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Critical line of He-H₂ up to 2500 K and the influence of attraction on fluid-fluid separation

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The Monte Carlo simulation method of Panagiotopoulos has been used to study the fluid-fluid phase behavior of the helium-hydrogen system up to high pressures and temperatures. The influence of the attractive part of the potential has been investigated by carrying out the simulations also for the purely repulsive system. It is shown that fluid-fluid equilibrium in the helium-hydrogen system persists up to at least 700 kbar and 2500 K. The attraction causes a shift of the critical line to higher temperatures. Implications of these results for models of the Jovian planets are discussed.

I. INTRODUCTION

Due to new experimental techniques, mixtures have received a great deal of interest the last decade. Binary mixtures in particular have been investigated at great length since, at high pressures, various phenomena occur that require a substantial extension of our present theoretical insights.¹ Of all binary mixtures, He-H₂ stands out for its importance: first because, despite its simplicity, it exhibits all the characteristic mixture features and secondly because it is of great importance to astrophysics;² the atmospheres around the inner cores of the planets Jupiter and Saturn consist of He-H₂ under extreme temperature and pressure conditions, several thousand K and millions of bars.

Unfortunately, these conditions have proven to be still unattainable for the present static laboratory research. In the diamond anvil cell one now reaches 2–3 Mbar at ambient temperatures in pure systems; for mixtures the pressures have been restricted so far to 100 kbar. In the (dynamical) shock-wave experiments one can realize high temperatures combined with high pressures but all in a less controllable way; the observation of fluid-fluid phase separation, for one thing, seems to be impossible. Therefore, it is clear that, in this field of molecular physics, computer simulations will play an increasingly important role. Due to the innovative simulation technique of Panagiotopoulos,³ one can now simulate fluid-fluid phase equilibria at computational costs which, with the present generation of computers, is manageable.

In an earlier paper⁴ we demonstrated the use of this simulation technique by calculating the fluid-fluid phase separation in He-H₂, interacting through the α -exp-6 potential, at 300 K and about 55 kbar. We found excellent agreement with the experimental data at room temperature, using the interaction parameters for He, H₂, and He-H₂ from literature. We compared our results with the earlier perturbation theory calculations of Van den Bergh and Schouten⁵ who calculated the demixing in He-H₂ up to 1 Mbar using the one-fluid approximation. We obtained much better agreement with the experimental data especially with respect to the width of the binodal curve. In that paper we also showed that attraction is not necessary for phase separation to occur since a system interact-

ing through the repulsive part of the α -exp-6 potential (using the same interaction parameters) also gave a clear phase separation at a somewhat higher pressure.

In the present paper we extend the simulation work on He-H₂ to higher temperatures and thus to higher pressures. We have determined the critical line of this system up to 2500 K and approximately 700 kbar. For the repulsive system we have also calculated the critical line up to 2500 K and to 750 kbar. In Sec. II we give the details on the simulation method used by us, in Sec. III we present the results on the full α -exp-6 system, and in Sec. IV we give the results on the repulsive α -exp-6 system; in both cases we used He-H₂ parameters. In Sec. V, we discuss our results and the consequences for astrophysics, in the case of He-H₂, and for molecular physics by comparison between the full and repulsive system.

II. SIMULATION TECHNIQUE

In this section we shall briefly outline the Gibbs Monte Carlo method of Panagiotopoulos and co-workers. For more details on this method we refer to Ref. 3 and for a theoretical description to Ref. 6.

Consider two simulation boxes, each with their own standard periodic boundary conditions. Box I contains N_I^A particles of species *A*, N_I^B particles of species *B*, and has a volume V_I . Analogously, box II contains N_{II}^A particles of species *A*, N_{II}^B particles of species *B*, and has a volume V_{II} . The total number of particles of either species is conserved. Both boxes have the same temperature *T* and experience the same external pressure *p*. A simulation cycle consists of four different steps: particle displacement, an attempted change in volume, particle transfer, and particle swapping. These steps will now be discussed in more detail.

Particle displacement. In each box separately, all particles are moved in a random fashion. The well-known acceptance probability for these steps is

$$P_{PD} = \min[1, \exp(-\beta\Delta E)] , \quad (1)$$

where ΔE denotes the change in configurational energy and $\beta \equiv 1/k_B T$.

Volume change. The volume is changed at random, for both boxes independently, to ensure that the internal

pressure equals the applied external pressure p . The acceptance probability is given by

$$P_{\text{VR}} = \min \left\{ 1, \exp \left[-\beta\Delta E + N \ln \left(\frac{V+\Delta V}{V} \right) - \beta p \Delta V \right] \right\}. \quad (2)$$

Here, ΔV denotes the change in volume.

Particle transfer. A particle is chosen at random from one of the two boxes and is transferred to the other box. The species of the particle (A or B) as well as the receiving box (I or II) is chosen with fixed (50%) probability. Due to these steps, the equality of the chemical potential of each species in both volumes is guaranteed. The acceptance probability for a transfer of an A particle from box II to box I is given by

$$P_{\text{PT}} = \min \left\{ 1, \exp \left[-\beta\Delta E_{\text{I}} - \beta\Delta E_{\text{II}} - \ln \left(\frac{V_{\text{II}}(N_{\text{I}}^A + 1)}{V_{\text{I}}N_{\text{II}}^A} \right) \right] \right\}, \quad (3)$$

where $\Delta E_{\text{I}} + \Delta E_{\text{II}}$ denotes the energy change due to the insertion of an additional A particle in box I and the extraction of this particle from box II.

At high fluid densities, the acceptance ratio for this step can become very small since many randomly chosen insertion spots will cause (partial-) overlap with the existing particles. To reduce the computational costs of this step we have used the excluded-volume map sampling technique (EVMS).⁷ The receiving box is covered by a $20 \times 20 \times 20$ grid and the positions of the particles are marked on this grid. Whenever a trial position is chosen, one first checks with the grid whether this position will cause overlap or not. If this is indeed the case, the costly calculation of the energy difference ΔE can be skipped and the trial move is rejected immediately. We refer to Ref. 7 for more details on this method.

Particle swapping. As already mentioned in the previous paragraph, the acceptance ratio for the particle transfer step can become quite small at high fluid densities. Another method of speeding up the exchange of particles, necessary for the equality of the chemical potentials, is to swap two particles of different species simultaneously. Since the insertion spot coincides with a newly created vacancy, the acceptance ratio will be much higher. The acceptance probability for a swap of a particle of species A from box I with a particle of species B from box II is given by

$$P_{\text{PS}} = \min \left\{ 1, \exp \left[-\beta\Delta E_{\text{I}} - \beta\Delta E_{\text{II}} + \ln \left(\frac{V_{\text{II}}(N_{\text{I}}^B + 1)}{V_{\text{I}}N_{\text{II}}^B} \right) + \ln \left(\frac{V_{\text{I}}(N_{\text{II}}^A + 1)}{V_{\text{II}}N_{\text{I}}^A} \right) \right] \right\}. \quad (4)$$

At modest pressure we started with an equimolar mixture of 256 particles in each box, randomly placed on an

fcc lattice; this then melted instantaneously. We then, after each run, augmented the pressure, using the end configuration of the lower-pressure run as starting configuration for the next run. Typically, a run consisted of 1000–2000 cycles for equilibration and another 1000–2000 cycles for production. In Ref. 4 it was demonstrated, by a concentration versus the number of cycles plot, that equilibrium established very fast in this system.

During each cycle, all particles in both boxes were attempted to be moved and the volume of the boxes was varied once. We tried to transfer a particle of species A or B (with equal probability) from one box to the other 20 000 times. The swapping of two particles between the boxes was attempted 2000 times. This resulted in several thousands of particles being transferred and several ten thousands of particles being swapped. Each run was divided into ten blocks and the estimated uncertainties in the thermodynamical properties correspond to the standard deviations of the block averages. Due to the attempted insertion of particles in both boxes, we found, at no additional costs, an estimate for the chemical potential μ of both species using the Widom test-particle method;⁸ these were used to check that μ was equal for both species in both boxes.

During the run a histogram was constructed on the mole fractions as they occurred in both boxes; this provides an easy check of whether or not the system prefers demixing above mixing. This is especially important when the system is close to the critical point since both boxes might swap identity during the simulation: e.g., from A rich to B rich. A typical example of such a histogram is shown in Fig. 1. At the end of a simulation we ran an additional 100 cycles with only particle displacement steps, enabling us to determine the radial distribution functions of the end configuration. These were used to check that the system was in the fluid phase.

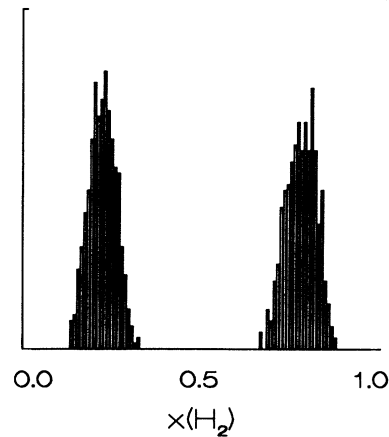


FIG. 1. Example of a concentration $x(\text{H}_2)$ histogram (arbitrary units) as they occurred during the simulation run for the full α -exp-6 system at $T=1500$ K and $p=425$ kbar (coming from ± 412 kbar). The preference for a 20%-80% demixing is clear.

TABLE I. The parameter values used for the α -exp-6 and the repulsive α -exp-6 potential for the system He-H₂ and their references.

Interaction	ε/k_B (K)	r^M (Å)	α	Ref.
H ₂ -H ₂	36.4	3.43	11.1	9
He-He	10.8	2.9673	13.1	10
He-H ₂	17.3	3.28	12.49	5

III. RESULTS FOR He-H₂

As an interaction for the He-H₂ mixture we used the well-known α -exp-6 potential which has proved to be accurate in describing the properties of the pure constituents as well as those of the mixture. It is given by

$$\phi_{ij}(r) = \frac{\varepsilon_{ij}}{\alpha_{ij}-6} \left\{ 6 \exp \left[\alpha_{ij} \left(1 - \frac{r}{r_{ij}^M} \right) \right] - \alpha_{ij} \left(\frac{r_{ij}^M}{r} \right)^6 \right\}, \quad (5)$$

where the parameter values ε_{ij} , α_{ij} , and r_{ij}^M are given in Table I.

For $T=1000$ and 1500 K we started at modest pressures in the homogeneous region of the phase diagram and then augmented the pressure until we found phase separation. Further increasing the pressure provided us with the binodal curve as is depicted for 1000 K in Fig. 2 and for 1500 K in Fig. 3. The critical point estimated for the lower temperature is $x(\text{H}_2)=0.40(5)$ and $p=230(10)$ kbar while for the higher temperature it is $x(\text{H}_2)=0.45(5)$ with a critical pressure of $p=385(10)$ kbar. The precise critical composition was difficult to determine and has been obtained using the fit for the binodal curve.

At temperatures of 2000 K and higher, complications arose since the α -exp-6 potential has an anomalous behavior at small intermolecular distances: at a certain distance r_c it reaches a maximum while in the limit for $r \rightarrow 0$ it even diverges to $-\infty$. All potentials using an exponential part to represent the short-range repulsion will suffer

from this drawback. Under normal conditions, where the densities and temperatures are not extremely high, this causes no problem: one simply forbids particles to come too close by replacing the α -exp-6 interaction by a hard-sphere interaction. Especially in the application of this potential form in Monte Carlo simulations this is a commonly used procedure. However, the point r_c , where $\phi(r)$ has its maximum, depends on the value of α ; the smaller, α , the larger r_c . For H₂, e.g., $r_c \simeq 0.36r^M \simeq 1.23$ Å. We noticed from the graphs of the radial distribution functions (see Fig. 4) that, at the higher temperatures, the fluid-fluid separation in He-H₂ occurred at pressures, and thus densities, so high that a small amount of molecules reached intermolecular distances of 1.23 Å and were "blocked" there due to the hard-sphere interaction replacing $\phi(r)$. We found this occurring at 2000 K and ca. 500 kbar for the He-H₂ system, conditions which are well below the extreme conditions used by Ross *et al.*⁹ in determining the H₂-H₂ interaction parameters. The reason these authors did not encounter similar problems is probably that they used a variational technique to relate the H₂ properties to the potential parameters and, in doing so, an effective hard-sphere repulsion was introduced which took care of the contributions at small distances. Instead of using a hard-sphere repulsion to prevent the molecules from getting too close, one can also gradually switch off the $1/r^6$ term in the intermolecular potential starting from a certain separation r_c . However, in any case, one still uses a potential which for $r < r_c$ has not been determined by comparison with experiments and hence might not describe the H₂-H₂ interaction appropriately.

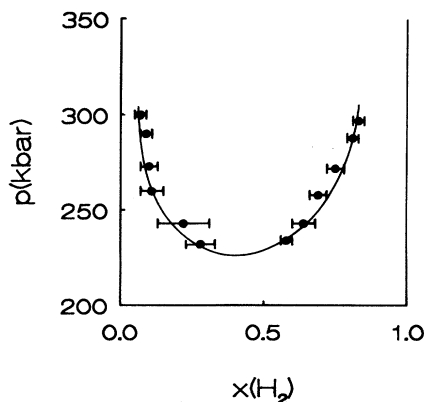


FIG. 2. The simulated binodal curve for He-H₂ at $T=1000$ K; the line serves as a guide to the eye.

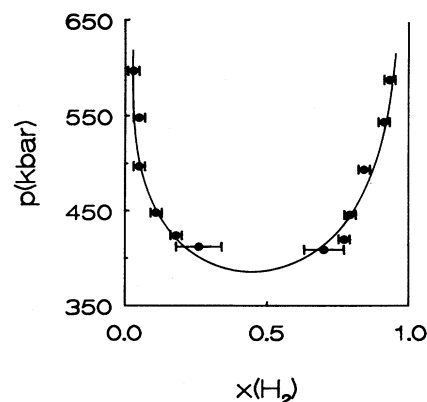


FIG. 3. The simulated binodal curve for He-H₂ at $T=1500$ K; the line serves as a guide to the eye.

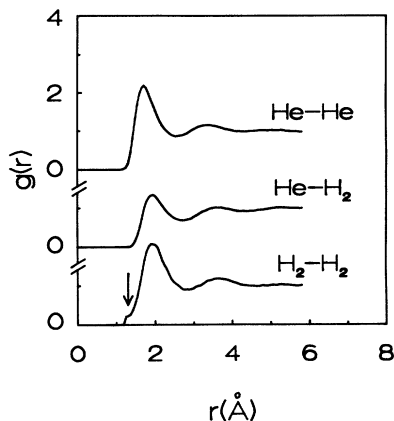


FIG. 4. Example of the partial radial distribution functions of the repulsive α -exp-6 system at $T=2000$ K and $p=580$ kbar. Notice the increased number of molecules located at $r=1.23\text{\AA}$ (indicated by the arrow) for the $\text{H}_2\text{-H}_2$ interaction; no such problems arise with the He-He and He- H_2 interactions.

In our simulations this anomalous behavior of the hydrogen potential became a problem since, once fluid-fluid separation occurred, the concentration of H_2 molecules in one of the boxes increased rapidly and so did the number of hydrogen molecules that started behaving as hard spheres thus preventing further demixing. We therefore decided not to pursue the binodal curve under these conditions since clearly the potential form no longer yielded reliable results for higher H_2 concentrations. Hence, for $T=2000$ and 2500 K, we did not determine the binodal curve but we simply give the pressures where we noticed that the system preferred a demixed over a mixed state.

$$\phi_{ij}(r) = \begin{cases} \frac{\epsilon_{ij}}{\alpha_{ij}-6} \left[6 \exp \left[\alpha_{ij} \left(1 - \frac{r}{r_{ij}^M} \right) \right] - \alpha_{ij} \left(\frac{r_{ij}^M}{r} \right)^6 \right] + \epsilon_{ij} & \text{if } r \leq r_{ij}^M, \\ 0 & \text{if } r > r_{ij}^M, \end{cases} \quad (6)$$

with the same parameter values as used in Eq. (5), given in Table I. In a previous paper⁴ we demonstrated that fluid-fluid phase separation does occur in this system and hence that attraction is not necessary for demixing. This in contrast to, e.g., the liquid-vapor phase separation where attraction is known to be of crucial importance. Our results on the 300-K isotherm indicated that the system interacting through Eq. (6) has a binodal curve with the same shape as the full system interacting through (5) but with a 20% higher critical pressure: $p^{\text{rep}}=65.6(4)$ kbar versus $p^{\text{full}}=53.6(4)$ kbar. The critical composition was the same for both systems: $x(\text{H}_2)=0.47(3)$.

Considering this analogy between the full and repulsive α -exp-6 system, we decided to determine the critical pressures of the purely repulsive system in exactly the same

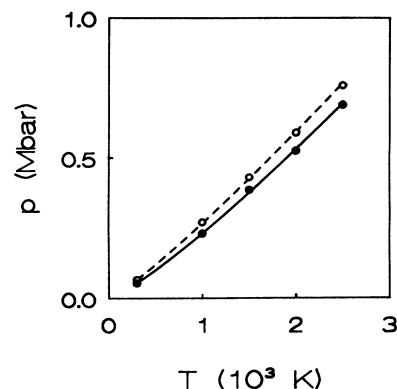


FIG. 5. The critical line of the He- H_2 mixture (solid circles) and of the repulsive α -exp-6 mixture (open circles); the lines serve as a guide to the eye.

Since there the concentration H_2 is approximately 50%, we expected few H_2 molecules to behave anomalously which was confirmed by the radial distribution functions. At 2000 K we found $p=525(10)$ kbar and at 2500 K, $p=690(10)$ kbar. At these temperatures we no longer have information available regarding the critical compositions. The calculated critical pressures are shown in Fig. 5 (lower curve), together with the results on $T=1000$ and 1500 K and the earlier result at $T=300$ K from Ref. 4.

IV. REPULSIVE α -EXP-6 SYSTEM

We have also performed simulations on the repulsive part of the He- H_2 interaction [Eq. (5)], given by

manner as for the He- H_2 system at the highest temperatures: we started in the homogeneous fluid phase and then augmented the pressure until we had proof of phase separation. The thus found critical pressures at $T=1000$, 1500 , 2000 , and 2500 K are depicted in Fig. 5 (upper curve), together with the earlier result at $T=300$ K.

V. DISCUSSION AND CONCLUSIONS

The results obtained in this investigation for the full α -exp-6 potential can be compared with calculations reported previously.⁵ As stated before, at $T=300$ K the critical pressures of both calculations are comparable with the experimental result but the simulations predict a

width of the binodal curve which is in much better agreement with experiment than the perturbation calculations. The critical line from the perturbation calculations is steeper than the curve shown in Fig. 5. For example, in this investigation the critical pressure at 2500 K is about 700 kbar while in an earlier work it was about 900 kbar. Also at higher temperatures, the width of the binodal is much larger in the case of the simulations. The critical composition determined through the Monte Carlo method at 300 K is in reasonable agreement with the experiment while this was within the experimental uncertainty in the case of the perturbation theory calculations. In conclusion, we believe that the computer simulations represent the fluid-fluid phase behavior of the system helium-hydrogen better than previous perturbation calculations. One of the reasons is that, in perturbation theory, the Van der Waals one-fluid approach is used. It is doubtful whether at these extreme high densities this approximation is still valid. Moreover, the use of variational perturbation theory itself might add to the uncertainty of the results.

The present models for the Jovian planets predict that, at about 2 Mbar and 8000–10 000 K the atmosphere of Jupiter, which consists of 90 mol % H₂ and 10 mol % He, will undergo a phase transition to solid hydrogen.¹¹ To check whether our present results support these models, we have extrapolated the critical line of the He-H₂ system to higher temperatures. We have used the well-known Simon-Glatzel type of equation, $p = a + bT^c$, where a , b , and c are constants. Using this equation, we arrive at a critical temperature of 6000 K at the aforementioned 2 Mbar. From the work of Van den Bergh and Schouten,⁵

we know that a reasonable extrapolation of the melting line of pure hydrogen lies at lower temperatures than the critical line of the He-H₂ mixture calculated through perturbation theory. Given a certain pressure, the critical temperature obtained from this work is even higher. On the other hand, at fixed pressure, the melting temperature of the 10% He mixture is definitely lower than the melting temperature of the pure hydrogen system.⁵ Moreover, it is also clear from the experimental results (Fig. 3 of Ref. 5) that the critical line and the 10% He fluid-solid phase-separation line diverge. Therefore, we can state that, at 2 Mbar, the phase transition of the 10% He mixture to solid molecular hydrogen will take place at a temperature well below the critical temperature; hence, well below 6000 K. As a consequence, we conclude that new models for our giant planets have to be developed.

The critical curve for the repulsive system is also depicted in Fig. 5. At any temperature its critical pressure is higher than for the full potential. This behavior resembles that of the melting line of the pure systems. In a recent paper¹² we demonstrated that the influence of attraction on the melting line appears to be a shift to higher temperatures. There is, however, a difference with the two critical lines depicted in Fig. 5: the two melting lines presented in Ref. 12 run parallel while the critical line of the repulsive system studied here runs steeper than for the full system. It was anticipated that these two critical lines would run parallel if the critical composition would be constant with temperature but due to large uncertainties in these quantities, definite conclusions cannot be drawn here. Roughly speaking, the difference in critical pressures at any temperature is about 20%.

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