a Gaussian to a Lorentzian lineshape indicates the crossover from a gas-like to a liquid-like diffusive dynamics of the molecules and occurs roughly at the pressure at which the Widom line intercepts the 200 K isotherm, indicating that the Widom line separates gas-like and liquid-like behaviours as concerns the self diffusion of  $\text{CH}_4$  in the vicinity of the critical temperature. **This result is exclusively based upon the experimental determination of a basic transport property as a function of the pressure and use the only available diffusive models available in literature, without resorting to any other external input or calculations.**

To our knowledge, the present work represents the first to employ the QENS technique to investigate a SCF sample in the vicinity of its critical point. The advantage of using neutrons to investigate the diffusion in a SCF resides in the fact that neutron scattering is a weak process and the sample response is linear. It follows that the measured dynamic structure factor is determined by the spectrum of the spontaneous correlations between molecules, and thus gives a fundamental information on the molecular interaction [52]. Along the thermodynamic path we followed, we could cross both the Widom and the Frenkel line. The picture that emerges is that at pressures below the Widom line, the molecular diffusion is basically governed by the harsh repulsive forces between molecules while the weaker, longer-ranged attractive forces have little influence on the dynamics. The system can be described as a dense (non-ideal) gas. Conversely, above the Widom line, the sharp increase in density makes the free path of the molecules to strongly decrease and the diffusion mechanism becomes sensitive to the longer-ranged molecular interaction and depends on the average molecular distances. The molecular diffusion can be thus described as that of a liquid and the Stokes–Einstein–Sutherland relation holds. This happens starting from much lower densities (by approximately a factor of 2) than those **typical for liquid methane.**

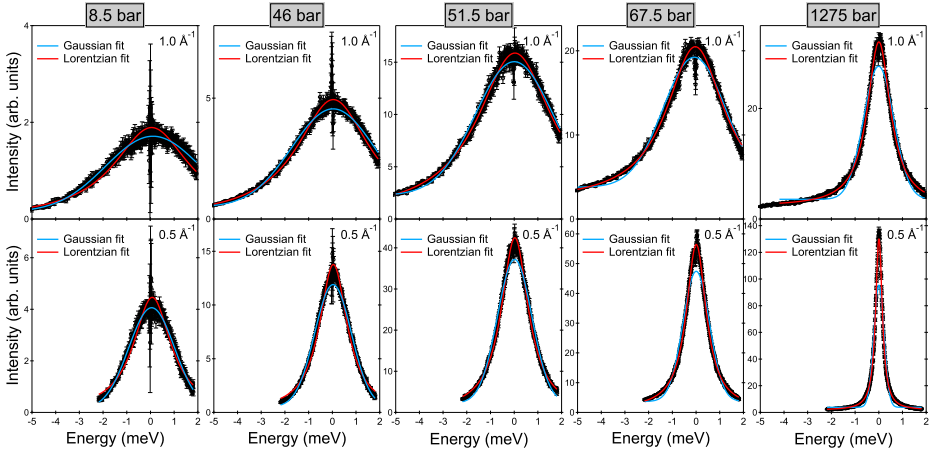
The presence of a Frenkel line does not seem to affect in a radical way **the pressure dependence of the diffusion coefficient nor the diffusion mechanism probed in the present measurements,** with the exception of a **shallow minimum**

320 in the trend of the in-cage molecular residence time  $\tau$  as a function of pres-  
321 sure. On the “non-rigid fluid” side of the Frenkel line, a competition between  
322 the repulsive potential and attractive Van der Waals forces between adjacent  
323 molecules undergoing diffusion is in place. Attractive Van der Waals forces  
324 dominate in the fluid at the lowest densities and lead the in-cage residence  
325 time of the molecules to decrease upon pressure increase [53]. Conversely, when  
326 crossing the Frenkel line,  $\tau$  increases with pressure because of the major role of  
327 the repulsive potential and the consequent stabilisation of the neighbour’s cage.  
328 As a consequence, the variation of the residence time as a function of pressure  
329 in an isothermal experiment can display a minimum as one proceeds from the  
330 non-rigid to the rigid fluid. **Future studies will be able to verify whether this**  
331 **intriguing observation is reproduced and matches the Frenkel line intercepts**  
332 **also along other isotherms.** At pressures above the Frenkel line, the (relatively)  
333 close packed arrangement of the molecules determines a much stronger inter-  
334 action between close neighbour molecules and the onset of long-living density  
335 fluctuation modes as well as of shear modes. The diffusion mechanism pro-  
336 gressively becomes more similar to the hopping observed in solids through  
337 vacancies and the system can be described as a “rigid” liquid on the short  
338 timescales here explored.

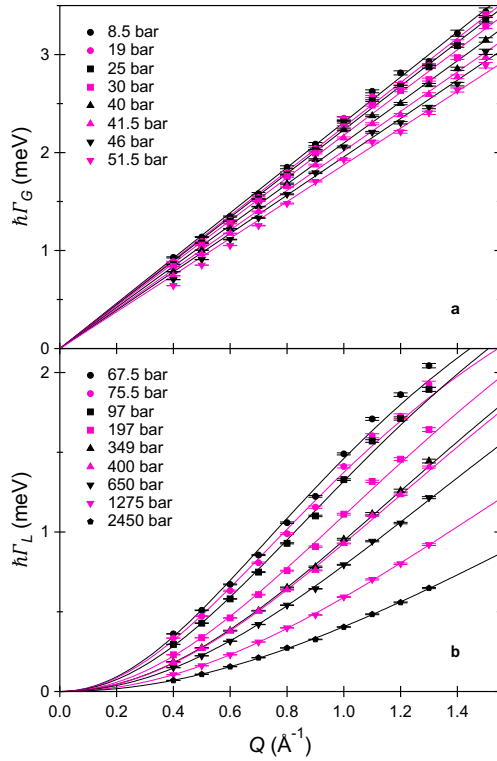
339 Concerning the Widom line, it is worth recalling that there is a group  
340 of lines emanating from the critical point which are associated with maxi-  
341 ma/minima in different thermophysical properties such as the speed of sound,  
342 isothermal compressibility, isochoric and isobaric heat capacities, which have  
343 all been named “Widom lines” [54]. Close to the critical point, as in the present  
344 experiment, the choice of the specific thermophysical property is relatively  
345 unimportant as all of the maxima/minima closely coincide, but far away from  
346 the critical point, the maxima in the response functions begin to deviate signif-  
347 icantly from each other. However, it is now generally agreed that the Widom  
348 line can be identified to a maximum in the correlation length characterizing the  
349 range of the molecular interactions which is here directly probed through the  
350 dynamic structure factor. In this extent, the dynamic structure factor turns  
351 out to be a pertinent physical observable **allowing us** to distinguish between  
352 a gas-like and a liquid-like behaviour within the supercritical fluid. Its change  
353 in lineshape when crossing the Widom line reflects a substantial change in the  
354 molecular interaction length scale with clear consequences in the transport  
355 properties of the system. This observation could have major consequences on  
356 the geodynamics of gas giant planets in our Solar System and beyond, and  
357 could be exploited to tailor the efficiency of supercritical fluids in industrial  
358 applications. It remains to be established how a planet-scale crossover through  
359 the Widom line would affect heat flow, like it is observed for Uranus.



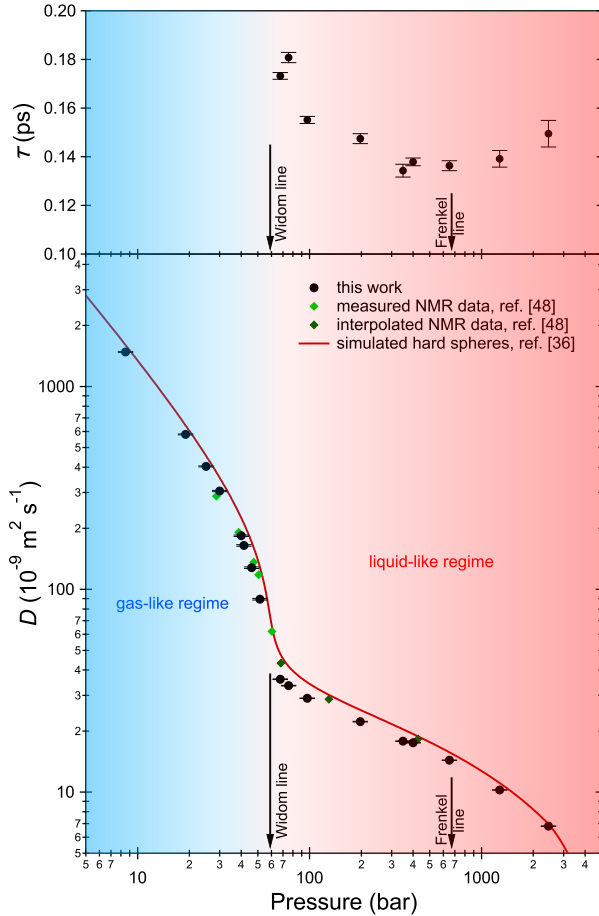
**Fig. 1: Phase diagram of methane.** Temperature-pressure phase diagram of methane including the Widom line (locus of the isobaric heat capacity maxima [31]) and the predicted Frenkel line from ref. [24]. The critical point is at 190.55 K and 46 bar. Symbols depict the pressure points measured (along the 200 K isotherm) in the present experiment. The density profile at 200 K from ref. [31] is reported on top of the phase diagram. Examples of QENS experimental spectra in logarithmic scale (empty circles) at two selected pressures on each side of the Widom line are also reported with their best Gaussian/Lorentzian fits (solid lines) to highlight the Gaussian-to-Lorentzian crossover upon compression. To improve statistics, these two spectra were obtained by summing up measurements in the  $0.55\text{--}0.85\text{ \AA}^{-1}$  exchanged wavevector range.



**Fig. 2: Examples of QENS spectra.** QENS spectra of the sample at 200 K at the indicated pressure and wavevector transfer values, collected using an incoming neutron wavelength of  $5.12 \text{ \AA}$  and an instrumental resolution of full width at half maximum equal to  $0.077 \text{ meV}$ . Experimental data (empty circles) are compared to the best Gaussian and Lorentzian fits (solid lines).



**Fig. 3: Wavevector transfer dependence of  $\Gamma_G$  and  $\Gamma_L$ .** Fitted Gaussian (panel a) or Lorentzian (panel b) half widths at half maximum (symbols) as a function of  $Q$ , at all investigated pressures. The best fits to the data at each pressure are shown as solid lines. For the Gaussian half widths, the fits are lines passing through zero whose slopes allowed us to extract  $D$  (see Eq. 4 and following discussion). The Lorentzian half widths were modelled using Eq. 6 with  $\tau$  and  $D$  as free parameters.



**Fig. 4: Pressure dependence of the mean residence time and of the diffusion coefficient at 200 K.** Top panel: Parameter  $\tau$  of the jump diffusion model as obtained from the fits shown in Fig. 3b. Bottom panel: Self-diffusion coefficient  $D$  (full circles) as obtained from the fits shown in Fig. 3. A gas-like (resp. liquid-like) regime is defined as being the regime where  $D$  was obtained using Gaussian (resp. Lorentzian) fits and the two regimes are indicated with different colors, with the blur in between indicating that the Gaussian-to-Lorentzian transition is progressive. The arrows indicate the intercepts of the Widom and Frenkel lines with the 200 K isotherm. We also report i) experimental NMR values for methane at 200 K (full diamonds) measured in ref. [48] or obtained in ref. [48] from interpolation of data measured at other temperatures and ii) simulated values for the hard sphere fluid from ref. [36] (full line), plotted here using  $T=200$  K,  $\sigma=3.61$  Å, and the mass of the methane molecule.

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## 506 Methods

507 **Experimental setup.** The measurements have been carried out at the  
 508 Institut Laue-Langevin large-scale facility in Grenoble, France, on the time-  
 509 of-flight neutron spectrometer IN6-SHARP. We set the wavelength of the  
 510 incoming neutron beam to 5.12 Å. Neutron scattering spectra of methane at  
 511  $200\pm 1$  K were recorded at pressures between 8.5 and 2450 bar with a typical  
 512 acquisition time of 3-4 hours per pressure point. The sample was contained  
 513 in a cylindrical pressure cell of aluminium alloy whose height was about 50  
 514 mm and whose internal diameter was 6 mm, and was compressed using a gas  
 515 compressor working with methane. In this setup, the sample volume does not  
 516 change upon pressure increase/decrease and the number of methane molecules  
 517 in the neutron beam increases with increasing pressure. To reduce the multi-  
 518 ple scattering contributions, we inserted a cylindrical aluminium spacer of 5  
 519 mm in diameter for the measurements at the following eight pressures: 46, 97,  
 520 197, 349, 400, 650, 1275, and 2450 bar. The nine pressure points measured  
 521 without aluminium spacer were: 8.5, 19, 25, 30, 40, 41.5, 51.5, 67.5, and 75.5  
 522 bar. The CH<sub>4</sub> (purity>99.95%) bottle was purchased from AirLiquide, Saint  
 523 Priest, France. Pressure was directly measured by a manometer attached to  
 524 the capillary connecting the gas compressor with the high-pressure cell. The  
 525 uncertainty on the pressure measurement was 1 bar. The sample temperature  
 526 was controlled using a standard “orange” cryostat. Empty-cell spectra were  
 527 measured with and without aluminium spacer.

528  
 529 **Data extraction and fitting.** For each pressure point, constant- $Q$  spectra  
 530 from 0.4 to 1.5 Å<sup>-1</sup> with 0.1 Å<sup>-1</sup> steps were extracted (except in Fig. 1 where  
 531 a larger integration range of 0.3 Å<sup>-1</sup> was used). Their intensity was normal-  
 532 ized using the measurement of a vanadium standard and the empty-cell signal  
 533 was subtracted using  $P$ - and  $Q$ -dependent transmission values (the spectra  
 534 reported in Figs. 1 and 2 are empty cell-subtracted).

535 The different possible motions of methane (vibrations, rotations and trans-  
 536 lations) lie on different time scales. The contribution of the vibrational motion  
 537 is very fast and can be approximated with a Debye–Waller factor. Rotations  
 538 are too fast to be properly resolved on IN6-SHARP and probably only con-  
 539 tribute as a very broad quasi-elastic signal appearing as a flat background in  
 540 our spectra. Therefore, only the vibrational and translational motions were  
 541 included in the fitting model, similarly to our previous QENS study of dense  
 542 supercritical methane at 300 K [43]. The accessible energy range is inherently  
 543 limited in time-of-flight neutron spectrometers and is rather narrow at small  
 544  $Q$ . For example, it goes from -2.2 to 1.8 meV at 0.5 Å<sup>-1</sup>, as can be seen in Fig.  
 545 2. To limit the effect that the rotational contribution might have on our results,  
 546 fits of the spectra at high  $Q$  were restricted over a reduced energy range.

547 Spectra are given in arbitrary units and were accordingly fitted using a  
 548 Gaussian or Lorentzian function multiplied by a scaling factor in arbitrary  
 549 units. A flat positive background  $B$  and a zero shift (small difference between  
 550 the values of the true and nominal zeros of the energy transfer axis) were

551 included. Moreover, in the fitting of the spectra, convolution of  $S_{\text{self}}(Q, \omega)$  with  
 552 the instrumental resolution function was taken into account. The resolution  
 553 function of the spectrometer  $R(E)$  was obtained by fitting the measurement  
 554 of the vanadium standard to a pseudo-Voigt distribution. Its full width at half  
 555 maximum was about 0.077 meV. Therefore, each constant- $Q$  spectrum was  
 556 fitted using either of the two formulas:

$$I^{\text{Gauss}}(E) = I_0^{\text{Gauss}} \exp\left(-\frac{\ln(2)(E - E_0)^2}{\hbar^2 \Gamma_G^2}\right) \otimes R(E) + B_0, \quad (7)$$

$$I^{\text{Lor}}(E) = \frac{I_0^{\text{Lor}}}{\pi} \frac{\hbar \Gamma_L}{(E - E_0)^2 + \hbar^2 \Gamma_L^2} \otimes R(E) + B_0. \quad (8)$$

557 Both Gaussian and Lorentzian fits have four parameters:  $I_0^{\text{Gauss}}$  or  $I_0^{\text{Lor}}$ ,  $\Gamma_G$   
 558 or  $\Gamma_L$ ,  $E_0$ , and  $B_0$ . The zero shift of the energy-transfer axis  $E_0$  was generally  
 559 left free to vary. However, it was systematically imposed at high  $Q$  in the  
 560 Gaussian fits to an extrapolation of the small  $Q$  values (it would otherwise  
 561 converge to relatively large values up to 0.2-0.3 meV). Similarly, to ensure a  
 562 smooth  $Q$  dependence, the flat background  $B_0$  was imposed to an extrapolation  
 563 of the higher  $Q$  values at small  $Q$  values in the Gaussian fits and at the smallest  
 564  $Q$  only in the Lorentzian fits (it would otherwise converge to larger values).  
 565 **Supplementary Figs. 10 and 11 report all  $B_0$  values.** We checked that both  
 566 of these choices (for zero shift and flat background) have only minor effects  
 567 on the determination of the diffusion coefficient. Intensities and widths were  
 568 always left as free parameters in the fitting. **Supplementary Fig. 12 reports the**  
 569 **fitted Lorentzian half widths at pressures where Gaussian fits were preferred**  
 570 **and the fitted Gaussian half widths at pressures where Lorentzian fits were**  
 571 **preferred (therefore complementing Fig. 3 of the main text).**

572 The obtained intensities  $I_0^{\text{Gauss}}$  and  $I_0^{\text{Lor}}$  are plotted as a function of  $Q$  in  
 573 Supplementary Fig. 13. They were fitted using:

$$I_0^{\text{Gauss}} \propto \frac{1}{Q} \exp(-Q^2 \langle u^2 \rangle / 3), \quad (9)$$

$$I_0^{\text{Lor}} \propto \exp(-Q^2 \langle u^2 \rangle / 3). \quad (10)$$

574  $I_0^{\text{Gauss}}$  corresponds to the height of the Gaussian function before convolu-  
 575 tion with the instrumental resolution and is proportional to the factor  $1/Q$   
 576 (see Eq. 3) multiplied by the Debye-Waller factor  $\exp(-Q^2 \langle u^2 \rangle / 3)$ .  $I_0^{\text{Lor}}$  cor-  
 577 responds to the area of the Lorentzian function before convolution with the  
 578 instrumental resolution and is simply proportional to the Debye-Waller factor.  
 579 The resulting values of  $\langle u^2 \rangle^{1/2}$  are reported as a function of pressure in Sup-  
 580 plementary Fig. 14. They amount to roughly 1 Å, which is a reasonable value  
 581 and within the range of values reported in the literature for example of liquid  
 582 water at ambient conditions, for which many QENS studies exist. We observe  
 583 an increasing trend for  $\langle u^2 \rangle^{1/2}$  with increasing pressure (see Supplementary  
 584 Fig. 14) in both estimations (from the Gaussian and Lorentzian intensities)

585 with a discontinuity between the Gaussian and Lorentzian estimations whose  
 586 origin is presently unclear.

587 The Gaussian half widths were fitted over the  $Q$  range from 0.4 to 1.5  $\text{\AA}^{-1}$ , as  
 588 shown in Fig. 3a. In the linear fits, the data points were not weighted according  
 589 to the estimated error in  $\Gamma_G(Q)$ . This choice moderates the weight of the low-  
 590  $Q$  points (having the smaller error), corresponding to the regime where the  
 591 theoretical ground for the Gaussian modelling is weaker. The Lorentzian half  
 592 widths were fitted over a slightly narrower  $Q$  range from 0.4 to 1.3  $\text{\AA}^{-1}$  (Fig.  
 593 3b), similarly to our previous work [43], in order to limit the potential effect  
 594 of the rotational contribution. This is because the rotational contribution i)  
 595 becomes slower with increasing pressure and might potentially approach the  
 596 timescale window accessible by the present experiment at our highest pressures  
 597 and ii) is known from analytical modelling to have increasing intensity with  
 598 increasing  $Q$ . The data points were weighted according to the estimated error  
 599 in  $\Gamma_L(Q)$ .

600 Finally, multiple scattering contributions to the spectra were ignored.  
 601 The multiple scattering was calculated following the established procedure  
 602 described in ref. [55] for a few selected pressure points and its subtraction was  
 603 observed to have negligible effect on the fits and on the determination of the  
 604 diffusion coefficient. This test was performed at three pressures: 67.5 bar (mea-  
 605 sured without the aluminium spacer in the high-pressure cell containing the  
 606 sample), and 97 and 1275 bar (both measured with the spacer). The calculated  
 607 multiple scattering is much weaker and broader than the single scattering and  
 608 included in the flat background over the considered energy range. This is con-  
 609 firmed by the observation that there is no inconsistency between the results for  
 610 the data measured with and without the aluminium spacer. In particular, the  
 611 results for the point at 46 bar, which was measured with the spacer, perfectly  
 612 interpolate in between the results for 41.5 and 51.5 bar, which were measured  
 613 without the spacer.

## 614 Data availability

615 Data were generated at the Institut Laue-Langevin large-scale facility and are  
 616 stored on the ILL data portal under doi 10.5291/ILL-DATA.6-01-332.

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 622 analysis, and L. Scaccia for her contribution to the Bayesian code.

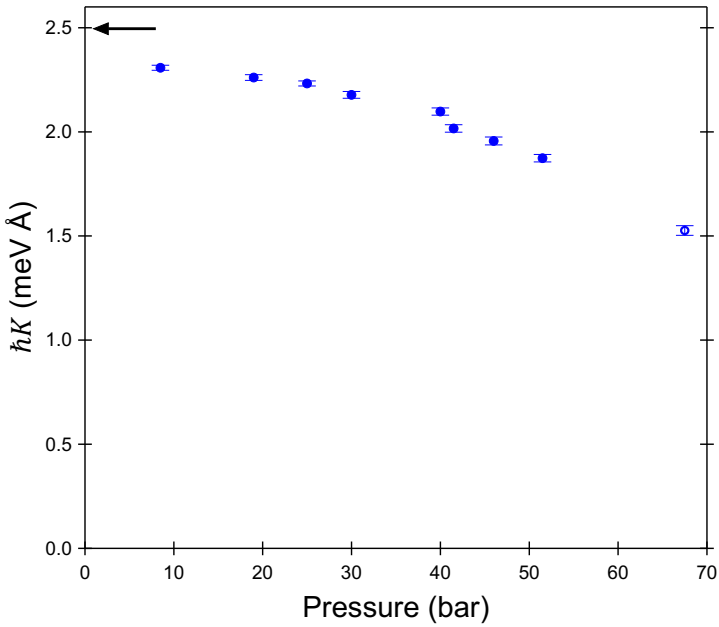
## 623 Author contributions

624 The project was conceived by F.F, F.A.G, M.S. and L.E.B.. The experiments  
 625 were performed by F.F., F.A.G., M.S., M.M.K., and L.E.B.. New analytic tools

626 have been provided by F.F. and L.E.B. The data were analysed and the figures  
627 produced by U.R., with contributions from F.F. and L.E.B.. **F. F performed**  
628 **the Bayesian analysis using the code written by A.D.F..** The manuscript was  
629 written by U.R. and L.E.B.. All authors discussed the results and commented  
630 on the manuscript.

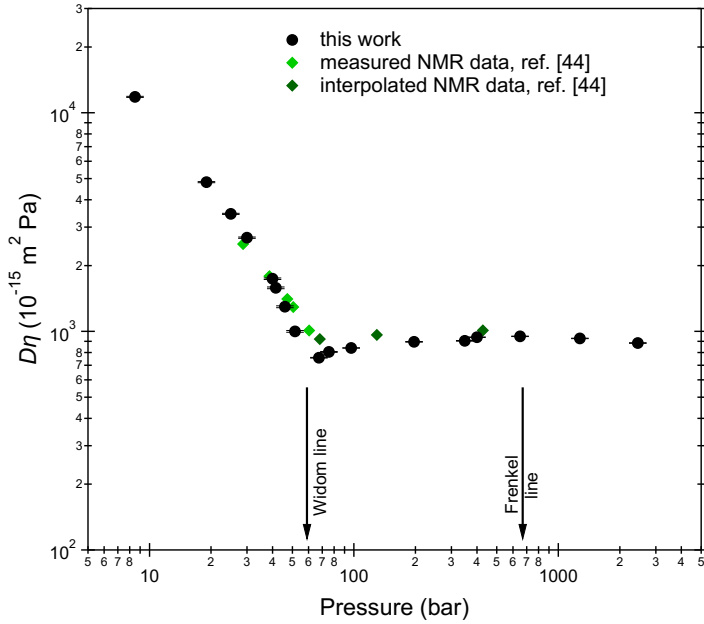
### 631 **Competing interests**

632 The authors declare no competing interests.



**Extended Data Fig. 1 | Slope parameter  $K$  appearing in Eq. 4.** Pressure dependence of the slope of the linear fits of the Gaussian half widths shown in Fig. 3a. 67.5 bar is also included. The arrow indicates the value calculated from the theoretical expression for ballistic diffusion (Eq. 1):  $K=(2\ln(2)k_{\text{B}}T/m)^{1/2}$ .





**Extended Data Fig. 2 | Test of the Stokes–Einstein–Sutherland relation.** Pressure dependence of the product between the self-diffusion coefficient  $D$  at 200 K (from this work and from ref. [48]) and the viscosity  $\eta$  at the same temperature from the equation of state-like viscosity model of ref. [50]. The error bars were obtained by propagating the errors in  $D$  only. The Stokes–Einstein–Sutherland relation predicts a constant product  $D\eta$  along isotherms.