Melting pressure of saturated helium mixture at temperatures between 10 mK and 0.5 K

J Rysti, J Tuoriniemi, A Salmela, and A Sebedash
Low Temperature Laboratory, Aalto University, PO Box 15100, 00076 Aalto, Finland
E-mail: juho.rysti@aalto.fi

Abstract. The melting curves of helium mixtures are, in general, equilibrium states between one or two liquid phases and one solid phase. In the case of a solubility saturated system, three phases coexist and the melting pressure depends uniquely on temperature. Thus, it forms a univariant system, and can be used as a thermometric standard. The melting pressure of the saturated helium mixture has been studied experimentally, but an independent calculation of this quantity supports its use in thermometry. We have calculated the melting pressure of the saturated helium mixture as a function of temperature between 10 mK and 0.5 K by using thermodynamic considerations and recently determined effective interaction potential between $^3$He quasiparticles in the liquid mixture.

1. Introduction
At low temperatures liquid helium mixtures are separated into two phases, provided that enough $^3$He is present. The so-called dilute phase is rich in $^4$He and the other phase is rich in $^3$He. As the pressure of the system is increased, a solid phase appears, and the system has reached the melting curve. Due to the lower melting pressure of pure $^4$He compared to $^3$He, the solid phase always contains $^4$He. At very low temperatures the melting pressure of a helium mixture increases quadratically as a function of temperature. This is because the melting curve is essentially determined by the entropy of $^3$He in the liquid phases. Then the solid phase can be assumed to be pure from $^3$He. As temperature is raised, increasing amount of $^3$He dissolves into the solid, whereby the melting pressure turns over and begins to decrease. The maximum is obtained at approximately 300 mK. The pressure drops below that of pure $^4$He at about 400 mK and reaches a minimum around 1 K, beyond which a positive slope is observed again. In the studied temperature range the energetically favorable crystal structure also changes from hcp to bcc.

The melting pressure of pure $^4$He at zero temperature is 2.532 MPa, and that of pure $^3$He is 3.44 MPa. The melting pressure of a mixture depends on the concentration of $^3$He, and increases from the value of pure $^4$He to 2.566 MPa. The increasing pressure due to additional $^3$He can be attributed to the increasing osmotic pressure in the liquid phase [1]. The melting pressure of pure $^3$He is commonly used as an empirical thermometric standard [2]. In a similar fashion, the melting pressure of a helium mixture can be used for the same purpose [3]. The saturated mixture is the preferred choice for this application, as the concentration of $^3$He in the system is set by nature. Since three phases are then present simultaneously at the melting curve, it represents a univariant relation, whose value is uniquely determined by temperature. Helium mixtures have the potential to offer better sensitivity compared to pure $^3$He at very
low temperatures and the relation between pressure and temperature in dilute mixtures can be computed from theory more easily.

We have calculated the melting pressure of the saturated helium mixture using an approach similar to Edwards and Balibar [4]. Below 0.5 K, phonon related effects can be neglected and thus all properties of \(^{4}\text{He}\) can be regarded as independent of temperature. In this paper, we also confine ourselves to temperatures above the superfluid transition of \(^{3}\text{He}\).

2. Calculations

In order to find the equilibrium state between the phases, we need the chemical potentials of both \(^{3}\text{He}\) and \(^{4}\text{He}\) in each of them. Since we are considering the saturated mixture, we have three phases, and subsequently four equations of the form \(\mu_{3,4}^A - \mu_{3,4}^B = 0\), where \(A\) and \(B\) denote two different phases. The four variables to be solved from this group of nonlinear equations are the melting pressure \(P_m\) and the concentrations \(x^D\), \(x^R\), and \(x^S\). The superscripts \(D\), \(R\), and \(S\) refer to the \(^{3}\text{He}\)-dilute liquid, \(^{3}\text{He}\)-rich liquid, and the solid, respectively.

The so-called regular solution model is adequate for describing the solid state, as shown by Edwards and Balibar. Therefore, the chemical potentials of the helium isotopes in the solid are rather straightforward to determine. The situation in the liquid phases is somewhat more involved. We have recently studied the effective interaction potential between \(^{3}\text{He}\) atoms in the dilute liquid [5]. The validity of our treatment extends over the entire pressure range of liquid mixtures, including the melting pressure. Thereupon, we can calculate the value of \(\mu_{3}^D\) considerably more accurately than previously. In comparison to Edwards and Balibar, we also benefit from more recent experimental data needed in the calculations. These include, for example, melting pressure of pure \(^{3}\text{He}\) and the effective mass and binding energy of \(^{4}\text{He}\) in the \(^{3}\text{He}\)-rich phase [2, 6]. Some of these data are quite different from those used by Edwards and Balibar.

The chemical potential of \(^{3}\text{He}\) in the dilute phase was obtained using the effective interaction potential, the Hartree-Fock approximation, and solving \(\mu_{3}^D\) from the Fermi-Dirac distribution function. This chemical potential can further be used to determine the change in the chemical potential of \(^{4}\text{He}\) in the same phase using the Gibbs-Duhem equation. This also trivially guarantees that the Gibbs-Duhem equation is satisfied; otherwise one might have trouble finding the phase equilibrium. The interaction potential includes a concentration dependence, whose validity is questionable at concentrations above 10 % and at temperatures above some 100 mK. Indeed, we faced difficulties in using this potential to calculate the melting pressure at higher temperatures (larger concentrations). The chemical potential has a maximum as a function of concentration. As this maximum is reached, the group of equations no longer has a solution. This problem arose at a temperature of 250 mK, which corresponds to a concentration of about 16 % in the dilute phase. Fortunately, we also have at our disposal an interaction potential, which does not include a concentration dependence, but still reproduces its determining experimental data quite well. The use of this potential could be extended to \(x^D \approx 30\%\), which in our case allowed the calculation of the melting pressure to temperatures close to 0.5 K. Since the concentration of \(^{4}\text{He}\) in the \(^{3}\text{He}\)-rich phase remains rather small below 0.5 K \((x^R > 0.98)\), we can use Maxwell-Boltzmann statistics, and the determination of \(\mu_{4}^R\) is more straightforward than that of \(\mu_{3}^D\).

3. Results and Conclusions

Figure 1 shows the univariant melting curve as a function of temperature. The curves for both crystal structures are shown separately. They have been extrapolated to zero temperature using a quadratic fit to the low temperature data. As the melting curves intersect (at \(T = 280\) mK), it becomes energetically favorable to change the crystal structure. The intersection in fact forms a quadrupole point, at which four phases (hcp, bcc, dilute, rich) can coexist. A discontinuity
in the concentration of $^3$He between the solid phases exists at the quadrupole point. It changes from $x^S = 3.7\%$ of hcp to $x^S = 7.2\%$ of bcc. In reality, one may enter a metastable state, where the new solid phase has yet to be nucleated. It is also somewhat unclear, whether the melting pressure actually follows the equilibrium curve when temperature is changed. The slow diffusion of $^3$He into the $^4$He-rich crystal creates concentration gradients within the solid. One may need to melt and regrow the crystal at different temperatures to guarantee a homogeneous system, which is in equilibrium. The calculated concentrations are shown in Fig. 2. The discontinuity of $x^S$ in the bcc crystal at $T \approx 380$ mK indicates that the rich bcc becomes the favorable phase. At this temperature, four phases can coexist simultaneously, rich and dilute liquids and rich and dilute bcc solids. The data are also listed in Table 1.

In conclusion, we have calculated the univariant melting pressure for the saturated helium mixture as a function of temperature between 10 mK and 0.5 K. The transition of the crystal structure from hcp to bcc at 280 mK might complicate the reliable use of the melting pressure of
| $T$ (mK) | $P_m$ (MPa) | $x_D$ (%) | $x_R$ (%) | $x_S$ (%) | $P_m$ (MPa) | $x_D$ (%) | $x_R$ (%) | $x_S$ (%) |
|--------|-------------|-----------|-----------|-----------|-------------|-----------|-----------|-----------|
| 0      | 2.566       | 8.10      | 100       | 0         | 2.599       | 8.07      | 100       | 0         |
| 20     | 2.567       | 8.12      | ≈100      | ≈0        | 2.591       | 8.08      | ≈100      | ≈0        |
| 40     | 2.568       | 8.16      | ≈100      | ≈0        | 2.593       | 8.13      | ≈100      | $10^{-8}$ |
| 60     | 2.571       | 8.23      | 99.999    | $10^{-6}$ | 2.596       | 8.20      | 99.999    | $10^{-5}$ |
| 80     | 2.574       | 8.35      | 99.996    | $10^{-4}$ | 2.600       | 8.32      | 99.996    | 0.001     |
| 100    | 2.579       | 8.54      | 99.99     | 0.004     | 2.605       | 8.51      | 99.99     | 0.01      |
| 120    | 2.585       | 8.80      | 99.97     | 0.02      | 2.611       | 8.77      | 99.97     | 0.07      |
| 140    | 2.591       | 9.12      | 99.95     | 0.07      | 2.617       | 9.09      | 99.95     | 0.21      |
| 160    | 2.598       | 9.52      | 99.92     | 0.19      | 2.623       | 9.48      | 99.92     | 0.47      |
| 180    | 2.605       | 9.96      | 99.87     | 0.41      | 2.629       | 9.94      | 99.88     | 0.92      |
| 200    | 2.611       | 10.48     | 99.82     | 0.74      | 2.634       | 10.45     | 99.82     | 1.58      |
| 220    | 2.618       | 11.04     | 99.76     | 1.22      | 2.636       | 11.02     | 99.77     | 2.49      |
| 240    | 2.623       | 11.67     | 99.70     | 1.86      | 2.637       | 11.66     | 99.70     | 3.70      |
| 260    | 2.627       | 12.36     | 99.62     | 2.67      | 2.635       | 12.35     | 99.62     | 5.24      |
| 280    | 2.630       | 13.12     | 99.54     | 3.68      | 2.630       | 13.12     | 99.54     | 7.18      |
| 300    | 2.631       | 13.95     | 99.45     | 4.88      | 2.621       | 13.96     | 99.45     | 9.59      |
| 320    | 2.630       | 14.87     | 99.35     | 6.30      | 2.608       | 14.89     | 99.35     | 12.61     |
| 340    | 2.627       | 15.88     | 99.25     | 7.94      | 2.590       | 15.91     | 99.24     | 16.49     |
| 360    | 2.622       | 17.02     | 99.14     | 9.80      | 2.567       | 17.04     | 99.13     | 21.77     |
| 380    | 2.615       | 18.30     | 99.02     | 11.90     | 2.536       | 18.31     | 99.00     | 30.60     |
| 400    | 2.606       | 19.79     | 98.90     | 14.24     | 2.486       | 19.77     | 98.87     | 68.63     |
| 420    | 2.594       | 21.59     | 98.78     | 16.81     | 2.429       | 21.41     | 98.73     | 67.56     |
| 440    | 2.582       | 24.00     | 98.65     | 19.59     | 2.381       | 23.42     | 98.59     | 66.53     |
| 460    | -           | -         | -         | -         | 2.335       | 26.21     | 98.45     | 65.89     |

Table 1. Calculated melting pressures and concentrations at various temperatures for the hcp and bcc solids.

helium mixtures as a thermometer around this temperature. On the other hand, this transition provides a specific point on the curve and increases the slope of the pressure towards higher temperatures. At temperatures below 1 mK, a helium mixture melting pressure thermometer may provide more sensitivity compared to pure $^3$He. We intend to extend the calculations to temperatures below the superfluid transition of $^3$He. These results and the details of the calculations will be published later.

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