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# Transport properties of supercritical methane

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Experimental results on molecular diffusion in supercritical methane over a wide pressure range reported by Ranieri *et al.* [Nature Communications **15**, 4142 (2024)] are compared with the theoretical expectations based on the Lennard-Jones model. In the low-pressure low-density limit the kinetic approach within the Chapman-Enskog approximation is shown to be adequate. At higher pressures and densities the freezing density scaling approach becomes appropriate. We analyse the transition from the gas-like to liquid-like dynamical behaviour from the perspective of Stokes-Einstein-Sutherland relation between the coefficients of self-diffusion and shear viscosity. This analysis locates the Frenkel dynamical crossover close to the transition from gas-like to liquid-like molecular diffusion in methane observed experimentally. The reported results provide a useful practical tool to estimate the transport properties of supercritical methane in parameter regimes where experimental results are not yet available.

## I. INTRODUCTION

Methane represents one of the most important substance relevant for our life. Its significance extends over areas such as climate and environment, energy sources, chemical industries, and extraterrestrial physics. Despite this importance our understanding of the thermophysical properties of methane remains elusive to a large extent, in particular in the high pressure regime [1]. New experimental results continue to improve our understanding of various important properties of methane [2–7].

In a recent paper, Ranieri *et al.* report measurements of the self-diffusion coefficient of the supercritical fluid methane along the  $T = 200$  K isotherm using the quasi-elastic neutron scattering [8]. A very wide pressure range is investigated, from 8.5 bar to 2450 bar. The molecular self-diffusion coefficient is derived from the best Gaussian (at low pressures) or Lorentzian (at high pressures) fits to the neutron spectra. The Gaussian-to-Lorentzian crossover is progressive and is indicative of the gas-like to liquid-like crossover in molecular transport properties.

The purpose of this work is to provide a theoretical interpretation of the experimental results by Ranieri *et al.* [8]. We demonstrate that the low-pressure results are consistent with the kinetic theory of self-diffusion in the rarefied Lennard-Jones (LJ) gas, while the high-pressure results are consistent with the freezing density scaling of transport coefficients in the LJ fluid. The transition

between the two regimes corresponds to the gas-like to liquid-like dynamical crossover [8].

Historically, a crossover of this kind has been attributed both to the crossing of the Widom line and to the Frenkel line on the phase diagram. The first one emerges from the critical point and represents the maxima or minima of certain thermo-physical properties. Crossing this line has been associated with several phenomena, including a shift in the anomalous dispersion (i.e., the difference between the unrelaxed and relaxed values) of the simulated THz sound velocity, the observation of pseudo-boiling, droplet formation, and changes in density fluctuation correlations [9–14]. The second is not directly related to the critical point and is linked to the change in the dynamical behaviour [15]. Above the Frenkel line, at high pressures, fluid dynamics is dominated by solid-like oscillations about temporary equilibrium positions and transverse acoustic excitations can be sustained [16–18]. Note that Frenkel line exists in fluids with purely repulsive interactions [19–21] where the critical point does not exist at all. In this sense the two lines discussed are quite different in nature.

In one of the approaches - following its initial definition [15]-, the location of the Frenkel line can be inferred from the analysis of the product of the self-diffusion and shear viscosity coefficients in the form of the Stokes-Einstein-Sutherland relation without the hydrodynamic radius [22–24]. In the following we refer to it as the Stokes-Einstein (SE) relation, because it is mainly based on the Stokes formula for a friction force experienced by a sphere moving through viscous medium and Einstein relation between mobility and diffusion coefficient.

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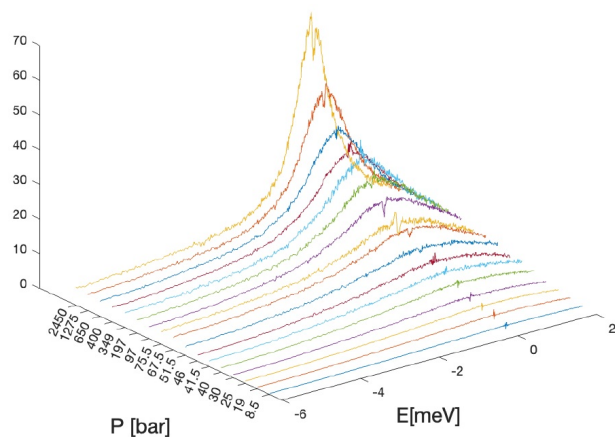


FIG. 1. (Color online) Evolution of scattered spectra of methane at  $200 \pm 1$  K across pressures from 8.5 to 2450 bar. Further details on the experiment can be found in Ref. [8].

cients. The control parameter is the dimensionless quantity  $D\eta(\Delta/k_B T) = \alpha_{SE}$ , where  $D$  is the self-diffusion coefficient,  $\eta$  is the shear viscosity coefficient,  $\Delta = \rho^{-1/3}$  is the average intermolecular separation,  $T$  is the temperature, and  $k_B$  is the Boltzmann constant. The quantity  $\alpha_{SE}$  decreases quickly with density in the gas-like regime and becomes constant in the high-density liquid-like regime. The transition between the two asymptotes serves as a reliable indication of the gas-like to liquid-like dynamical crossover and this is supported by the experimental results [8]. Previously, some aspects related to the diffusion, viscosity, and Stokes-Einstein relation in dense supercritical methane were discussed in Ref. [25], based on experimental results for the  $T = 300$  K isotherm [5]. New experimental results from Ref. [8] cover much wider region of pressures and densities and deserve new consideration.

## II. EXPERIMENT

Quasi-elastic neutron scattering (QENS) measurements were conducted at the Institut Laue-Langevin in Grenoble, France, using the IN6-SHARP time-of-flight neutron spectrometer, providing direct measurements of molecular diffusion at picosecond timescales and  $\text{\AA}$ -length scales [8]. A neutron wavelength of  $5.12 \text{ \AA}$  was employed to record scattering spectra of methane at  $200 \pm 1$  K across pressures from 8.5 to 2450 bar. The methane sample was contained in an aluminum alloy pressure cell with constant volume during pressure adjustments. Nine pressure points were measured without an aluminum spacer and eight with it. Methane purity exceeded 99.95%, and a cryostat was used to maintain temperature stability. Pressure was monitored with a 1-bar accuracy, and empty-cell spectra were recorded for calibration. Evolution of the spectra is demonstrated in Fig. 1.

Constant- $Q$  spectra ( $0.4\text{--}1.5 \text{ \AA}^{-1}$ ) were extracted and normalized using a vanadium standard, with empty-cell signals subtracted. The study revealed a gradual transition in the self-dynamic structure factor, from a Gaussian shape, describing molecular diffusion in a gas, to a Lorentzian shape, characteristic of liquid diffusion. This transition took place at pressures around 60 bar (see Fig. 1).

In dilute fluids, molecular collisions are infrequent, allowing molecules to follow ballistic motion between collisions, meaning both velocity and trajectory can be defined. As a result, the mean square displacement (MSD) of molecules shows a  $\propto t^2$  dependence over time. Experimentally, this behavior translates into the free-particle (ideal gas) expression for the self-dynamic structure factor  $S_{\text{self}}(Q, \omega)$ , which is a Gaussian function of the frequency  $\omega$ , centered at  $\omega = 0$ . The values of the half width at half maximum  $\gamma_G(Q)$  obtained from the Gaussian fits of the measured spectra displayed a linear trend with  $Q$ , as shown in Fig. 3(a) of Ref. [8]. From the values of the linear fit slope, the diffusion coefficient  $D$  for each pressure point in the gas-like regime was estimated using the density values from the National Institute of Standards and Technology (NIST) Chemistry WebBook [26]. As the density increases to the liquid-like range, the frequency of molecular collisions rises significantly. During typical experimental timescales, molecules undergo multiple uncorrelated collisions, leading to random Brownian motion. This motion is characterized by a linear, rather than quadratic, time dependence of the MSD. Consequently, the self-dynamic structure factor takes on a Lorentzian shape, centered at zero frequency. This is the model commonly used to analyze QENS data for bulk liquid samples [5, 27–29]. In this liquid-like regime the half width at half maximum  $\gamma_L(Q)$  typically follows a  $Q^2$  dependence at small  $Q$ , consistent with Fickian diffusion. However, at higher  $Q$  values, where shorter distances are probed and microscopic details of the motion become important,  $\gamma_L(Q)$  deviates from this simple behavior and lies below the expected  $Q^2$  trend. The relationship can be modeled by the formula [30]:

$$\Gamma_T(Q) = \frac{D Q^2}{1 + \tau D Q^2}. \quad (1)$$

Both the diffusion constant  $D$  and the characteristic diffusion time  $\tau$  can then be estimated.

## III. THEORY

### A. Low densities

To describe the self-diffusion and viscosity coefficients in the low-density regime we use the dominant (first-order) terms in the Chapman-Enskog pair collision ap-

proximation [31]. The diffusion coefficient is

$$D = \frac{3\sqrt{\pi}}{8} \frac{(k_B T)^{1/2}}{\rho m^{1/2} \sigma^2 \Omega_D}, \quad (2)$$

where  $m$  is the molecular mass,  $\sigma$  is the molecular length scale, and  $\Omega_D$  is the reduced diffusion (momentum transfer) integral. Similarly, the shear viscosity coefficient can be approximated by

$$\eta = \frac{5\sqrt{\pi}}{8} \frac{(k_B T)^{1/2} m^{1/2}}{\sigma^2 \Omega_\eta}, \quad (3)$$

where  $\Omega_\eta$  is the viscosity (energy transfer) integral. The transport integrals are

$$\Omega_D = \frac{1}{2} \int_0^\infty x^2 e^{-x} \sigma_D(x) dx, \quad (4)$$

and

$$\Omega_\eta = \frac{1}{2} \int_0^\infty x^3 e^{-x} \sigma_\eta(x) dx. \quad (5)$$

Here  $x = \mu v^2 / 2k_B T$  is the relative reduced kinetic energy and  $\mu$  is the reduced mass ( $\mu = m/2$  for identical molecules).

The system-dependent momentum transfer  $\sigma_D$  and energy transfer  $\sigma_\eta$  cross sections are required to evaluate the transport integrals. We use the cross sections for the LJ potential derived in Ref. [32] to evaluate the self-diffusion and viscosity coefficients at low-densities. LJ parameters for methane are  $\epsilon/k_B = 174$  K and  $\sigma = 0.36652$  nm [1]. In Ref. [8] a hard-sphere model with  $\sigma = 0.361$  nm has been chosen to approximate the diffusion coefficient using the simulated hard-sphere fluid values from Ref. [33].

It is convenient to operate with dimensionless units. In the following we use macroscopically reduced self-diffusion and shear viscosity coefficients, which are defined as  $D_R = D/\Delta v_T$  and  $\eta_R = \eta \Delta^2 / m v_T$ , where  $v_T = \sqrt{k_B T / m}$  is the thermal velocity. This normalization is essential in Rosenfeld's excess entropy scaling of transport coefficients [34, 35], hence the subscript ‘‘R’’ is used. The advantage of these units is that they are system-independent and thus can be used to compare the behaviour of transport coefficients in different systems.

Rewriting Eqs. (2) and (3) in reduced units we obtain  $D_R \sim 1/(\rho^*)^{2/3} \Omega_D$  and  $\eta_R \sim 1/(\rho^*)^{2/3} \Omega_\eta$ , where  $\rho^* = \rho \sigma^3$  is the reduced density. The transport integrals do not depend on the density. Therefore, both the self-diffusion and viscosity coefficients decrease with density as  $(\rho^*)^{-2/3}$  in the considered low-density limit. Their product in the form of the SE relation without the hydrodynamic radius decreases even faster:

$$\alpha_{SE} = D_R \eta_R \propto (\rho^*)^{-4/3}. \quad (6)$$

In this sense, the SE relation appears violated at low densities. This result is quite general, while the coefficient of proportionality in Eq. (6) is system-dependent. For example, in a dilute gas of hard spheres  $\alpha_{SE} \sim 0.037(\rho^*)^{-4/3}$  [36].

## B. High densities

In the high-density regime we make use of the freezing density scaling (FDS) approach. In Ref. [36] it has been demonstrated that macroscopically reduced transport coefficients (self-diffusion, shear viscosity, and thermal conductivity) of the LJ fluid along isotherms exhibit quasi-universal scaling on the density divided by its value at the freezing point. Thus, the transport coefficients depend on a single variable,  $\mathcal{R} = \rho/\rho_{fr}$ , where  $\rho_{fr}$  is the density at the freezing point. Originally, FDS has been proposed as a merely empirical observation, complementing the freezing temperature scaling discussed by Rosenfeld and others [37–39]. Recently, this scaling has been rationalized and discussed in terms of the Rosenfeld's excess entropy scaling [34, 40] and isomorph theory of Roskilde-simple systems [41]. It appears that the lines corresponding to constant ratios  $\rho/\rho_{fr}$  in the LJ phase diagram correspond also to approximately quasi-universal values of excess entropy [42, 43]. These lines are thus approximate isomorphs, along which certain macroscopically reduced structural and dynamical properties remain invariant to a good approximation [41, 44]. So far, FDS has been demonstrated to apply not only to the LJ fluid [36, 45], but also to the Weeks–Chandler–Andersen fluid [46], and noble gases [42, 43]. FDS of transport coefficients in the hard-sphere fluid is similar, although not exactly the same [36]. Thus, we may expect FDS to be to some extent universal concept. There have been indications that it applies to methane, too [25, 42]. It has been recently demonstrated that FDS can be improved by using the average of the freezing and melting densities instead of the freezing density alone [47]. Here we use the original version of FDS, because it provides a sufficient accuracy for supercritical temperatures.

Technically, the FDS approach represents just an appropriate mapping between the LJ and methane fluids. Importantly, LJ energy and length scales parameters are not required in this case. For a given density we calculate the density scaling parameter  $\mathcal{R} = \rho/\rho_{fr}$ , with the freezing mass density  $m\rho_{fr} \simeq 0.545$  g/cm<sup>3</sup> at  $T = 200$  K, according to REFPROP 10.0 NIST database [48]. For the obtained  $\mathcal{R}$  we then evaluate the corresponding reduced transport coefficients of the LJ fluid. In particular, we use molecular dynamics (MD) results along the slightly supercritical isotherm  $T^* = 1.5$  from Ref. [49] (diffusion) and Ref. [50] (viscosity). The exact value of the temperature is not very important. According to the FDS approach, temperature only affect  $\rho_{fr}$ , not affecting reduced transport properties otherwise. This approach provides theoretical expectations for the reduced transport coefficients of methane at sufficiently high densities. As pointed above, FDS does not use any effective diameter, energy, or any other free parameters and hence is very simple and transparent.

The dynamics of molecules in the high-density liquid regime is dominated by solid-like vibrations of atoms around their temporary equilibrium positions [15, 51].

These temporary equilibrium positions of atoms do not form any regular structure and are not fixed, unlike in solids. Instead, they are allowed to diffuse and this is why liquids can flow. However, this diffusive motion is characterized by much longer time scales compared to those of solid-like oscillations. The time separation between the fast oscillation and slow relaxation processes is essential in the vibrational paradigm of dense liquids dynamics [52]. Within this paradigm, self-diffusion of molecules can be considered as a random walk process [53]. The characteristic length-scale of the process corresponds to the amplitude of solid-like vibrations. The characteristic time scale is the Maxwellian shear relaxation time,  $\tau = \eta/G_\infty$ , where  $G_\infty$  is the infinite frequency shear modulus [54]. As a result the relation between the self-diffusion coefficient, shear viscosity, density, and temperature of dense liquids emerges (see Ref. [53] for further details):

$$D \propto \frac{k_B T}{\eta \Delta}. \quad (7)$$

This proportionality implies that the SE relation without the hydrodynamic radius holds in dense liquids. Zwanzig explained why it should be approximately so [22]. He also derived the lower and upper boundaries for the SE parameter,  $0.13 \lesssim \alpha_{SE} \lesssim 0.18$ . The topic received considerable attention over years [23, 24, 55–59]. Recently, it has been demonstrated that in addition to simple atomic fluids, the SE relation without the hydrodynamic radius can remain valid in various dense non-spherical molecular liquids [60]. Among recent examples are water [61, 62] and methane [25].

### C. Frenkel line

Frenkel line is introduced as a dynamical crossover line in the supercritical state [15, 19, 51, 63]. It separates the high density liquid regime where the molecular motion is dominated by solid-like vibrations with much slower diffusion from the low-density liquid regime where the molecular motion is purely diffusive like in gases [51]. Sometimes these regimes are referred to as “rigid” and “non-rigid” fluids, respectively. The canonical definition of the Frenkel line is the equality of the liquid relaxation time and the period of solid-like oscillations. This is an approximate qualitative criterion useful for illustration purposes, but tricky in practical implementation [51, 63]. The two quantitative criteria highlighted by Trachenko [51] are based on the disappearance of the oscillations and minima of velocity autocorrelation function (VAF) and a threshold value of the specific heat at constant volume,  $c_v = 2$ . However, these are not truly universal. For instance, they cannot be applied to the important model system in condensed matter – the fluid of hard spheres [64]. Many more qualitative definitions for the Frenkel line have been proposed over the years, including for example specific values of diffusion constant

and speed of sound [63], excess entropy [65], equality of kinetic and potential contribution to viscosity and the minima of the kinematic viscosity [66], minima of the properly reduced viscosity and thermal conductivity coefficients [67], etc. These different criteria predict somewhat different location for the Frenkel line on the phase diagram. This is not a severe issue since the crossover is considered.

The location of the Frenkel line on the phase diagram of important systems such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_4$  is investigated in Ref. [18]. MD simulation are performed to calculate VAF. Frenkel line is then located based on the disappearance of oscillations and minima of VAF. This location is used in Ref. [8]. Dealing with the data for the diffusion and viscosity coefficient in the wide density and pressure range opens an attractive alternative. It is possible to estimate the transition between the gas-like and liquid-like dynamical regimes from the intersection of the gaseous and liquid asymptotes of the SE product. This method has been previously tested on various model systems such as Coulomb and Yukawa fluids, the hard-sphere fluid, the LJ fluid, and delivered consistent results [59].

## IV. RESULTS

The reduced self-diffusion and viscosity coefficients of methane at  $T = 200$  K versus the density scaling parameter  $\mathcal{R}$  are shown in Fig. 2. Here the circles correspond to the experimental data for the self-diffusion coefficient [8]. The squares are the literature data for the shear viscosity coefficient, summarized in the Supplementary Table 1 of Ref. [8]. The solid curves correspond to our calculation based on the FDS approach using available MD data. The dashed curves correspond to low-density gaseous asymptotes calculated from Eqs. (2) – (5).

First of all, the qualitative behaviour of the reduced diffusion and viscosity coefficients is quite representative of simple fluids [52, 67]. The reduced diffusion coefficient decreases monotonously on approaching the fluid-solid phase transition. The reduced viscosity coefficient first decreases with density in the low-density gas-like regime, experiences a minimum at an intermediate density and then increases towards the fluid-solid phase transition. The existence of the minimum is a generic property of liquids [51, 67, 68]. The minimum corresponds to the transition between two different mechanisms of momentum transfer in gas-like and liquid-like regimes. Hence, its position can serve as a rough indicator of the location of the Frenkel line on the phase diagram [10, 66]. However, the observed minimum is rather shallow and thus the accuracy of this indicator may not be high.

Regarding the comparison between the experiment and theory, we observe that in both low-density and high-density regimes there is a reasonably good agreement between the experiment and theoretical predictions based

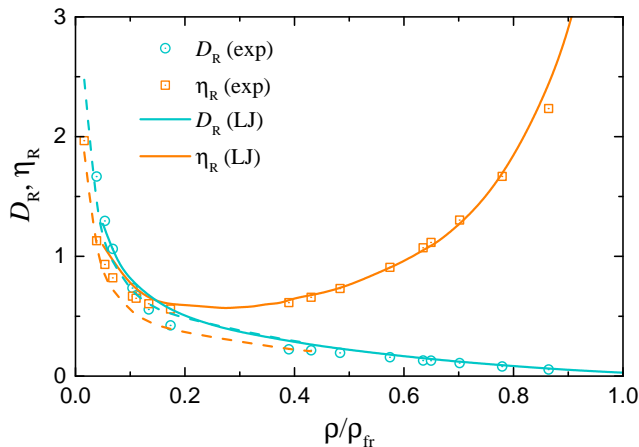


FIG. 2. (Color online) The self-diffusion and viscosity coefficients of supercritical fluid methane along the  $T = 200$  K isotherm. Circles and squares denote the experimental self-diffusion and viscosity coefficients, respectively. Solid curves represent the FDS scaling for a supercritical LJ fluid at  $T^* = 1.5$ . The data are from Refs. [49] (self-diffusion) and Ref. [50] (shear viscosity), respectively. Dashed curves represent the low-density gaseous asymptotes, as discussed in the text.

on the LJ model fluids. At intermediate densities the self-diffusion experimental data are slightly below the theoretical expectation. From the experimental side, this is where the transition from the Gaussian to the Lorentzian shape of the neutron spectra occurs and the results can be not so accurate as in the respective limits of low- and high-density. From the theoretical side, it cannot be excluded that the pairwise LJ potential is only a rough approximation in this regime. Note that the Chapman-Enskog low-density approach for the diffusions coefficients matches very well the FDS approach at low and moderate densities. Remarkably, it remains a rather good approximation even at densities exceeding the critical point density, as shown in Fig. 2. In the case of the shear viscosity coefficient, the situation is different. The LJ FDS scaling describes the literature data relatively well in the entire density regime. The low-density Chapman-Enskog approximation describes the data well in the low-density limit, but becomes unreliable for  $\mathcal{R} \gtrsim 0.05$ , far below the density at which the minimum in the reduced shear viscosity coefficient is reached.

The SE product  $\alpha_{SE}$ , evaluated using the data for diffusion, viscosity and density, tabulated in the Supplementary Table 1 of Ref. [8], is plotted in Fig. 3 as a function of methane mass density. Symbols correspond to the experimental results. The dashed lines are the theoretical asymptotes. In the low-density regime the calculation is done using Eqs. (2) - (5). In the high-density regime a constant value  $\alpha_{SE} \simeq 0.15$  is expected [59]. The experimental results are in reasonable agreement with these expectations. **At a very high pressure the SE coefficient**

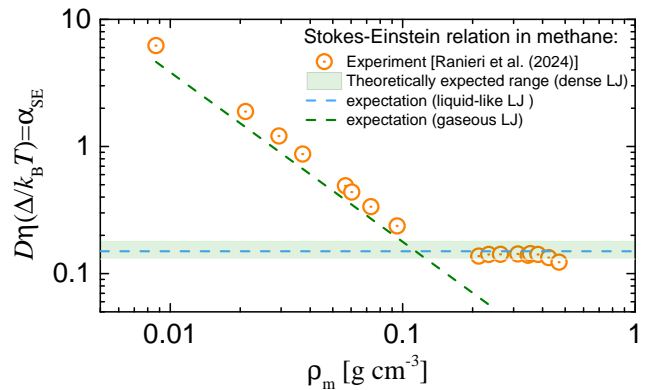


FIG. 3. (Color online) Stokes-Einstein product  $D\eta(\Delta/k_B T) \equiv \alpha_{SE}$  in supercritical methane along the  $T = 200$  K isotherm versus the mass density  $\rho_m$ . Circles are plotted using the data for self-diffusion and viscosity coefficients as well as mass density tabulated in the Supplementary Table 1 of Ref. [8]. Shaded region correspond to the theoretical expectation,  $0.13 \lesssim \alpha_{SE} \lesssim 0.18$  in the high density fluid region of the phase diagram. The horizontal dashed line shows the SE coefficient for the LJ fluid,  $\alpha_{SE} \simeq 0.15$ .

**drops somewhat below expectations and this might signal the approach to the super-cooled regime, where SE relation breaks down.** Taking into account uncertainties, the intercept of the two asymptotes occurs in the interval  $\rho_m \simeq 0.1 - 0.2$  g/cm<sup>3</sup>. In the LJ fluid the dilute gaseous and dense liquid asymptotes for  $\alpha_{SE}$  intersect at  $\rho/\rho_{fr} \simeq 0.35$  [69]. This can serve as an indicator of the Frenkel line as proposed in Ref. [59] and further elaborated in Ref. [69]. Translated into the case of methane fluid at  $T = 200$  K this estimate gives  $\rho_m \simeq 0.19$  g/cm<sup>3</sup> and  $P \simeq 6.3$  MPa, **according to recommended values from the REFPROP 10.0 database.** This brings Frenkel line close to the location of the crossover from gas-like to liquid-like diffusion in methane detected experimentally [8]. Previous estimates based on the disappearance of oscillations and minima of VAF resulted in considerably higher pressures and densities of the Frenkel line [18].

## V. DISCUSSION AND CONCLUSION

The main result of this work is the demonstration that the experimental results on the self-diffusion in supercritical methane along the  $T = 200$  K isotherm reported in Ref. [8] can be relatively well reproduced using the LJ fluid model. In the low-density limit the Chapman-Enskog pair collision approximation can be used with the momentum transfer cross section derived for the LJ potential. The LJ potential parameters  $\epsilon/k_B = 174$  K, and  $\sigma = 0.36652$  nm, suggested in Ref. [1], seem appropriate for this purpose. At higher densities the freezing density scaling approach does a rather good work. This approach does not require introduction of LJ potential parameters

or any other free parameters. It is even not very sensitive to the exact shape of the interaction potential. Density divided by its value at the freezing point serves as a single control parameter for mapping between the LJ and methane fluids. The same is essentially true for the literature data on the shear viscosity coefficient, except the Chapman-Enskog approximation is violated at considerably lower densities than in the case of diffusion.

The Stokes-Einstein product without the hydrodynamic radius,  $D\eta(\Delta/k_B T) = \alpha_{SE}$ , exhibits two distinct asymptotes. At low densities  $\alpha_{SE} \propto (\rho^*)^{-4/3}$  as the the Chapman-Enskog approximation predicts. At higher density the SE parameter reaches a constant value  $\alpha_{SE} \simeq \text{const}$  corresponding to the validity of the SE relation without the hydrodynamic radius. The intersection of the two asymptotes can serve as an indication of the gas-like to liquid-like dynamical crossover. This idea has been tested on several model fluids, including the LJ fluid, in Ref. [59].

If the mapping between the LJ and methane fluid is adopted, then the location of the Frenkel line in the LJ fluid proposed in Ref. [69] would almost ideally match the crossover from gas-like to liquid-like diffusion in methane observed experimentally [8]. Previous estimates based on the disappearance of oscillations and minima of the velocity autocorrelation function predicted considerably higher pressures and densities for the locations of the Frenkel line [18].

Our explanation for this discrepancy is as follows. Following the discussion in Ref. [52] we suggest that actually two useful lines on the phase diagram can be identified. The first corresponds to the intersection of gas-like and liquid-like asymptotes of reduced dynamical characteristics (such as the macroscopically reduced shear viscosity and thermal conductivity coefficients, or dimensionless Stokes-Einstein product in our case). This occurs at a

fixed density ratio  $\rho/\rho_{fr} \simeq 0.35$  for the LJ fluid [69]. This implies that the first line occasionally emanates from the vicinity of the critical point in the LJ-like fluids. The second line corresponds to about twice higher density ratio and marks the onset of solid-like vibrational dominance and the applicability of the vibrational model of transport and thermodynamics of dense fluids. It is this second line that corresponds to the specific heat criterion  $c_v = 2$  in simple fluids (see Fig. 14 from Ref. [52]). This line better describes the transition from a “non-rigid” to “rigid” fluid, rather than gas-like to fluid-like crossover. In the experiment it is the first line that has been identified from the analysis of the molecular diffusion. As it emanates from the vicinity of the critical point it lies closely to the Widom line [8]. But it should be stressed that this is just a coincidence, because gas-like to fluid-like dynamical crossover also occurs for simulated fluids, which do not have critical point and Widom line at all. The criterion based on the disappearance of oscillations and minima of the VAF is likely more applicable to the transitions between “non-rigid” to “rigid” fluids and thus corresponds to considerably higher pressures and densities.

Altogether, our observations shed some new light on the transport properties of the supercritical methane fluid. They open up a possibility to predict the coefficients of diffusion and viscosity in parameter regimes where experimental results are still missing. This can be of certain value in understanding transport properties of supercritical fluids, their industrial applications, as well as geodynamics of gas giant planets in our Solar System and beyond.

The authors have no conflicts of interest to disclose.

All data reported in this study can be obtained from the corresponding authors upon request.

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- [1] D. G. Friend, J. F. Ely, and H. Ingham, “Thermophysical properties of methane,” *J. Phys. Chem. Ref. Data* **18**, 583–638 (1989).
  - [2] E. H. Abramson, “Viscosity of methane to 6 GPa and 673 K,” *Phys. Rev. E* **84**, 062201 (2011).
  - [3] E. H. Abramson, “Melting curves of argon and methane,” *High Pressure Research* **31**, 549–554 (2011).
  - [4] D. Smith, M. A. Hakeem, P. Parisiades, H. E. Maynard-Casely, D. Foster, D. Eden, D. J. Bull, A. R. L. Marshall, A. M. Adawi, R. Howie, A. Sapelkin, V. V. Brazhkin, and J. E. Proctor, “Crossover between liquidlike and gaslike behavior in CH<sub>4</sub> at 400 K,” *Phys. Rev. E* **96**, 052113 (2017).
  - [5] U. Ranieri, S. Klotz, R. Gaal, M. M. Koza, and L. E. Bove, “Diffusion in dense supercritical methane from quasi-elastic neutron scattering measurements,” *Nature Commun.* **12**, 1958 (2021).
  - [6] D. W. Meyer, W.-P. Hsieh, H. Hsu, C.-Y. Kuo, and J.-F. Lin, “Thermal conductivity and compressional velocity of methane at high pressure: Insights into thermal transport properties of icy planet interiors,” *J. Geophys. Res.: Planets* **127**, e2021JE007059 (2022).
  - [7] T. G. White, H. Poole, E. E. McBride, M. Oliver, A. Descamps, L. B. Fletcher, W. A. Angermeier, C. H. Allen, K. Appel, F. P. Condamine, C. B. Curry, F. Dallari, S. Funk, E. Galtier, E. J. Gamboa, M. Gauthier, P. Graham, S. Goede, D. Haden, J. B. Kim, H. Lee, B. K. Ofori-Okai, S. Richardson, A. Rigby, C. Schoenwaelder, P. Sun, B. L. Witte, T. Tschentscher, U. Zastrau, B. Nagler, J. B. Hastings, G. Monaco, D. O. Gericke, S. H. Glenzer, and G. Gregori, “Speed of sound in methane under conditions of planetary interiors,” *Phys. Rev. Research* **6**, L022029 (2024).
  - [8] U. Ranieri, F. Formisano, F. A. Gorelli, M. Santoro, M. M. Koza, A. De Francesco, and L. E. Bove, “Crossover from gas-like to liquid-like molecular diffusion in a simple supercritical fluid,” *Nat. Comm.* **15**, 4142 (2024).
  - [9] G. G. Simeoni, T. Bryk, F. A. Gorelli, M. Krisch, G. Ruocco, M. Santoro, and T. Scopigno, “The Widom

- line as the crossover between liquid-like and gas-like behaviour in supercritical fluids,” *Nature Phys.* **6**, 503–507 (2010).
- [10] F. A. Gorelli, T. Bryk, M. Krisch, G. Ruocco, M. Santoro, and T. Scopigno, “Dynamics and thermodynamics beyond the critical point,” *Sci. Rep.* **3**, 1203 (2013).
- [11] F. Maxim, C. Contescu, P. Boillat, B. Niceno, K. Karalis, A. Testino, and C. Ludwig, “Visualization of supercritical water pseudo-boiling at Widom line crossover,” *Nature Commun.* **10**, 4114 (2019).
- [12] F. Maxim, K. Karalis, P. Boillat, D. T. Banuti, Jose I. Marquez D., B. Niceno, and C. Ludwig, “Thermodynamics and dynamics of supercritical water pseudo-boiling,” *Adv. Sci.* **8** (2020), 10.1002/adv.202002312.
- [13] V. Pipich and D. Schwahn, “Densification of supercritical carbon dioxide accompanied by droplet formation when passing the widom line,” *Phys. Rev. Lett.* **120**, 145701 (2018).
- [14] A. A. Arai, T. Morita, and K. Nishikawa, “Investigation of structural fluctuation of supercritical benzene by small-angle x-ray scattering,” *J. Chem. Phys.* **119**, 1502–1509 (2003).
- [15] Y. Frenkel, *Kinetic theory of liquids* (Dover, New York, NY, 1955).
- [16] V. V. Brazhkin, Yu. D. Fomin, A. G. Lyapin, V. N. Ryzhov, and E. N. Tsiok, “Widom line for the liquid–gas transition in Lennard-Jones system,” *J. Phys. Chem. B* **115**, 14112–14115 (2011).
- [17] V. V. Brazhkin, A.G. Lyapin, V. N. Ryzhov, K. Trachenko, Y. D. Fomin, and E. N. Tsiok, “Where is the supercritical fluid on the phase diagram?” *Phys.-Usp.* **182**, 1137–1156 (2012).
- [18] C. Yang, V. V. Brazhkin, M. T. Dove, and K. Trachenko, “Frenkel line and solubility maximum in supercritical fluids,” *Phys. Rev. E* **91**, 012112 (2015).
- [19] V. V. Brazhkin, Yu. D. Fomin, A. G. Lyapin, V. N. Ryzhov, E. N. Tsiok, and K. Trachenko, “Liquid-gas” transition in the supercritical region: fundamental changes in the particle dynamics,” *Phys. Rev. Lett.* **111**, 145901 (2013).
- [20] D. Huang, M. Baggioni, Sh. Lu, Z. Ma, and Y. Feng, “Revealing the supercritical dynamics of dusty plasmas and their liquidlike to gaslike dynamical crossover,” *Phys. Rev. Research* **5**, 013149 (2023).
- [21] N. Yu, D. Huang, S. Lu, S. Khrapak, and Y. Feng, “Universal scaling of transverse sound speed and its isomorphic property in Yukawa fluids,” *Phys. Rev. E* **109**, 035202 (2024).
- [22] R. Zwanzig, “On the relation between self-diffusion and viscosity of liquids,” *J. Chem. Phys.* **79**, 4507–4508 (1983).
- [23] L. Costigliola, D. M. Heyes, T. B. Schröder, and J. C. Dyre, “Revisiting the Stokes-Einstein relation without a hydrodynamic diameter,” *J. Chem. Phys.* **150**, 021101 (2019).
- [24] S. Khrapak, “Stokes–Einstein relation in simple fluids revisited,” *Mol. Phys.* **118**, e1643045 (2019).
- [25] S.A. Khrapak, “Diffusion, viscosity, and Stokes-Einstein relation in dense supercritical methane,” *J. Mol. Liq.* **354**, 118840 (2022).
- [26] P. Linstrom, en“Nist chemistry webbook, nist standard reference database 69,” (1997).
- [27] S. Klotz, T. Strässle, and L. E. Bove, “Quasi-elastic neutron scattering in the multi-GPa range and its application to liquid water,” *Applied Physics Letters* **103**, 193504 (2013).
- [28] L. E. Bove, S. Klotz, Th. Strässle, M. Koza, J. Teixeira, and A. M. Saitta, “Translational and rotational diffusion in water in the gigapascal range,” *Physical Review Letters* **111**, 185901 (2013).
- [29] K. Amann-Winkel, M. Bellissent-Funel, L. E. Bove, T. Loerting, A. Nilsson, A. Paciaroni, D. Schlesinger, and L. Skinner, “X-ray and neutron scattering of water,” *Chemical Reviews*, *Chemical Reviews* **116**, 7570–7589 (2016).
- [30] K. S. Singwi and A. Sjölander, “Diffusive motions in water and cold neutron scattering,” *Physical Review* **119**, 863–871.
- [31] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases - An Account of the Kinetic Theory of Viscosity, Thermal Conduction and Diffusion in Gases* (Cambridge University Press, Cambridge, 1990).
- [32] S. A. Khrapak, “Accurate transport cross sections for the Lennard-Jones potential,” *Eur. Phys. J. D* **68**, 276 (2014).
- [33] S. Pieprzyk, M. N. Bannerman, A. C. Brańka, M. Chudak, and D. M. Heyes, “Thermodynamic and dynamical properties of the hard sphere system revisited by molecular dynamics simulation,” *Phys. Chem. Chem. Phys.* **21**, 6886–6899 (2019).
- [34] Y. Rosenfeld, “Relation between the transport coefficients and the internal entropy of simple systems,” *Phys. Rev. A* **15**, 2545–2549 (1977).
- [35] Y. Rosenfeld, “A quasi-universal scaling law for atomic transport in simple fluids,” *J. Phys.: Condens. Matter* **11**, 5415–5427 (1999).
- [36] S. A. Khrapak and A. G. Khrapak, “Transport properties of Lennard-Jones fluids: Freezing density scaling along isotherms,” *Phys. Rev. E* **103**, 042122 (2021).
- [37] Y. Rosenfeld, “Excess-entropy and freezing-temperature scalings for transport coefficients: Self-diffusion in Yukawa systems,” *Phys. Rev. E* **62**, 7524–7527 (2000).
- [38] Y. Rosenfeld, “Quasi-universal melting-temperature scaling of transport coefficients in Yukawa systems,” *J. Phys.: Condens. Matter* **13**, L39–L43 (2001).
- [39] L. Costigliola, U. R. Pedersen, D. M. Heyes, T. B. Schröder, and J. C. Dyre, “Communication: Simple liquids’ high-density viscosity,” *J. Chem. Phys.* **148**, 081101 (2018).
- [40] I. H. Bell, R. Messerly, M. Thol, L. Costigliola, and J. C. Dyre, “Modified entropy scaling of the transport properties of the Lennard-Jones fluid,” *J. Phys. Chem. B* **123**, 6345–6363 (2019).
- [41] J. C. Dyre, “Hidden scale invariance in condensed matter,” *J. Phys. Chem. B* **118**, 10007–10024 (2014).
- [42] S. A. Khrapak and A. G. Khrapak, “Freezing temperature and density scaling of transport coefficients,” *J. Phys. Chem. Lett.* **13**, 2674–2678 (2022).
- [43] S. A. Khrapak and A. G. Khrapak, “Freezing density scaling of fluid transport properties: Application to liquefied noble gases,” *J. Chem. Phys.* **157**, 014501 (2022).
- [44] N. Gnan, T. B. Schroder, U. R. Pedersen, N. P. Bailey, and J. C. Dyre, “Pressure-energy correlations in liquids. IV. Isomorphs in liquid phase diagrams,” *J. Chem. Phys.* **131**, 234504 (2009).
- [45] D. M. Heyes, D. Dini, S. Pieprzyk, and A. C. Brańka, “Departures from perfect isomorph behavior in Lennard-

- Jones fluids and solids,” *J. Chem. Phys.* **158**, 134502 (2023).
- [46] S. A. Khrapak and A. G. Khrapak, “Freezing density scaling of transport coefficients in the Weeks-Chandler-Andersen fluid,” *J. Chem. Phys.* **160**, 134504 (2024).
- [47] D. M. Heyes, D. Dini, S. Pieprzyk, A. C. Brańka, and L. Costigliola, “Models to predict configurational adiabats of lennard-jones fluids and their transport coefficients,” *J. Chem. Phys.* **161**, 084502 (2024).
- [48] E. W. Lemmon, I.H. Bell, M. L. Huber, and M. O. McLinden, “NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 10.0, National Institute of Standards and Technology,” (2018).
- [49] V.G. Baidakov, S.P. Protsenko, and Z.R. Kozlova, “The self-diffusion coefficient in stable and metastable states of the Lennard-Jones fluid,” *Fluid Phase Equilibria* **305**, 106–113 (2011).
- [50] V. G. Baidakov, S. P. Protsenko, and Z. R. Kozlova, “Metastable Lennard-Jones fluids. I. Shear viscosity,” *J. Chem. Phys.* **137**, 164507 (2012).
- [51] K. Trachenko, *Theory of liquids: From excitations to Thermodynamics* (Cambridge University Press, Cambridge, England, 2023).
- [52] S.A. Khrapak, “Elementary vibrational model for transport properties of dense fluids,” *Phys. Rep.* **1050**, 1 (2024).
- [53] S. A. Khrapak, “Self-diffusion in simple liquids as a random walk process,” *Molecules* **26**, 7499 (2021).
- [54] S. A. Khrapak and A. G. Khrapak, “Quasiuniversal behavior of shear relaxation times in simple fluids,” *Phys. Rev. E* **110**, 054101 (2024).
- [55] U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon Press, Oxford, 1994).
- [56] U. Balucani, R. Vallauri, and T. Gaskell, “Generalized Stokes-Einstein relation,” *Berichte der Bunsengesellschaft für physikalische Chemie* **94**, 261–264 (1990).
- [57] N. Ohtori, S. Miyamoto, and Y. Ishii, “Breakdown of the Stokes-Einstein relation in pure Lennard-Jones fluids: From gas to liquid via supercritical states,” *Phys. Rev. E* **95**, 052122 (2017).
- [58] N. Ohtori, H. Uchiyama, and Y. Ishii, “The Stokes-Einstein relation for simple fluids: From hard-sphere to Lennard-Jones via WCA potentials,” *J. Chem. Phys.* **149**, 214501 (2018).
- [59] S. A. Khrapak and A. G. Khrapak, “Excess entropy and Stokes-Einstein relation in simple fluids,” *Phys. Rev. E* **104**, 044110 (2021).
- [60] N. Ohtori, Y. Kondo, K. Shintani, T. Murakami, T. Nobuta, and Y. Ishii, “The Stokes-Einstein relation for non-spherical molecular liquids,” *Chem. Lett.* **49**, 379–382 (2020).
- [61] S. A. Khrapak and A. G. Khrapak, “Stokes-Einstein relation without hydrodynamic diameter in the TIP4P/Ice water model,” *J. Chem. Phys.* **158**, 206101 (2023).
- [62] S. A. Khrapak, “System size dependence of the diffusion coefficients in MD simulations: A simple correction formula for pure dense fluids,” *J. Phys. Chem. B* **128**, 287–290 (2024).
- [63] V. V. Brazhkin, Yu. D. Fomin, A. G. Lyapin, V. N. Ryzhov, and K. Trachenko, “Two liquid states of matter: A dynamic line on a phase diagram,” *Phys. Rev. E* **85**, 031203 (2012).
- [64] C. G. Pruteanu, M. N. Bannerman, M. Kirsz, L. Lue, and G. J. Ackland, “From atoms to colloids: Does the frenkel line exist in discontinuous potentials?” *ACS Omega* **8**, 12144–12153 (2023).
- [65] I. H. Bell, G. Galliero, S. Delage-Santacreu, and L. Costigliola, “An entropy scaling demarcation of gas- and liquid-like fluid behaviors,” *J. Chem. Phys.* **152**, 191102 (2020).
- [66] I. H. Bell, S. Delage-Santacreu, H. Hoang, and G. Galliero, “Dynamic crossover in fluids: From hard spheres to molecules,” *J. Phys. Chem. Lett.* **12**, 6411–6417 (2021).
- [67] S. A. Khrapak and A. G. Khrapak, “Minima of shear viscosity and thermal conductivity coefficients of classical fluids,” *Phys. Fluids* **34**, 027102 (2022).
- [68] K. Trachenko, M. Baggioli, K. Behnia, and V. V. Brazhkin, “Universal lower bounds on energy and momentum diffusion in liquids,” *Phys. Rev. B* **103**, 014311 (2021).
- [69] S. A. Khrapak, “Gas-liquid crossover in the Lennard-Jones system,” *J. Chem. Phys.* **156**, 116101 (2022).