P. Carelli, I. Modena and F. P. Ricci:
SELF-DIFFUSION IN KRYPTON AT INTERMEDIATE DENSITY

Self-Diffusion in Krypton at Intermediate Density

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The self-diffusion coefficient in Kr has been measured throughout a large range of densities (0.85 < ρ < 2 g/cm³) at temperatures near the critical point. The results are compared with molecular-dynamic calculations and with the CH₄ behavior. Although the qualitative agreement is good, disagreement from a quantitative point of view was found. The "normal behavior" of the self-diffusion coefficient in the critical region has been deduced.

INTRODUCTION

At present the "computer experiments" seem to be the most powerful way for investigating the static and the dynamic behavior of the dense fluids. Some of the numerical predictions must, however, be compared with real experiments. This ensures that the hypothesis about the intermolecular potential on which the model is based gives a correct description of the world around us.

Recently a thorough study has been published on the self-motion of atoms in a Lennard–Jones fluid; the study was carried out using computer experiments. These "experiments" have a range of 0.72 ≤ T* ≤ 5.09 and 0.30 ≤ ρ* ≤ 0.85, where T* = kₜ T/ε and ρ* = ρε²/m are the reduced temperature and density, ε and σ the depth and the core of the Lennard–Jones potential, m the atomic mass, and kₜ the Boltzmann constant.

Noble gases Ar, Kr, and Xe are the substances which should be described by a classical Lennard–Jones fluid. The authors compare the numerical results of the self-diffusion constant with some experiments on Ar² and claim a very good agreement. However, these experiments cover a small range of densities and temperatures since 0.725 ≤ T* ≤ 0.925 and 0.763 ≤ ρ* ≤ 0.835; that is, the measurements are only near the triple point. Since suggestions have been made that at intermediate densities many-body forces become important, it is worthwhile to measure the self-diffusion coefficient in Kr for a large range of densities (0.1 ≤ ρ* ≤ 0.7). Moreover, if the experimental data are taken at a temperature near the critical temperature T_c, but outside the critical region [i.e., (T − T_c)/T_c > 3%], we obtain the "normal" behavior of the self-diffusion coefficient in the critical region. This point is quite important since the deduction of an anomalous behavior of the self-diffusion coefficient at the critical point depends upon a good knowledge of the "normal" behavior. This problem has caused erroneous statements in the past.¹,5 Finally, we wish to point out that extensive measurements are available for the self-diffusion in CH₄⁶ at various temperatures and for 0.07 ≤ ρ* ≤ 0.82.

Since CH₄ is a polyatomic molecule, the comparison between the behavior of Kr and CH₄ will give us an idea of the importance of the internal degrees of freedom in the self-diffusion process.

EXPERIMENTAL APPARATUS

The capillary method of Anderson and Saddington¹ has been used. Since we were interested in
obtaining high densities at temperature near $T_c$, the apparatus was built to hold pressures up to 400 atm and to perform the diffusion experiments down to the liquid-nitrogen temperature. The block diagram of the whole apparatus is shown in Fig. 1 and details of the diffusing cell are illustrated in Fig. 2. The experiment was carried out as follows.

(i) After evacuating the system and closing SV, the mixture of Kr-Kr$^{85}$ held in the reservoir Z is condensed in the basin V through valve 14. $T_1$ is used as a cryogenic compressor. The pressure in V is given by TX1.

(ii) After closing SC and opening SV for a short time, a sample of the condensed solution which we call “standard” is taken out. It is transferred through SC, 4, 3, and 2 to $T_2$. If $T_2$ is immersed in the liquid nitrogen, it works as a cryogenic pump taking at least $99\%$ of the fluid contained in the capillary. The condensation in $T_2$ can be followed, since the pressure can be read from TX2. When the condensation is complete, we close valve 4. We warm up $T_3$ to room temperature, and the sample is transferred to CG (the volume of $T_3$ is $2\%$ of the volume of CG). The pressure in CG is read using TX2. The piston $P_1$ changes the volume of the analyzing region and allows the determination of the radioactivity of the gas in CG at the different pressures. The radioactivity of the gas in CG is measured by G. The vessel CG has an end window, in front of G, made of Mylar, 0.025 mm thick. Since Kr$^{85}$ emits $\beta^-$ of 0.67 MeV, the absorption by the two windows is negligible. $C_s$ is the specific
activity of the standard.

(iii) After evacuating the capillary line, we fill the capillary C with natural Kr from T₂. The filling pressure is read from M₁ and is made equal to the pressure in V, read from TX₁. Therefore, the densities in C and V are the same. Then SC is closed.

(iv) SV is opened. At this point the diffusion period begins. To avoid turbulence the opening time is not less than 20 sec. Also, the SO opening system was built in such a way (see Fig. 2) that there is no variation in the basin volume during the opening of SV.

(v) SV is closed. The time between steps 4 and 5 is the diffusion time.

(vi) After evacuating the capillary line, the fluid from C is transferred to CG as in step (ii). However, in this case, the Kr⁴⁰ concentration was not homogeneous along the capillary since there will be a small amount of gas remaining in the capillary line, perhaps with Kr⁴⁰ concentration different from the average; we homogenize the fluid contained in the capillary by moving the piston P, up and down after opening SC but before condensing the Kr in T₁. We control the degree of homogenization by measuring the activity of partial withdrawals of the same sample. We wish to point out that if P₁ is in a fixed position we can derive, from the reading of TX₂ (which measures the pressure in CG) the Kr density in which the diffusion process took place. This pressure is much smaller than one atmosphere even for high-density runs. This method is very convenient and it generally gives the density value within 1%.

This value is in agreement with this 1% limit, with the density value derived from PVT.¹⁰ C₀ is the specific activity of the diffusion sample.

(vii) Step (ii) is repeated; this makes it possible to check that the Kr⁴⁰ concentration in V is maintained constant during the diffusion process.

The temperature of the diffusion cell is measured by a Pt thermometer¹¹ with a sensitivity of ± 0.01 °K; this thermometer is held mechanically very tight to the diffusion cell. We also checked that along our diffusion cell the temperature gradients were less than 0.01 °K. This indicates, as does the very good reproducibility of Table I, that we can exclude thermal convection. The temperature control is obtained by regulating the vapor pressure over the CHClF₂ (freon 22) bath by a bellows manostat¹² capable of controlling the pressure to better than 0.4 Torr. This value at 220 °K gives ΔT ≈ 0.02 °K. This stability limit is in agreement with the response of the Pt thermometer. As mentioned before, the pressure of Kr in V is read from TX₁ which has a precision of 2 × 10⁻⁶ atm.

The knowledge of the temperature allows us to derive the density using the PVT data available in the literature.¹⁰ Taking into account the errors in T, in p, and in the graphic interpolation of the data, we find the following results for D in CG.

<table>
<thead>
<tr>
<th>Run</th>
<th>P (atm)</th>
<th>T (°K)</th>
<th>ρ (g/cm³)</th>
<th>t (sec)</th>
<th>D (cm² sec⁻¹)</th>
<th>Dp(T²)⁰.⁵² (g cm⁻³ sec⁻¹)</th>
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<tbody>
<tr>
<td>1</td>
<td>65.88</td>
<td>232.99</td>
<td>0.46 ± 0.01</td>
<td>1198</td>
<td>5.69 ± 0.34</td>
<td>2.47 ± 0.22</td>
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<tr>
<td>2</td>
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<td>232.97</td>
<td>0.455 ± 0.01</td>
<td>3361</td>
<td>6.08 ± 0.35</td>
<td>2.63 ± 0.21</td>
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<tr>
<td>3</td>
<td>67.45</td>
<td>232.04</td>
<td>0.85 ± 0.01</td>
<td>1799</td>
<td>3.22 ± 0.17</td>
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<tr>
<td>4</td>
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<td>0.367 ± 0.007</td>
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<td>2.42 ± 0.29</td>
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<tr>
<td>5</td>
<td>71.0</td>
<td>223.3</td>
<td>0.74 ± 0.01</td>
<td>1800</td>
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<tr>
<td>6</td>
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<td>0.75 ± 0.01</td>
<td>1319</td>
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<tr>
<td>7</td>
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<td>1.307 ± 0.005</td>
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<td>1.85 ± 0.09</td>
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<td>1.285 ± 0.005</td>
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<td>1.185 ± 0.005</td>
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<td>2.36 ± 0.12</td>
<td>2.81 ± 0.15</td>
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<td>11</td>
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<td>1.12 ± 0.01</td>
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<td>2.47 ± 0.16</td>
<td>2.78 ± 0.20</td>
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<td>1804</td>
<td>3.05 ± 0.21</td>
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<td>1.533 ± 0.005</td>
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<td>1.99 ± 0.02</td>
<td>3125</td>
<td>0.615 ± 0.026</td>
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<td>1.45 ± 0.06</td>
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<tr>
<td>18</td>
<td>97.35</td>
<td>183.57</td>
<td>1.91 ± 0.02</td>
<td>2408</td>
<td>1.51 ± 0.07</td>
<td>2.13 ± 0.11</td>
</tr>
<tr>
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<td>220.25</td>
<td>1.228 ± 0.010</td>
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<td>2.04 ± 0.11</td>
<td>2.59 ± 0.15</td>
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<td>3.62 ± 0.40</td>
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available PVT data, we derive the density with a maximum error of 2% at low densities and 0.5% at high densities. These density values agree very well, within the stated errors, with those derived from the measurement of the total amount of the capillary content, as we said in step (vi). For details and drawings on the experimental apparatus, we refer the reader to our internal report LNF 71/33 of the National Laboratory of Frascati.

**EXPERIMENTAL RESULTS**

The self-diffusion coefficient $D$ can be evaluated by solving the Fick law in the case of a one-dimensional capillary connected to an infinite source:

$$
\frac{C_t - C_0}{C_s} = \frac{8}{\pi} \frac{t}{L} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2}{4L^2} \frac{(n_L + \Delta n_L)^2}{D_L} \right),
$$

where $L$ is the effective capillary length (in our case the capillary has a diameter of 0.07 cm and an effective length of 4.6 cm after one correction for the penetration of SV and SC in C1, $t$ is the diffusion time, and $C_0$ and $C_t$ are the activities of the standard and diffusion samples. $C_0$ and $C_t$ are measured in counts per minute per Torr in CG. The counts are corrected for the background and the dead time of the counter. The errors in $C_0$ come from the statistical error of the counts and from the error in the value of the pressure in CG obtained from TX2 (the sensitivity of TX2 is $\sim 50$ mTorr). The indeterminacy in the knowledge of the value of $L$ affects the absolute value of $D$ by an error which is smaller than 2%. The error on $t$ is smaller than 0.5% in every run and therefore is negligible with respect to the other errors. The values of $D$, calculated from Eq. (1), according to our measurements are reported in Table I. Since the errors in $C_0$, $C_t$, and $\rho$ increase with the decrease of $\rho$, we cannot measure $D$ with an accuracy of better than 10% at densities lower than 0.35 g/cm$^3$ using the diffusion cell we have at our disposal.

From Table I we can see the reproducibility of $D$ is very good, even for diffusion times changing by a factor of 3.

Until now, few experimental data on self-diffusion in Kr are available in the literature. In particular, data are given only at room temperature for densities lower than the critical density and at temperatures near the triple point for high density. Our data are in good agreement with the literature if the correction for the temperature difference is taken into account.

**DISCUSSION**

To describe the data of Table I it is necessary to choose the more representative thermodynamic variables. Recently it has been shown that for the transport properties in dense fluids the most significant thermodynamic variables are density and temperature. Moreover, the dependence on the density is much stronger than the dependence on the temperature. Our self-diffusion data enable us to analyze only the dependence of $D$ on the density. For this reason we prefer to scale these data at exactly the same temperature, i.e., 220 °K. The temperature correction can be made quite confidently using the results either of the molecular-dynamic computations or of the self-diffusion in CH$_4$. In both cases we find that, at least in our range of densities and temperatures, the behavior of $D$ at $\rho = \text{const}$ is of the type $D = A T^{0.3}$, where $A$ is a constant dependent only on the density. This relationship should not be considered a physical law but rather a useful interpolation formula.

Furthermore, we wish to point out that a change in the power of $T$ from 0.7 to 1.1 does not imply a change in the self-diffusion coefficient greater than the experimental error of $D$. This is true for our case since the temperatures of the various measurements do not differ much from 220 °K.

In Fig. 3 our experimental values of $D$, reduced at 220 °K, are reported together with those obtained from the molecular-dynamic values given in Table I of Ref. 2. The curve shown in Fig. 3 is the third-order polynomial best fit, which has been reported to describe the self-diffusion in CH$_4$. The polynomial has been converted for Kr at 220 °K using the principle of corresponding states.

First of all, we want to consider the comparison between our experimental data and the molecular-dynamic results. We see that at high densities the agreement is rather good, as has already been shown for the case of Ar. At intermediate densities there seems to be a discrepancy outside the experimental errors. Unfortunately, there are not enough data available for the molecular-

![Fig. 3. Self-diffusion in Kr at 220 °K: (1) dots with vertical bar, the experimental results of the present work; (2) stars, results from molecular dynamics as in Table I of Ref. 2; (3) solid line, behavior of self-diffusion following the CH$_4$ results (Ref. 17).](image_url)
dynamic calculations in this density region to allow us to establish this discrepancy in a definite way. However, if this disagreement were confirmed, we would have to conclude that it is not correct to use the Lennard–Jones potential for describing a noble-gas fluid in a large range of density.

From the comparison between the behavior of the self-diffusion in Kr and in CH₄, we can see that the qualitative shape is the same. However, from a quantitative point of view there is a progressive disagreement in the high-density region. Also, around the critical density the small bump present in Kr is completely outside the CH₄ behavior.

A very interesting situation has been pointed out by Alder and Wainwright concerning the atomic motion in dense fluids. Analyzing their computer experiments on hard-sphere fluids, they found that at intermediate densities there is an unexpected long persistence of velocity correlations which leads to enhanced transport coefficients with respect to the ENSKOG values. Moreover, analyzing the CH₄ self-diffusion experiments, it has been found that the same phenomenon is also present.

The same analysis was made for all the experimental results of the self-diffusion in Kr. In Fig. 4 we report the behavior of the hard spheres and the data for CH₄, Ar, Krypton, and Kr, all as the ratio of the diffusion coefficient to the ENSKOG value, as a function of the density.

To evaluate the diffusion coefficient from the ENSKOG theory in the case of Ar, Krypton, and CH₄ we need the effective core sizes which are deduced from equilibrium data within the framework of the van der Waals theory. This can be done from a plot of $pV/Nk_B T$ against $1/T$ at a given density. The core size is then determined at that density and at a given temperature from the high-temperature intercept of the slope at the temperature with the known hard-sphere equation of state. The $PVT$ data used for Ar are taken from Ref. 21 and those for Kr from Ref. 10; the calculations for CH₄ are available in Fig. 1 of Ref. 20. These values of effective core sizes for Kr turn out to be 3.40 Å at 308.2 °K, 3.45 Å at 222 °K, and 3.50 Å at 125 °K. The values of $g(0)$ have all been taken from Monte Carlo calculations.

Looking at Fig. 4 we can notice the following features:

(a) The experimental points of Ar and Kr fit rather well the same curves as predicted by the principle of corresponding states.

(b) Hard spheres, CH₄, and noble gases behave qualitatively in the same way. For all of them $D/D_E$, as a function of the density, goes through a maximum greater than 1 at densities greater than the critical density, and then decreases very rapidly in the high-density region.

(c) However, the behavior of hard spheres, CH₄, and noble gases is quantitatively different. The width of the curves decreases and their maximum decreases as we move towards lower densities as we consider the hard-sphere curve, the CH₄ curve, and the noble-gases curve, respectively.

Three possible reasons can be suggested for these differences: (i) the presence of an attractive part in the intermolecular potential; (ii) the presence of internal degrees of freedom; (iii) a different behavior of the repulsive part of the interatomic potential.

We do not think point (i) is relevant. In fact, although CH₄ and noble gases both have an attractive part in the interatomic potential, we find the same discrepancy between them as between hard spheres and CH₄. Point (ii) also seems to us to be irrelevant, since according to this hypothesis it is not clear why CH₄ must have an intermediate behavior between hard spheres and noble gases. Point (iii) seems to us to be more reasonable. In fact, previous measurements of the pressure dependence of the diffusion coefficient have been interpreted in terms of the greater steepness of the repulsive part of the interatomic potential in the CH₄ with respect to noble gases.

Finally we want to note that, looking at Fig. 3,
the "normal behavior" of $D$ for noble gases in the critical region seems to be represented by $D_0$
slowly increasing with $\rho$ at constant temperature. The choice of the normal behavior as $D_0 = \text{const.}$
as found in the CH$_4$ case, would imply an under-estimate of about 15%. We want to stress that
our data have been taken at a temperature 4.76% higher than $T_c$, which is quite well outside the
critical region, as we can deduce from the equilibrium properties and the thermal conductivity
measurement. As a result no noticeable critical effects are present. On the other hand, we are
very near to $T_c$ as far as the temperature dependence of the normal behavior is concerned.

Finally we would like to mention the density expansion of the transport properties. We do not
try to fit our data with a polynomial of powers of density. We think that, in order to proceed cor-
rectly with such a development, the behavior of low density must be known very well. Otherwise all
the coefficients derived are meaningless.

CONCLUSION

The experimental results of self-diffusion in Kr clearly require more molecular-dynamic calcula-
tions for a Lennard–Jones fluid at intermediate range of density. Such calculations are needed
both for understanding the possible failure of the two-body potential and for clarifying the situation
of vortices in fluids where a Lennard–Jones potential is present. The behavior of polyatomic
molecules seems to be different from the behavior of the monatomic molecules only for details. The
"normal behavior" in the critical region has been indicated.

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Rowlinson, and G. S. Rushbrooke (North–Holland, Amsterdam, 1968), Chaps. IV and V.


4J. D. Noble and M. Bloom, Phys. Rev. Letters 14, 445 (1965); for the criticism see p. 429 or Ref. 6.


8The natural Kr has been supplied by Rivoira with a
99.9% parity. Kr$^{85}$ has been supplied by The Radio-
chemical Centre of Amersham.

9$\alpha$ is a Geiger–Muller counter tube with end window 2
mg/cm$^2$ thick.


11Rosemount platinum resistance thermometer model No.
118G; $R (0 ^\circ \text{C}) = 100 \Omega$.

12H. White, Experimental Techniques in Low Tempera-
Chap. VII.


16To use the molecular-dynamics computations for Kr we
used the values $\epsilon/k_B=165$ $\text{K}$ and $\sigma=3.85$ Å. These
values have been deduced from the critical-point and the
triple-point parameters [J. De Boer, Physica 14, 139 (1948)]. They also agree quite well with the values
deduced from the second virial coefficient [N. J. Trappenier,

17The polynomial used, $D_0=0.55 \times 0.25 \rho -0.01 \rho^2$
$-0.20 \rho^3 \times 10^{-4}$, has been scaled from Ref. 6 with the
CH$_4$ parameters $\epsilon/k_B=147$ $\text{K}$ and $\sigma=3.71$ Å.

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