Ex4552: Liquid He3, cooling by adiabatic pressurization

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The phase-diagram of ^{3}He is displayed in the figure below. Assume that the liquid phase can be described as a low temperature ideal Fermi gas with $T_F \approx 5\,°\mathrm{K}$, while the solid phase is described as a set of spins. Assume that $T > 0.01\,°\mathrm{K}$, such that antiferromagnetic order is diminished and the spins can be treated as non-interacting. In this region the $P(T)$ coexistence solid-liquid curve exhibits a minimum at temperature T^*. This implies an anomaly: as the temperature is raised, keeping the pressure constant, the liquid is "frozen" into solid, and only later melts back into a liquid. This is the regime of interest for this question.

In particular we are interested in method of cooling by pressurization. Consider N Helium particles in the the liquid phase with temperature lower than T^*. The system is pressurized adiabatically. Once the liquid becomes a solid, the temperature drops down to a lower value.

(a) Express the entropy $S_\ell(T, P)$ in the liquid phase and the entropy $S_s(T)$ in the solid phase. Determine the temperature T^* for which both phases have the same entropy.

(b) Use Clapeyron's relation to deduce the shape of the $P(T)$ coexistence solid-liquid curve near T^*. Assume that $P^* \equiv P(T^*)$ is known. Assume that the difference Δv of the specific volumes is temperature independent and that the solid is denser.

(c) Of what order is the liquid-solid transition? Evaluate the jump in the specific heat.

(d) Find the trajectory $T(P)$ for an adiabatic process in the liquid phase region, starting at some initial state (T_0, P_0). Assuming that (T^*, P^*) are known, determine the condition that this process leads to cooling via solidification.

(e) If the condition in (d) is satisfied, what will happen to the $T(P)$ trajectory after it hits the $P(T)$ coexistence curve?
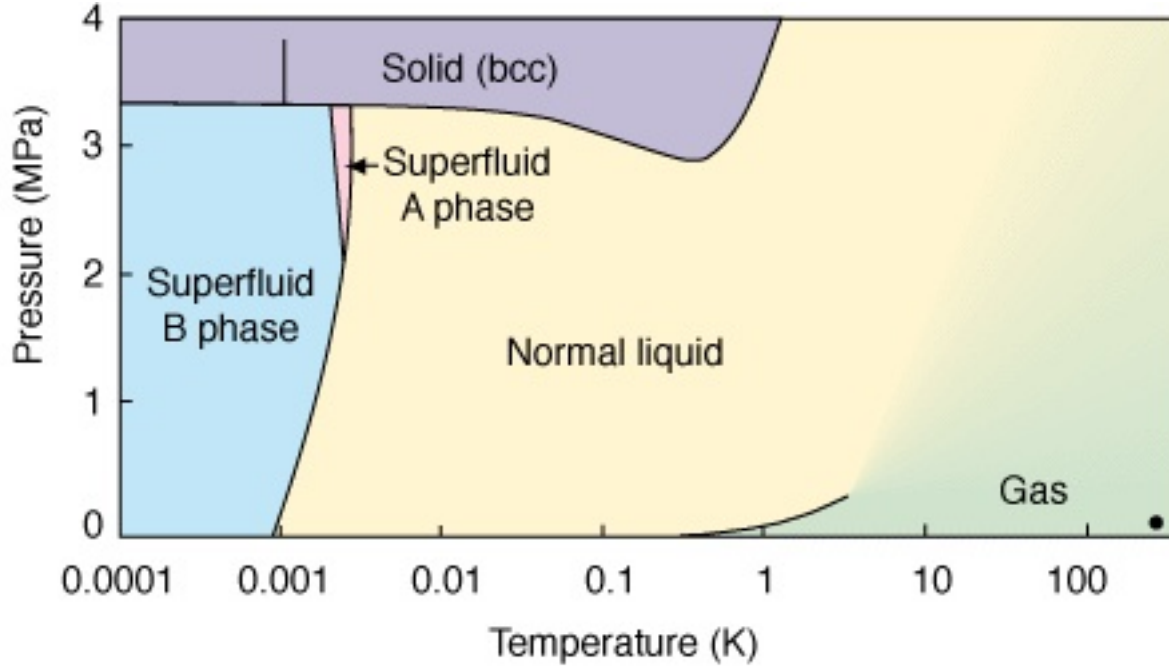
Figure 1: The phase diagram above is for a Helium 3 isotope

1 The Solution:

(a) Helium atoms have a magnetic moment, subsequently the solid phase can be thought of as a set of spins, such that each spin can be oriented either up or down irrespective of neighboring spins.

The partition function for an individual spin:

$$Z = \sum_{\sigma=\pm1} = 2 \tag{1}$$

The partition function of N non-interacting spins factorizes, as a result the partition function of N independent spins is simply the product of each individual partition function. Thus $Z_N = Z_1^N$. Given a partition function the Entropy is $\frac{\partial}{\partial T}Tln(Z^N)$:

$$S_s = Nln(2) \tag{2}$$

For low temperatures the He^3 liquid may be considered as a Fermi gas. The free energy of a low temperature Fermi gas is written as:

$$F(T) = \left(\frac{3N\epsilon_f}{5}\left(1 - \frac{5\pi^2}{12}(\frac{T}{\epsilon_f})^2 + o(T^2)\right)\right) \tag{3}$$

The entropy of the system is defined as the minus derivative of the Free energy with respect to Temperature $S_l = -\left(\frac{\partial F(T)}{\partial T}\right)$. This yields :
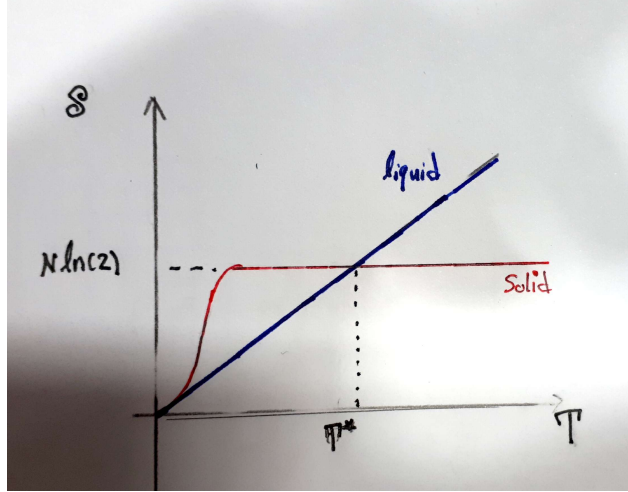
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Figure 2: Entropy as a function of Temperature

$$S_l = -\left(\frac{\partial F(T)}{\partial T}\right) = -\frac{\partial}{\partial T}\left(\frac{3N\epsilon_f}{5}\left(1 - \frac{5\pi^2}{12}(\frac{T}{\epsilon_f})^2 + o(T^2)\right)\right) = \frac{N\pi^2}{2}(\frac{T}{\epsilon_f}) \tag{4}$$

The Fermi energy and Pressure of a low temperature Fermi gas are:

$$P = \frac{1}{5m}(6\pi^2)^{\frac{2}{3}}\left(\frac{N}{V}\right)^{\frac{5}{3}} \tag{5}$$

$$\epsilon_f = \frac{1}{2m}(6\pi^2)^{\frac{2}{3}}\left(\frac{N}{V}\right)^{\frac{2}{3}} \tag{6}$$

leading to the relation:

$$\epsilon_f = \Lambda P^{\frac{2}{5}}$$

Λ is a constant Thus the resultant entropy is:

$$S_l = \frac{N\pi^2}{2}(\frac{T}{\Lambda})p^{\frac{-2}{5}} \tag{7}$$

Equating equations (2) and(4) we can find the Temperature T*:

$$T^* = \frac{\epsilon_f}{\pi^2}ln(4) \tag{8}$$

In the proceeding discussion we will substitute the Fermi energy with the Fermi temperature, while absorbing the Boltzmann constant into the definition of the fermi temperature.

(b) The Clausius Claperon relation describing the coexistence curve is written as:

$$\left(\frac{\partial P}{\partial T}\right)_{CoexistenceCurve} = \left(\frac{\Delta S}{\Delta V}\right)_{s \to l} = \frac{\frac{\pi^2 T}{2T_f} - ln(2)}{\Delta v} \tag{9}$$

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Note we divided by the total number of particles for both the numerator and denominator.

Re-writing the expression we find that

$$\frac{\partial P}{\partial T} = \frac{\pi^2}{2\Delta v}\left(\frac{T - T^*}{T_f}\right) \tag{10}$$

After integration with respect to temperature:

$$P(T) = \frac{\pi^2}{4T_f\Delta v}\left(T^2 - 2T^*T\right) + Const \tag{11}$$

It is known that $P(T^*) = P^*$.

$$P^* = -\frac{\pi^2}{4T_f\Delta v}T^{*2} + const \tag{12}$$

This leads to the result:

$$P(T) = \frac{\pi^2}{4T_f\Delta v}\left(T - T^*\right)^2 + P^* \tag{13}$$

(c) In this problem we have a first order phase transitions, due to the discontinuity of the Entropy (first order derivative of the Helmholtz Free energy function), excluding the transition at (P*,T*) where the entropy is continuous.

The specific heat is the product of Temperature and the derivative of entropy with respect to Temperature , that is $C = T\left(\frac{\partial S}{\partial T}\right)$

The specific heat of the liquid is:

$$C_{liquid} = \frac{N\pi^2}{2}\left(\frac{T}{T_f}\right) \tag{14}$$

The specific heat of the solid is:

$$C_{solid} = 0 \tag{15}$$

The jump in the specific heat as we migrate from one phase to another is given by:

$$\Delta C = C_{liquid} - C_{solid} = \frac{N\pi^2}{2}\left(\frac{T}{T_f}\right) \tag{16}$$

(d) For adiabatic processes $S_l(T,P) = const.$ As a result the ratio between Temperature and Pressure in the form remains unchanged during the entire process - $\frac{T}{p^{\frac{2}{5}}} = const$ -.It follows that the P(T) trajectory is described by the equation:

$$T = cP^{\frac{2}{5}} \tag{17}$$

Recall that initially the curve began at the point (T_0, P_0). Subsequently, this enables us to find the constant, $c = \frac{T_0}{P_0^{\frac{2}{5}}}$. The resultant trajectory is written as:

$$T = T_0 \Big(\frac{P}{P_0}\Big)^{\frac{2}{5}} \tag{18}$$

We will assume cooling occurs when the trajectory comes into contact the the liquid-solid coexistence curve, in particular when slope of the phase transition is negative $\frac{\partial P}{\partial T} < 0$ -anomalous region- . In the proceeding clause we will explain.

According to figure 3, the condition is satisfied for trajectories at lower temperatures than the critical trajectory $T_C = T^* \big(\frac{P}{P*}\big)^{\frac{2}{5}}$, therefore we will demand $T(P) < T_C(P)$

$$T_0 \Big(\frac{P}{P_0}\Big)^{\frac{2}{5}} < T^* \Big(\frac{P}{P*}\Big)^{\frac{2}{5}} \tag{19}$$

Which yields:

$$\frac{T_0}{T^*} < \Big(\frac{P_0}{P*}\Big)^{\frac{2}{5}} \tag{20}$$

(e) Our trajectory describes adiabatic compression. It will follow the trajectory $P = P_0 \big(\frac{T}{T_0}\big)^{\frac{2}{5}}$ until it reaches the phase transition curve. At that point the compression can continue via solidification of the helium. Which leaves the liquid with less entropy which at lower temperatures than the Fermi temperature, $T \propto S$, allows a pressure increase since $\frac{\partial P}{\partial T} < 0$. Meaning the process will proceed left along the phase transition curve.
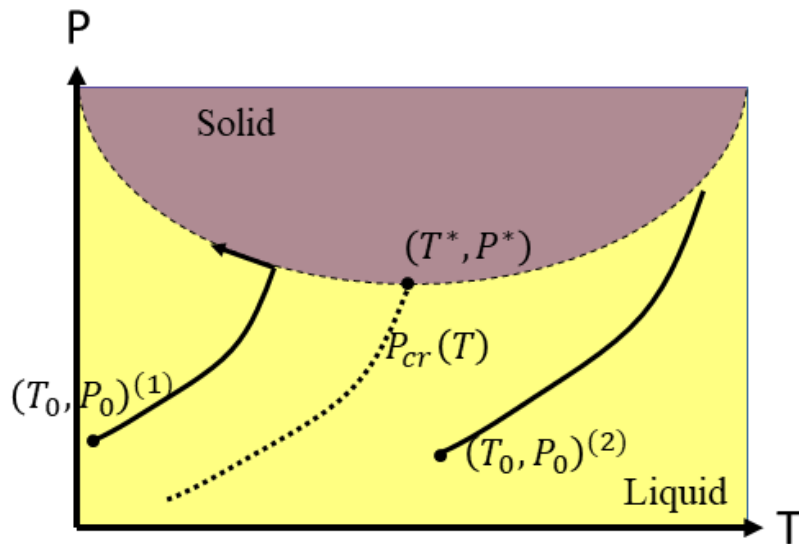
He_3 phase diagram around (T^*, P^*) with adiabatic compression trajectories, $P \propto T^{\frac{5}{2}}$. Trajectories with starting point above the critical trajectory (1) hit the phase transition where the slope is negative. Those with starting point below hit the transition line where the slope is positive (2). Additionally, trajectory 1 can continue with adiabatic compression via solidification (left pointing arrow)

Figure 3: