

Wetting in Binary Fluid Mixtures: Recent Results in H₂/He on Cesium

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We present the results of an experiment on the wetting of liquid hydrogen on a cesium substrate using helium as a surfactant. In contrast to the previously studied case of ³He-⁴He mixtures on cesium, there is less ambiguity about the concentration dependence of the liquid-solid surface tension, suggesting that the results may be more easily interpreted; however, the relatively high temperatures and pressures complicate both experiment and calculation. The thermal expansion of the liquid turns out to be a major contribution to the temperature variation of the liquid-solid surface tension. When this is taken into account, there is excellent agreement between the observed variation of the wetting temperature with helium concentration ($-.31 \pm 0.01$ K/bar) and the calculated value ($-.30$ K/bar).

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1. INTRODUCTION

Several previous experiments¹⁻⁴ and calculations⁵⁻¹¹ have explored the surface tension between liquid helium and solid cesium through the study of contact angles and wetting transitions. Specifically, the difference $\Delta\sigma$ between the liquid-solid surface tension $\sigma_{\ell s}$ and the solid-vapor surface tension σ_{sv} can be determined from Young's equation,

$$\Delta\sigma \equiv \sigma_{sv} - \sigma_{\ell s} = \sigma_{\ell v} \cos \theta. \quad (1)$$

Since $\sigma_{\ell v}$ is known, measurements of the contact angle θ determine $\Delta\sigma$. In the case of isotopic mixtures of ^3He and ^4He , varying the concentration introduces a new thermodynamic variable, which one may use to vary the wetting temperature for additional information. Measurement of the wetting temperature T_W as a function of the ^3He concentration X_3 determines $\Delta\sigma$ along a curve in the X_3-T plane. Since $\cos\theta = 1$ at the wetting temperature,

$$\Delta\sigma(X_3, T_W(X_3)) = \sigma_{\ell v}(X_3, T_W(X_3)). \quad (2)$$

A strong dependence on X_3 would arise from the existence of a bound state of ^3He at the $^4\text{He}/\text{Cs}$ interface, predicted by Pavloff and Treiner.¹² A strong temperature dependence was predicted by Pricaupenko and Treiner.⁷ However, the experiments have not been consistent with one another. For instance, quartz microbalance measurements by Ross *et al.*² of the wetting curve indicated that the sum of the X_3 and T dependences of $\Delta\sigma$ is small. Optical measurements of θ for pure ^4He indicated that the T dependence is small, implying that the X_3 dependence must also be small, and the bound state of ^3He weak or absent. However, $\theta(T)$ has been shown to be strongly substrate dependent.¹³ A capacitance measurement of the contact angle in the non-wetting region of the X_3-T plane by Klier *et al.*³ indicated that the dependence of $\Delta\sigma$ on both X_3 and T was strong. Remarkably, the wetting temperature measured in this experiment was in excellent agreement with the results of Ross *et al.*².

In order to use measurements of $\theta(T)$, one has to assume that the advancing contact angle is equal to the equilibrium contact angle, which appears in Young's equation. This assumption is by no means obvious, though it is generally argued that for a heterogeneous substrate, the advancing contact angle is close to the equilibrium contact angle of the less wettable patches.¹⁴ Furthermore, the hysteresis is rather small for H_2/Cs , and using the value of the receding contact angle would not lead to drastic changes in the slope $d\cos\theta/dT$ (see fig. 4 in ref. 15). On the other hand, it has been suggested that while the contact angle is very sensitive to substrate disorder, the wetting temperature is not, being governed by the least wettable parts of the surface.¹⁶ If so, wetting measurements are a more reliable probe of $\Delta\sigma$ than contact angle measurements, though only along the wetting curve. In order to separate the dependence of $\Delta\sigma$ on T and concentration using T_W only, it is necessary to vary the system. For this reason, we have performed an experiment to measure contact angles and wetting temperatures for the system of solutions of ^4He in liquid H_2 on cesium. The advantage of this system is that it is unlikely that $\sigma_{\ell s}$ depends significantly on the concentration of the solution, as will be explained below.

2. APPARATUS AND METHODS; SOME GENERAL OBSERVATIONS

The experimental apparatus is similar to one described previously.⁴ The cesium surface is formed by deposition at low temperature from a commercial getter.¹⁷ The cell was modified to allow deposition of the cesium at more nearly normal incidence, making the film more uniform, and to permit direct measurement of the cesium film thickness during deposition using a quartz microbalance. For the experiment presented in this paper, a cesium film of 84 layers was deposited on an optically polished silicon wafer at a rate of 0.7 layers per minute at a cell temperature of less than 20 K.

The contact angle is measured interferometrically. The cesium film forms an interferometric cavity with a semi-reflecting plate. The presence of liquid hydrogen alters the optical path length; for laser light of $\lambda=633$ nm, one interference fringe represents a change in depth of the liquid of $2.78 \mu\text{m}$ at 17 K, and $2.93 \mu\text{m}$ at 20 K.¹⁸ Because the index of refraction of liquid hydrogen is significantly greater than that of the vapor, large contact angles cause the beam reflected from the cesium surface to be refracted away from the window, eliminating the interference fringes. For this reason, the present experiment was restricted to contact angles less than 13° .

The wetting temperature was taken to be the temperature at which the contact angle became too small to be measurable by interferometry and the liquid near the meniscus became so thin that interference fringes due to reflections at the liquid-vapor interface were visible in incoherent light. At the same temperature, the line of contact became quite irregular, and droplets of liquid appeared at certain points on the surface. These points are presumably defective parts of the surface slightly more wettable than the rest; this would only be noticeable sufficiently close to the wetting temperature. The behavior of the contact line above and below the wetting temperature is illustrated in Fig. 1. The uncertainty in the measurement of the wetting temperature was about ± 0.05 K in each case.

It was not possible to measure receding angles, because the apparatus was not designed to control the rate of evacuation of the cell. However, it was observed that the receding angle of pure H₂ typically became zero at a temperature T_R about 1 K below T_W . Above T_R , once a part of the surface has been in contact with the liquid, it remains covered with a thin film of liquid, for if the receding contact angle is zero, the film cannot recede. The film is too thin to be visible, but if the meniscus advances again over this part of the surface, the advancing contact angle is zero, showing that the state of the surface is different from the bare substrate. The only way to completely dry the surface is to lower the temperature below T_R , or evaporate all the

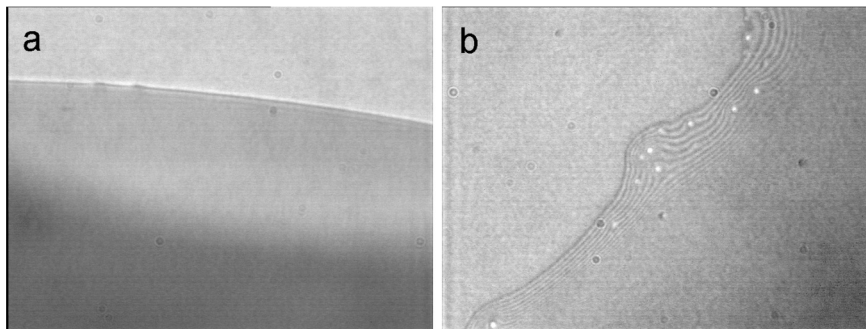


Fig. 1. The meniscus in yellow incoherent light, (a) below the wetting transition ($T=18.10$ K, $p=4.46$ bar) and (b) above the wetting transition ($T=18.75$ K, $p=4.76$ bar). The liquid is at the bottom of the image. The darkness of the lower part of (a) is due to the reflected light being refracted away from the window, as described in the text. Scale: 6.4 mm \times 4.8 mm.

liquid in the cell and bring the pressure below the saturated vapor pressure. Once this is done, previous values of the advancing angle are recovered.

When pure hydrogen was admitted to the cell, a mist of droplets condensed on the substrate when the saturated vapor pressure was reached. This was presumably due to small temperature gradients in the cell. The difficulty of drying the surface after it has been wet made it necessary to prohibit the formation of the mist by heating the substrate during condensation (less than 2 mW). As experiments have shown that the contact angle can be altered by substrate heating,¹⁹ it was necessary to check that the heating was always small enough not to affect the measurement. The problem of mist was much less severe in hydrogen/helium mixtures; this must be due to the fact that for hydrogen to condense on the substrate from the mixed vapor, it has to diffuse through the background helium.

To produce the mixtures, it was necessary to add the helium before the hydrogen; for if liquid hydrogen is introduced first, and then the pressure is raised by the addition of helium, the pressure raises the chemical potential of the liquid, the liquid evaporates, and the meniscus recedes. So the experimental procedure was to fill the cell with a background pressure of helium (as much as 5 bar at 17 K) and then to admit hydrogen through a flow meter until the liquid level in the cell was high enough that a meniscus appeared in the field of view. The hydrogen was supplied from an intermediate high-pressure storage bottle, to eliminate the possibility of contamination of the main hydrogen cylinder with helium backstreaming through the flow meter. The storage bottle was evacuated before being replenished from the main

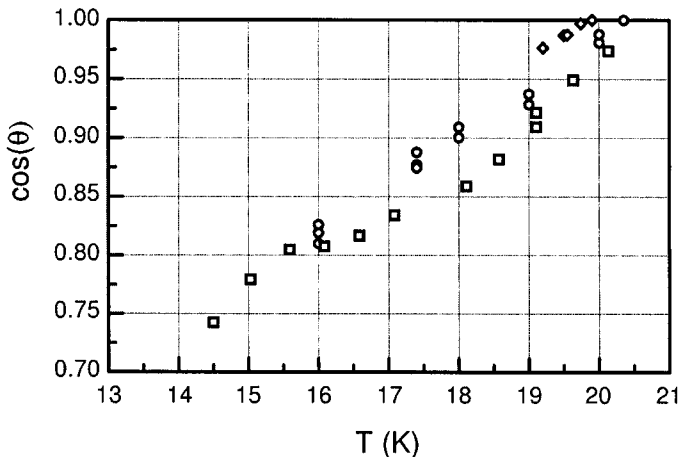


Fig. 2. Contact angles for pure H_2 on three different cesium substrates. Diamonds: present work ($T_W = 19.9 \pm 0.05$ K). Circles: previous work by Poujade, Rolley and Guthmann,²⁰ using a different cesium substrate ($T_W = 20.35 \pm 0.1$ K). Squares: Ross *et al.*²¹ ($T_W = 20.57 \pm 0.05$ K).

cylinder.

Once the meniscus was visible and the contact angle measured, the temperature was raised to the next measurement point. The pressure increases also, of course. At low temperatures, the decrease in contact angle with rising temperature was enough to advance the meniscus, but at higher temperatures it was necessary to add hydrogen to replenish that lost from the liquid by evaporation.

3. RESULTS AND ANALYSIS

Pure H_2 . Advancing contact angles for pure hydrogen are displayed in Fig. 2. We present the data as $\cos \theta$, since it is closely related to the quantity of interest, $\Delta\sigma = \sigma_{lv} \cos \theta$, but θ is the experimentally measured quantity. We find a wetting temperature of $T_W = 19.9 \pm 0.05$ K. For comparison, the figure also shows data from a previous experiment by Poujade, Rolley and Guthmann using a different cesium substrate,²⁰ and from Ross *et al.*²¹ Table 1 presents the slope, $d \cos \theta / dT$, for each substrate.

If we consider the data for $T > 18$ K to represent the limit as $T \rightarrow$

Table 1. Comparison of three different cesium surfaces.

| T_W (K) | $d \cos(\theta)/dT$ (K^{-1}) for $T > 18$ K | substrate |
|--------------------|--|-------------------------------------|
| 19.9 ± 0.05 K | 0.035 | present work |
| 20.35 ± 0.1 K | 0.040 | Poujade <i>et al.</i> ²⁰ |
| 20.57 ± 0.05 K | 0.058 | Ross <i>et al.</i> ¹³ |

Table 2. Measured contact angle as a function of pressure and temperature.

| p (bar) | T (K) | θ (degrees) | p (bar) | T (K) | θ (degrees) |
|-----------|---------|--------------------|-----------|---------|--------------------|
| 0.70 | 19.2 | 12.4 | 2.82 | 18.46 | 12.1 |
| 0.77 | 19.5 | 9.25 | 2.88 | 18.652 | 10.4 |
| 0.78 | 19.55 | 9 | 2.95 | 18.87 | 7.7 |
| 0.83 | 19.74 | 4.5 | 3.02 | 19.065 | 3.3 |
| 0.87 | 19.9 | 0 | 3.05 | 19.16 | 0 |
| 4.5 | 18.11 | 11 | 6.54 | 17.29 | 11.4 |
| 4.57 | 18.31 | 7.6 | 6.83 | 17.5 | 8.75 |
| 4.64 | 18.5 | 4.45 | 6.87 | 17.71 | 7 |
| 4.71 | 18.62 | 2.8 | 6.92 | 17.84 | 4.05 |
| 4.73 | 18.66 | 4 | 6.97 | 17.94 | 2 |
| 4.76 | 18.72 | 0 | 7.01 | 17.99 | 0 |

T_W , then there is a trend in Table 1 that $d \cos \theta / dT|_{T_W}$ increases with the wetting temperature of the substrate, as previously remarked by Ross *et al.*¹³ in another work. The H_2 case is apparently similar to that of He: the temperature dependence of θ varies with substrate more than T_W , whose spread is only 4 percent. The main difference between the two cases is the magnitude of the hysteresis. For H_2 the difference in $\cos \theta$ between advancing and receding contact angles is of the order of 0.05 near T_W ,^{15,20} while for He it is at least two times larger for the less hysteretic evaporated substrates¹⁵ (here we consider only evaporated Cs substrates).

Wetting temperature for mixtures. The results of the wetting temperature measurement are shown in Fig. 3. Contact angle measurements are listed in Table 2. Also shown are the results of a calculation, based on the model of ref. 10, assuming a wetting temperature of 19.9 K for pure hydrogen. The slope of the data is -0.31 ± 0.01 K/bar, while the original model predicts -0.17 K/bar. The discrepancy is due to the effect of thermal expansion of the liquid, which was neglected in the previous calculation.

The original model is described in detail in ref. 10 (however, the pre-

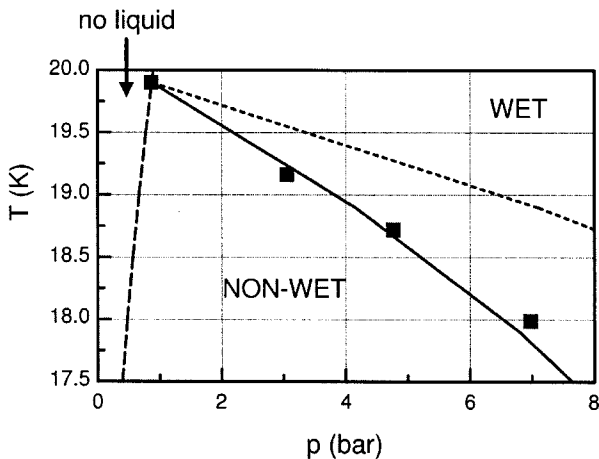


Fig. 3. Phase diagram for H₂/He mixtures on Cs. The points represent the experimentally measured wetting temperature; the uncertainty is equal to the size of the symbol. Solid curve, new model; dotted curve, old model; dashed curve, saturated vapor pressure of pure H₂.

viously published calculation is for H₂/He mixtures on rubidium). Starting from eq. (2), it is possible to solve for the wetting temperature if the surface tensions σ_{ls} , σ_{lv} and σ_{sv} are known. For solutions of He in H₂, σ_{lv} has been measured over the range of interest by Paine and Seidel.²² They worked with para-hydrogen and helium, while our hydrogen is normal; we assume that the effect of helium on the surface tension can be simply added to the surface tension of normal hydrogen, which we take to be $\sigma_{lv}^0(T) = (5.293 - 0.1634T/K)$ mN/m.²³ For σ_{sv} , our model is $\sigma_{sv}(T) = \sigma_{sv}(0) - a_1T^3 - n_{sv}k_B T - n'_{sv}k_B T$. The T^3 term represents the free energy of vibrations of the solid, with a coefficient a_1 computed by Shchegrov.²⁴ The last two terms represent the spreading pressure of the surface excess of hydrogen n_{sv} and helium n'_{sv} in the potential of the substrate. The potentials of Chizmeshya *et al.*²⁵ were used to compute these two quantities using both classical and quantum statistical mechanics. The classical result relates the surface excess to the vapor density n_v far from the surface: $n_{sv} = n_v \int_{z_{cutoff}}^{\infty} [\exp(-V(z)/kT) - 1] dz$ and similarly for n'_{sv} . The quantum result is slightly smaller than the classical result, in agreement with the observation of Shi *et al.*¹¹ that zero point energy effectively prevents the molecules from approaching the substrate too closely.

For $\sigma_{\ell s}$, the original model was $\sigma_{\ell s}(T) = \sigma_{\ell s}(0) - a_2 T^3 - n'_{\ell s} k_B T$. The T^3 term represents the free energy of vibrations of the liquid-solid interface, with a coefficient a_2 calculated by Hawkins *et al.*,²⁶ and $n'_{\ell s}$ is the adsorption of helium at the liquid-solid interface. The latter can be calculated in the classical limit,²⁷ where the displacement of a solvent molecule by a solute molecule is a thermally activated process, taking into account the difference in molecular volumes, in the potential of the substrate. $n'_{\ell s}$ is small because the concentration of helium in the solution is small (less than 0.7 percent), and negative because hydrogen is more attracted to the substrate than helium.

To complete the calculation requires a knowledge of the equation of state of the gas – we use the virial expansion to second order from Paine and Seidel²² – and the concentration of liquid and vapor as a function of the measured variables, p and T . For the latter, we use the data of Strett *et al.*²⁸ The final result is an implicit equation for the wetting temperature as a function of pressure,

$$(a_2 - a_1)T^3 - n_{sv}k_B T - n'_{sv}k_B T - \sigma_{lv}(p, T) + n'_{\ell s}k_B T = \text{const} \quad (3)$$

The various surface densities, of course, are functions of p and T .

Let us consider two new terms that must be added to the model of the liquid-solid surface tension. First, when the pressure over the solution is increased, the liquid becomes denser by an amount Δn_ℓ because of its compressibility, and $\sigma_{\ell s}$ increases by an amount $\Delta n_\ell \int V(z) dz$ because of the attractive potential of the substrate. This adds a free energy of $\alpha(p - p_{\text{sat}}(T))$ to $\sigma_{\ell s}$, where $\alpha = -4.8 \times 10^{-3}$ mN/m per bar. It would favor wetting as the pressure increases, thus enhancing the effect of helium on the wetting temperature. Second, when the temperature decreases, the density of the liquid increases, also enhancing wetting (because of the attractive potential of the substrate); the effect is to add βT to $\sigma_{\ell s}$, where $\beta = 0.068$ mN/m per K. Since raising the helium pressure lowers the wetting temperature, and the thermal expansion further lowers the surface free energy at lower temperature, the thermal expansion also increases the effect of helium on T_W . The new model is thus

$$(a_2 - a_1)T^3 - n_{sv}k_B T - n'_{sv}k_B T - \sigma_{lv}(p, T) + n'_{\ell s}k_B T - \alpha(p - p_{\text{sat}}(T)) - \beta T = \text{const} \quad (4)$$

The combination $a_2 - a_1$ turns out to be simply $\zeta(3)k_B^3/8\pi\hbar^2c^2 \approx 9 \times 10^{-6}$ mN/m/K³, where c is the speed of sound in the liquid. The thermal expansion effect is much more important than the T^3 term, and has the opposite sign. Unfortunately, it would be rather difficult to separate the T^3 term

from the linear term experimentally. Including the new terms improves the calculated low-pressure limit of dT_W/dp to -0.30 K/bar. Thus, with no adjustable parameters except the wetting temperature of pure H₂, the new model is in excellent agreement with the experimental value in the limit of low pressures. The point at highest pressure is not in as good agreement with the model, but as there may be virial corrections to the two-dimensional spreading pressure, or other effects not taken into account, the model is most reliable in the limit of low pressure.

The agreement with the contact angle is not quite as good, however. The slope of the data for pure H₂ is $d \cos \theta / dT|_{T_W} = 0.035/\text{K}$ experimentally, while the model gives $0.040/\text{K}$, a 15 percent discrepancy. For the substrate of Ross *et al.*, the calculated slope is $0.035/\text{K}$, compared to the empirical value of $0.058/\text{K}$. It is not possible to adjust the parameters of the model to fit the slopes for all three of the substrates in Fig. 1 simultaneously. As we have remarked, the contact angle appears to be more substrate-dependent than the wetting temperature.

Without any characterization of the substrates, we can only conclude that the various experiments, as well as the model, consistently show that the temperature variation of $\Delta\sigma$ is significant, as first noted by Ross *et al.*²¹

4. CONCLUSIONS AND APPLICATION TO HELIUM

We have measured the effect of helium on the wetting temperature of liquid hydrogen on cesium to be $dT_W/dp = -0.31 \pm 0.01$ K/bar. The result is in excellent agreement with the model if thermal expansion of the liquid, an important factor not previously considered, is taken into account. The model has no free parameters, except the wetting temperature for pure H₂.

Since the model works so well for hydrogen, we attempt now to apply it to helium. We calculate the magnitude of some of the terms in eq. 4 for pure ⁴He:

(1) $a_2 - a_1$. For He/Cs, the coefficient $a_2 - a_1$ has the value 2.46×10^{-4} mN/m/K³ and this term contributes a difference of -0.002 mN/m to $\sigma_{\ell s}$ over the temperature interval from 1 K to 2.1 K. This result is almost exactly one quarter of the temperature dependence proposed by Pricaupenko and Treiner,⁷ who neglected the contribution of the bulk phonons to the surface free energy.

(2) Thermal expansion (βT). Dupont-Roc and Demolder²⁹ considered the thermal expansion term for helium, but argued that below T_λ it would be offset by changes in the density of the gas and be very small. In our model, it contributes a change $\Delta n_\ell \int V(z) dz$ of about -0.005 mN/m to $\sigma_{\ell s}$

between 1 K and 2.1 K. It has the opposite sign from the H₂ case, because the thermal expansion of helium is negative below the lambda point.

(3) n_{sv} . The adsorption of He on the bare substrate was considered by Dupont-Roc and Demolder²⁹ and Klier *et al.*³. In our model, it contributes a change of -0.02 mN/m to σ_{sv} between 1 K and 2.1 K. This is quite large: roughly a third of the variation of σ_{lv} over the same temperature interval.

This result is rather interesting when applied to the case of ³He-⁴He mixtures, since the evidence for the existence of a bound state of ³He at the ⁴He/Cs interface¹² depends in part on the interpretation of wetting temperature measurements in mixtures (as well as on the conflicting contact angle measurements). As discussed in the introduction, wetting temperature measurements for mixtures¹⁻³ indicate that the variation of $\Delta\sigma(X_3, T)$ along the wetting curve $X_3, T_W(X_3)$ is small – comparable to the term $a_2 - a_1$ calculated above, at most. However, the calculated dependence on n_{sv} is much larger than this. If our model applies to helium, then in order to explain the experimental results for T_W , the temperature dependence of $\Delta\sigma$ must be approximately cancelled by the concentration dependence along the wetting curve. The existence of the ³He bound state is the most likely explanation. To use our model to analyze the wetting temperature data, to determine properties of this bound state such as its binding energy, it would be necessary to take into account also the effect of ³He adsorption at the solid-vapor interface.

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