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Abstract. The properties of dense H₂–He mixtures have been measured in a diamond anvil cell (DAC) at $T = 296$ K by direct visualization and Raman spectroscopy. The discrepancies that existed between the two previous high-pressure works have been resolved; they stemmed from an underestimation of the homogenization time of the mixture which is prepared for loading the DAC. The Raman spectroscopy measurements confirm the existence of a cusp on the fluid–fluid coexistence curve. The miscibility of one component in the solid of the other has also been investigated.

1. Introduction

Among dense binary systems, H₂–He mixtures are probably of the greatest physical interest. First of all, they should be the most amenable to a theoretical description, owing to the conceptually simple electronic configurations of their two components. That is why the results of measurements of their properties under pressure are generally used as reference data for testing dense mixture theories, which is all the more important because numerical experiments by simulation are very difficult for dense mixtures [1]. In addition, a wide variety of physical phenomena, which extends from those of pure solid H₂ to those of a H₂ molecule in a He matrix, can be probed on the same dense systems, with, at the present time, a special interest in the evolution of the electronic properties and metallization of solid H₂ [2]. Finally, H₂–He mixtures have an enormous cosmological importance: the Jovian planets are essentially constituted of H₂ and He and the recent observational data have put severe constaints on the models of their interiors. Measurements of the phase diagram, sound velocity or equation of state of H₂–He mixtures under very high pressures are certainly needed for improving these interior models [3].

The first measurements of the H₂–He binary phase diagrams carried out under pressure were performed by Streett with a vapour recirculation system up to 0.9 GPa and 100 K [4]. Thanks to the development of the DAC some ten years ago, experimentalists were given a new opportunity to considerably extend their (P, T) domain of investigation [5]. The H₂–He mixtures were then the first mixtures to be studied in a DAC: two groups have independently measured the H₂–He binary phase diagram up to 373 K and 15 GPa [6, 7]. In both cases, the binary phase diagram around room

temperature was found to be of the eutectic type with a fluid–fluid separation of phases. However, large differences existed between the results reported by the two groups, as if the two binary phase diagrams were shifted one from the other along the He concentration axis. It seems that these discrepancies stemmed from errors made in the determination of the *in situ* concentration of the sample which cannot be measured directly. However, the reasons for that error were not clear. Besides the will to understand such a problematical disagreement, the present study was motivated by the fact that, since H_2–He systems were the first mixtures to be studied in a DAC, the usefulness of this set up for the study of dense mixtures had still to be proved and that, in addition, reliable experimental data were needed in order to unambiguously test the recent theories of dense mixtures which were practically all applied to H_2–He binary systems.

Firstly, in section 2, we present measurements of the homogenization time of the initial mixture which is used to load the DAC. This explains the disagreement between the two previous determinations. The new measurements of the properties of the H_2–He mixtures at 296 K will then be reported and discussed.

2. Analysis of the discrepancies

Streett has measured with great accuracy the properties of H_2–He mixtures at temperatures below 100 K and up to about 0.9 GPa [4]: the H_2–He binary phase diagram was found to be of the eutectic type with a fluid–fluid separation of phases. The critical point was around 58 mol% He and the composition of the H_2-rich fluid at the triple point changed from 5 mol% He at 0.06 GPa to 19 mol% He at 0.95 GPa. In a first examination, the two subsequent DAC determinations of the H_2–He binary phase diagram at higher pressures [6, 7] seem to be in good agreement: in both cases, the binary phase diagram was found to be of the eutectic type with a fluid–fluid separation of phase and the (P, T) loci of the critical and triple points fall on the extrapolation of the low temperature measurements of Streett. However, strong disagreements appear if the third parameter, the He concentration, is considered. More explicitly, the He concentration of the critical point and of the H_2-rich fluid phase at the triple point were respectively 60 mol% and 22 mol% in the work of Schouten *et al* [6] instead of 70 mol% and 50 mol% in the work of Loubeyre *et al* [7]. It therefore seems as though there have been lax measurements and control of the *in situ* He concentration in either one or both experiments.

The *in situ* concentration of He cannot be directly measured but it is assumed to be equal to that of the initial gas mixture that is made in a gas container under a pressure of roughly 10 MPa. Still, changes of concentration can occur in the loading of the cell or upon variations of pressure during the experimental run. Before the present study was done it was very difficult to discriminate between these two sets of data. On one hand, H_2 is known to diffuse easily in metals and so the leaking out of H_2 during the loading of the DAC or in the metallic gasket which confines the sample could be the most simple explanation for the uncontrolled changes of the He concentration. This would then give a measured binary phase diagram in which the transition lines are systematically shifted to the low-He-concentration region, and hence would tend to give credit to the measurements of Loubeyre *et al* [7]. However, great care was paid by the two groups to check for this problem, mainly by testing the reproducibility of their measurements for various loadings, and nothing wrong was detected in either case. On the other hand, the results
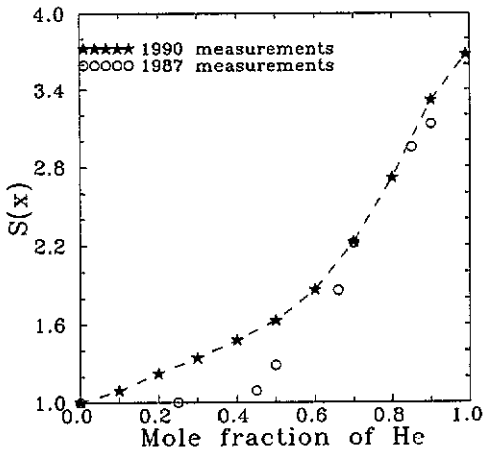
Figure 1. The ratio, $S(x)$, of the shift with pressure of the vibron frequency $Q_1(1)$ of the H_2 molecule in H_2–He fluid mixtures to that in pure H_2 plotted against the He concentration. The stars correspond to the present study and the circles to our previous measurements [7].
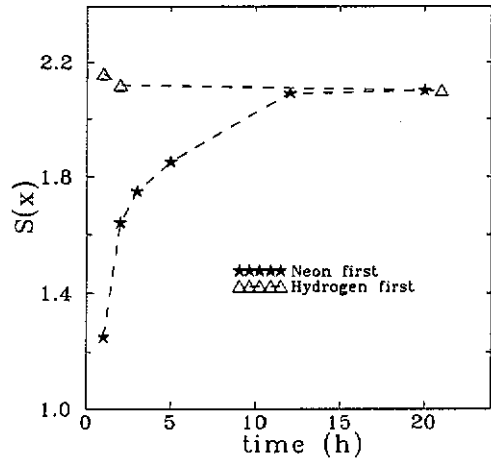
Figure 2. Value of $S(x)$ in the homogeneous H_2–Ne fluid mixture after its loading into the DAC plotted against the time over which the initial mixture has been stabilized. The stars or the triangles represent the loading of initial mixtures for which Ne or H_2, respectively, was put in the gas container first.

of Schouten *et al* [6] seem to agree much better with the extrapolation of the low-temperature measurements of Streett [4] which suggest that the critical and the triple compositions should not change much at higher pressures and should be around 60 mol% He and 20 mol% He, respectively.

H_2 and He can be considered as almost ideal gases for pressures below 10 MPa and the mole concentration of the initial mixture is calculated to a very good approximation with the ratio of the partial pressures of the two components. One difference between our experimental procedure and that of Schouten *et al* is that we kept the initial mixture for about 5 h before loading it in the DAC (in the following this time will be called the stabilization time) whereas Schouten *et al* waited at least overnight before loading the cell.

In our recent measurements of the H_2–Ne binary phase diagram [8] in a DAC, we found that the stabilization time of the initial mixture had an influence on the measurements. We then tried to measure this effect with the help of the $S(x)$ function. As explained below, the $S(x)$ function, which was introduced in our first article on H_2–He mixtures [7], quantifies the contribution to the shift of the vibron frequency of the H_2 molecule that is due to the effect of the He (or Ne) concentration of the surrounding mixture. $S(x)$ is independent of pressure and, as seen in figure 1, is a univocal strongly increasing function of the He (or Ne) concentration of the mixture, and therefore can be used as a sensitive *in situ* concentration gauge.

In figure 2, the value of $S(x)$, measured in the H_2–Ne homogeneous fluid mixture contained in the DAC just after its loading, is plotted as a function of the time over which the initial mixture of known partial pressures of H_2 and Ne was stabilized. This curve shows that the initial mixture takes a very long time to become homogeneous: for long enough stabilization times, independently of which component is put first in the gas

cylinder, the $S(x)$ value is always the same and corresponds to the concentration of the homogeneous initial mixture that is given by the ratio of the partial pressures of the two components, H_2 and Ne in this case. However, for shorter stabilization times, the initial mixture is heterogeneous: if the partial pressure of Ne is put first in the gas cylinder, a smaller $S(x)$ value is measured in the sample chamber, which means that the loaded concentration is richer in H_2. This means that the Ne gas has somehow stayed at the bottom of the gas cylinder. Conversely, when the H_2 gas is put first, the loaded concentration is richer in Ne. This effect, which has been quantitatively studied in the H_2–Ne case, is also valid in the H_2–He case. As a proof, one can see in figure 1 that the $S(x)$ function, determined previously in our 1987 study [7] of H_2–He, is systematically lower than that found using the present determination. In the previous case the He gas was put first in the gas container, and the stabilization time was around 4 h; whereas in this case at least 24 h elapsed before loading the DAC. The H_2–He mixtures were then not homogeneous, the He being at the bottom of the gas container, and the loaded mixture being thus richer in H_2. We were thus measuring the properties of mixtures having different He concentrations from those predicted. This explains why the determination of the H_2–He binary phase diagram made by Schouten *et al* was correct and ours in error concerning the He concentration parameter.

However, another discrepancy was existing between these two determinations which cannot be resolved by the analysis of errors presented above: we have reported a cusp on the He-rich side of the fluid–fluid coexistence curve that Schouten *et al* did not. We could point out such a feature by measuring the He concentration continuously in both separated fluid phases with the $S(x)$ *in situ* concentration gauge. Indeed, the direct visualization method is not very suitable for the detection of such fine details of the phase diagram, and it is not surprising that Schouten *et al* [6] did not report such a cusp. It was important to repeat these measurements carefully in order to confirm the existence of such a cusp because, as it was explained in our previous article, this could be the signature of an interesting evolution with temperature of the binary phase diagam towards a topology with a re-entrant fluid phase and three critical points. In the next section we present our new measurements made using direct observation and Raman spectroscopy. They have been extended in the solid phase and now constitute a complete and accurate determination of the properties of H_2–He mixtures at high density and at 296 K.

Firstly, however, it is interesting to wonder if we can understand the curve reported in figure 2. We are going to estimate the homogenization time of an H_2–Ne mixture under a pressure of 10 MPa by considerations of elementary transport theory. Using Fick's well-known second law of diffusion, it is easily shown that a concentration disturbance of wavevector K decays in a time τ equal to $1/(D_{12}K^2)$, where D_{12} is the diffusion coefficient of the mixture [9]. D_{12} for the H_2–Ne mixture at 10 MPa can be easily estimated [9] and was found to be equal to 0.0054 cm^2 s^{-1}. In our experiment, the H_2–Ne mixture was prepared in a gas container 50 cm long, and consequently the largest wavelength of the concentration gradient at the beginning, which thus gives the longest decay time, is 100 cm. With such input data, we found that the time after which the H_2–Ne mixture should be homogeneous, is 13 h, which is in very good agreement with the present observation, as seen in figure 2. The same calculation performed for H_2–He mixtures, with a diffusion coefficient $D_{12} = 0.0037$ cm^2 s^{-1} [9] gives a homogenization time of 19 h.

The result of this section is that the homogenization time of a simple molecular mixture under 10 MPa is longer than what we previously assumed. It can be estimated by simple transport considerations, and so when doing any study of dense mixture in a

DAC, one should verify that the initial mixture is stabilized over a long enough time before it is loaded into the DAC.

3. Measurements

For generating high static pressures, the membrane DAC (MDAC) has been used. Its design and loading system have been presented elsewhere [10]. Suffice to say, that the MDAC is particularly well adapted for such studies of dense mixtures: the force on the piston is supplied by an inflated membrane which allows very smooth variations of pressure. The phase transitions can thus be finely probed at a given temperature, whereas with other types of DAC one has to monitor them by varying the temperature. The initial mixture was made in a gas container under a pressure of 10 MPa. The concentration of the mixture was calculated to a very good approximation, by the ratio of the partial pressure of its two components, H_2 and He, and the maximum error then made has been estimated from second virial calculation to be of the order of 3×10^{-3}. The initial mixture was stabilized for at least 20 h before its loading through a compressor in the DAC. Beryllium–copper gaskets were used in order to prevent any diffusion of H_2. The pressure was measured by the ruby scale with a coefficient $0.0757 \text{ cm}^{-1} \text{ GPa}^{-1}$.

Two kinds of measurements were performed: the determination of the pressure of the phase transitions that were detected by the visual observation of the sample chamber through a microscope, and the Raman spectroscopy of the Q_1 vibron mode of the H_2 molecule. In our previous work [7], we have shown that the Q_1 vibron frequency was strongly dependent on the He concentration of the fluid mixture surrounding the H_2 molecule. In figure 3, we have reported the Raman frequency of the Q_1 vibron of H_2 in mixtures of various He concentrations as the pressure is increased. In the homogeneous fluid phase the measurements are denoted by crosses and in the fluid–fluid separated domain above 5.4 GPa they are plotted as triangles. The strong shift of the frequency of the Q_1 vibron mode with the He concentration is clearly demonstrated here. This is quantified by the $S(x)$ function, which has been defined in our first paper [7], and is given by:

$$S(x) = (Q_1(x, P) - Q_1(0, 0))/(Q_1(0, P) - Q_1(0, 0))$$

where $Q_1(x, P)$ is the Raman frequency of the vibron Q_1 mode of H_2 at a pressure P in a mixture of He concentration x, and $Q_1(0, 0)$ is the frequency of the isolated H_2 molecule. The $S(x)$ function is plotted in figure 1 and this clearly shows why the $S(x)$ function can be used as a very sensitive *in situ* concentration gauge.

In the region of fluid–fluid phase separation, two Raman measurements were performed: one in the He-rich fluid, F_2 and one in the H_2-rich fluid, F_1. On the F_2 branch, one can clearly see in figure 3 that there is a cusp at 6.25 GPa of 8 cm^{-1} in magnitude outside the error bars, which are of the order of 2 cm^{-1}. This confirms what we had previously found [7], although the cusp is much less accentuated in the present case. This difference stems from the fact that the Raman peak is very broad with a width of 50 cm^{-1} and very weak at such a small concentration of H_2. Since 1987 we have modified our optical set up and we now use selected diamonds with a very low luminescence level, which cuts down the interference pattern out of which it was sometimes difficult to extract the Raman peak. In doing so the quality of the Raman spectra was greatly improved. A graph of a series of Raman spectra at increasing pressures in the vicinity of the cusp is given in figure 4. One can see that the peaks are now well resolved and that
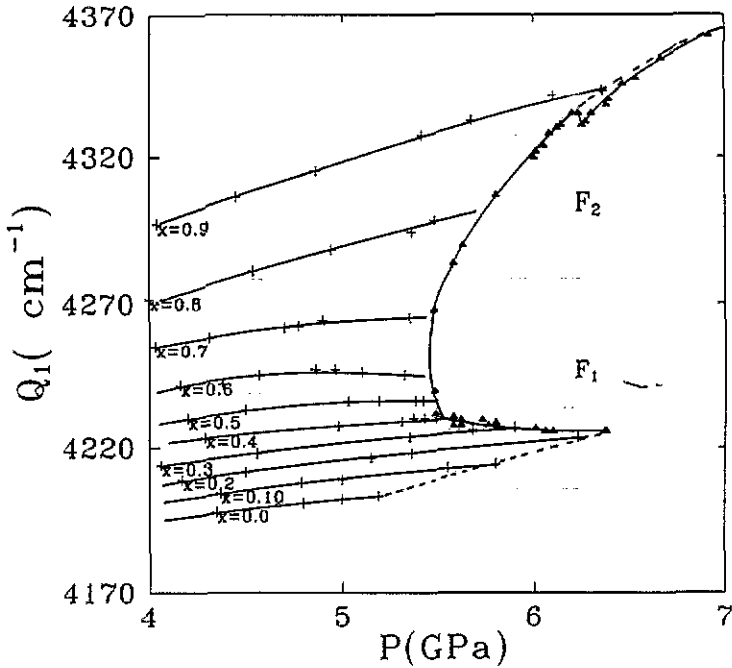
Figure 3. Evolution with pressure of the Raman frequency of the Q_1 vibronic mode of H_2 in H_2–He fluid mixtures of various He concentration, x. The crosses correspond to the homogeneous fluid phase and the triangles to the two branches, F_1 and F_2, of the fluid–fluid coexistence curve. On the F_2 branch there is a cusp at 6.25 GPa.

their positions, which are related by a broken line, clearly present a cusp-type evolution with pressure. Our 1987 measurements were only qualitatively correct. With the $S(x)$ concentration gauge, the $F_1 + F_2$ fluid–fluid coexistence curve could be inverted from the Raman data, plotted as triangles in figure 3. Ideally, in a single run one could determine continuously the $F_1 + F_2$ coexistence curve, since when crossing it at a given pressure any mixture will separate into the same two fluids whose concentrations are given by the intersection of the line representing the pressure of the mixture with the fluid–fluid coexistence curve, but whose relative amounts are given by the lever rule. In figure 5, the direct-visualization measurements of the $F_1 + F_2$ coexistence curve are compared with its determination by Raman measurements; the agreement is very good. More interestingly, it is seen that this curve is pinched on the He-rich fluid side at around 6.25 GPa. This feature is directly obtained from the cusp observed in figure 3 on the curve of the vibron frequency of H_2 in the separated fluid F_2. As reported in our previous article, we have observed once more that the fluid always separates in a He-rich fluid bubble surrounded by a H_2-rich fluid, which means that the surface tension is larger in the He-rich fluid than in the H_2-rich one. We also observed a density inversion just above the critical point: that is, below 5.47 GPa the fluid richer in H_2 is denser than the one richer in He, this being contrary to what is expected from an ideal mixture. Finally, our direct observation measurements of the fluid–fluid coexistence curve are now in very good agreement with the ones of Schouten *et al* [6].

We have also searched for the solubility of H_2 in solid He and for that of He in solid H_2 by looking at the phase transitions of binary mixtures of various low He or high He
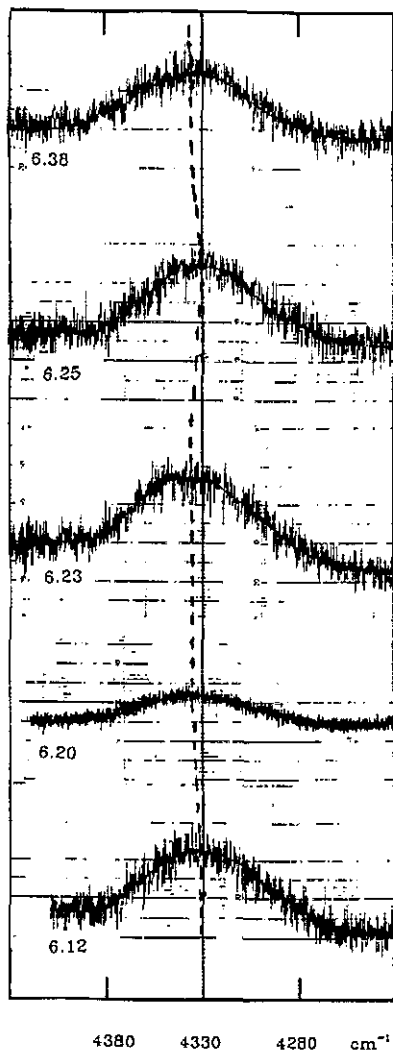
Figure 4. The graph of a series of Raman spectra of the Q_1 vibron mode of H$_2$ in the F$_2$ fluid phase at increasing pressure in the vicinity of the cusp. Their intensity is plotted, in arbitrary units, against the frequency, in cm^{-1}. The pressure is indicated in GPa and the broken line interpolates between the position of the peaks at the different pressures.

concentrations. Below 12 GPa, the separated solid phase rich in H$_2$, S$_1$, can only be in equilibrium with a fluid, as seen in figure 6. The $S(x)$ concentration gauge is not sensitive enough in the low He concentration range, and this renders impossible any determination of the He concentration of S$_1$ by Raman measurements. The direct-observation method is also not very accurate because the separated fluid in equilibrium with S$_1$ generally forms a layer which is hard to detect when in small amounts. Despite that, we have found that the He concentration of S$_1$ is less than 3% when in equilibrium with fluid F$_1$. This concentration then decreases with pressure. Above 12 GPa the mixture separates into two solids and the immiscibility of H$_2$ and He is practically total: there is less than 1% He in solid H$_2$ and *vice versa*. We have also determined two triple points: the first one, S$_1$ + F$_1$ + F$_2$, at a pressure of 6.4 GPa with the He concentration of the H$_2$-rich fluid phase F$_1$ equal to 23 mol%, and the other one, S$_1$ + F$_2$ + S$_2$, at 11.9 GPa with the He concentration of the He rich fluid phase F$_2$ equal to 99 mol%. The complete binary phase diagram at $T = 296$ K is reported in figure 6.
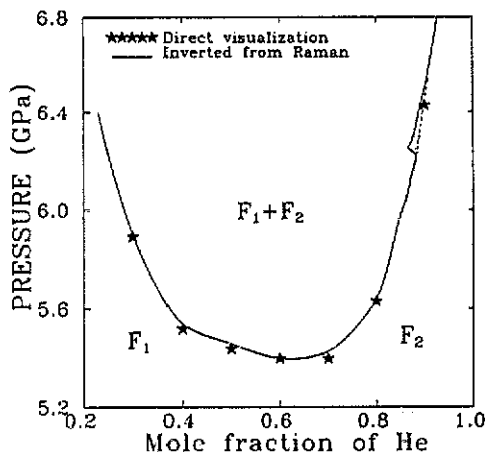
Figure 5. The fluid–fluid coexistence curve of the H$_2$–He binary phase diagram at 296 K. The stars represent direct visualization measurements and the solid curve is inferred from the Raman measurements.
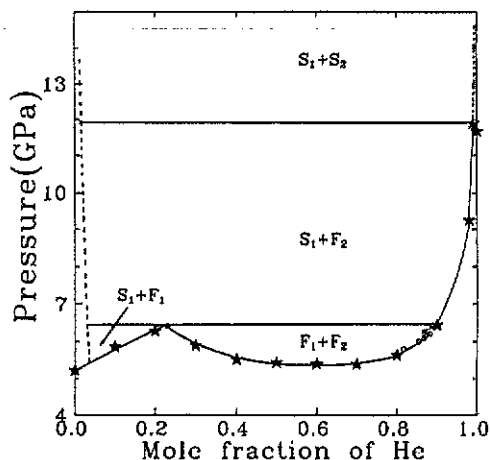
Figure 6. The H$_2$–He binary phase diagram at 296 K. The stars are direct visualization measurements, and the circles are inferred from Raman measurements. The broken lines show the upper limits of the miscibility in the solid phase.

4. Discussion

DAC measurements of the H$_2$–He binary phase diagram stand out as resulting from the highest-pressure experiments on fluid mixtures, with the significant result that they exhibit a supercritical fluid phase separation in the (P, T) region where molecular interactions are almost totally repulsive. Such a fluid–fluid coexistence does not exist for binary mixtures of hard spheres and so has been neglected in many available theoretical works. Recently, various theoretical calculations have aimed to reproduce these H$_2$–He DAC experimental data. In the fluid phase, the first calculations were performed with variational perturbation theory in conjunction with the Van der Waals one-fluid approximation (VDW1F) [11, 12]. In these calculations, the parameters of the H$_2$–He interaction were determined by matching calculations to experimental data. A general good agreement with the experimental fluid–fluid coexistence curve was then obtained. Other calculations were performed with the HMSA integral equation method [13] and the same parameters of the binary potential; they are also in fair agreement with experiment and moreover they can give the structural properties of the fluid mixture. These two calculations were coupled to an empirical freezing rule so as to obtain the liquidus of the solid–fluid equilibria. However, in order to address the question of the solubility of one component in the solid of the other, solid mixture theories are needed. Two such calculations were recently performed: the first, the density functional theory of freezing [13], was applied to H$_2$–He mixtures but gives only a semi-quantitative agreement with experiment. The second was the one-component description of the mixture extended in the solid phase with a correlated cell-model calculation [14]. In the latter, the agreement with the present experimental data is as good as in the fluid phase: a solubility of 4% He in the H$_2$-rich solid S$_1$ is obtained when it is in equilibrium with the fluid phase F$_1$, which then evolves to a practically total separation of solid phases above 12 GPa with less than 1% solubility of one component, H$_2$ or He, in the solid of the other.

But none of these calculations gives a cusp on the He-rich side of the fluid–fluid coexistence curve, which is in opposition to what is observed experimentally. This cannot be imputed to the possible errors of the above-mentioned calculations of the H_2–He binary phase diagram since they are in good agreement with the quasi-exact results of simulations [11, 13]. If the parameters of the unlike interaction are changed, the shape of the fluid–fluid surface remains essentially the same with only a change in its (P, T) locus. Consequently, the existence of the cusp suggests that the interactions of H_2–He mixtures are not as simple as the pair-potential forms assumed. It is probable that more complicated intermolecular potentials would have to be considered.

In our previous paper, we interpreted the cusp on the fluid–fluid coexistence curve as an intermediate stage in the evolution of the fluid–fluid domain towards its closing up at higher densities [7]. The binary phase diagram would then present a reappearing fluid phase and three critical points. The estimation of the temperature above which this would occur was certainly underestimated in our previous study at 295 K and 373 K because the magnitude of the cusp was largely overestimated, as discussed above. Temperatures much higher than 373 K are certainly needed in order to confirm this hypothesis but this is going to be technically very demanding because gasket material other than BeCu would have to be used, and also because at high temperatures the H_2 chemically reacts with diamond.

5. Conclusion

In the present work we have carefully redone the measurements of the H_2–He binary phase diagram at $T = 296$ K. The puzzling discrepancies between the concentration measurements of the two previous DAC experimental works have been resolved: the initial mixture has to be stabilized for a long enough time before its loading into the DAC, and this was underestimated in our previous study. We have shown that the homogenization time of the initial mixture made in a gas container, can be estimated by simple transport theory considerations. Such an estimation should now be performed as a preliminarily stage to any study of dense mixtures with a DAC. Also, suspicions about the usefulness of the DAC for studying dense mixtures were unjustified; it is very well adapted for such experimental work. The present measurements are now in very good agreement with the ones of Schouten *et al* as regards the direct visualization in the fluid phase. They are, however, more complete since by doing Raman spectroscopy measurements, finer features of the binary phase diagrams were obtained. In particular, the cusp on the He-rich fluid side of the $F_1 + F_2$ coexistence curve, already reported in our previous study, was confirmed. This is a possible indication that the fluid–fluid coexistence curve will close up at high temperatures. The investigation was also extended in the solid domain, and a very small miscibility of each component (H_2 or He) in the solid phase of the other was found. The present work should motivate further theoretical and experimental studies. Experimentally, the properties of H_2–He mixtures should be investigated at high temperatures in order to see if their binary phase diagram evolves toward the suggested, very interesting topology of a reappearing fluid phase with three critical points. Theoretically, the physical properties of dense H_2 should be carefully

analysed in order to determine any deviation from a pair potential description of its interaction which could explain such a cusp on the fluid–fluid coexistence curve.

Acknowledgments

References

[1] Ree F H 1989 *Simple Molecular Systems at Very High Density* (New York: Plenum)
[2] Mao H K and Hemley R J 1989 *Science* **244** 1462
[3] Hubbard W B 1989 *Simple Molecular Systems at Very High Density* (New York: Plenum)
[4] Streett W B 1973 *Astrophys. J.* **186** 1107
[5] Jayaraman A 1983 *Rev. Mod. Phys.* **55** 65
[6] Schouten J A, van den Bergh L C and Trappeniers N J 1985 *Chem. Phys. Lett.* **144** 40; 1987 *Physica* A **141** 524; 1986 *Fluid Phase Equilibria* **32** 1
[7] Loubeyre P, LeToullec R and Pinceaux J P 1985 *Phys. Rev.* B **32** 7611; 1987 *Phys. Rev.* B **36** 3723
[8] Loubeyre P, Jean-Louis M, LeToullec R and Pinceaux J P unpublished
[9] Hirschfelder J O, Curtiss C F and Byron Bird R 1964 *Molecular Theory of Gases and Liquids* (New York: Wiley) ch 8
[10] LeToullec R, Pinceaux J P and Loubeyre P 1988 *High Press. Res.* **1** 77
[11] Ree F H 1983 *J. Chem. Phys.* **87** 2846
[12] van den Bergh L C and Schouten J A 1988 *J. Chem. Phys.* **89** 2336
[13] Vos V L, de Kuijper A, Barrat J L and Schouten J A 1991 preprint
[14] Charon L, Loubeyre P and Jean-Louis M *Proc. 28th EHPRG Conf. (Bordeaux, 1990)* unpublished