

PHASES OF HELIUM-3

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.34.

Helium has peculiar properties at very low temperatures. In fact, the two main isotopes of helium ^3He and ^4He , have quite different behaviour. Looking at the phase diagram (a plot of phases on a pressure-temperature diagram) for ^3He in Schroeder's Figure 5.13, we see that the liquid-solid phase boundary has a horizontal slope at $T = 0$, then has a negative slope up to around $T = 0.3$ K, then has a minimum and turns upwards with a positive slope for $T > 0.3$ K.

In all these regions, if we look at some fixed temperature and increase the pressure, we always make a transition from liquid to solid. As I can't think of any situation in which increasing the pressure on a sample can *increase* its volume, it seems reasonable that at any temperature, the solid phase occupies a smaller volume, and thus has a higher density, than the liquid phase.

Note that this behaviour is different from that of water (shown in Schroeder's Figure 5.11). In the $P - T$ phase diagram for water, the phase boundary between liquid and solid also has a negative slope, but in this case, the liquid phase is *above* the solid phase, so that increasing the pressure causes a transition from solid to liquid. Liquid water therefore has a higher density than solid water.

From the fact that solid ^3He is denser than the liquid, we can use the Clausius-Clapeyron relation in the form that relates the entropies and volumes of the solid and liquid phases to the slope of the phase boundary

$$(0.1) \quad \frac{dP}{dT} = \frac{S_s - S_\ell}{V_s - V_\ell}$$

We see that on the phase boundary in the negative slope region, $S_s - S_\ell$ must have the opposite sign to $V_s - V_\ell$. For a fixed number of atoms, $V_s < V_\ell$, so $S_s > S_\ell$. That is, solid ^3He actually has a higher entropy than the liquid.

From the third law of thermodynamics, which states that as $T \rightarrow 0$, $S \rightarrow 0$, we see that both $S_s \rightarrow 0$ and $S_\ell \rightarrow 0$, so $\frac{dP}{dT} \rightarrow 0$ as $T \rightarrow 0$, which explains the horizontal slope at $T = 0$.

The curious behaviour of the entropy can be used to cool ^3He . If we compress liquid ^3He adiabatically, then we do so with no heat transfer and therefore with no change in entropy. If we begin with liquid ^3He in the region below 0.3 K where the P versus T phase boundary has a negative slope and increase the pressure adiabatically until we get a solid, the solid must have the same entropy as the liquid. As we've seen above, increasing the pressure isothermally produces a solid with a *higher* entropy than the liquid, so an adiabatic compression must produce a solid with a lower temperature in order to obtain the lower entropy that matches the entropy of the liquid before it solidified. [I'm not sure just how you'd do the adiabatic compression. Perhaps it works in a way similar to that for an ideal gas, where we can compress the gas quickly, but not so quickly that the gas doesn't have time to come to equilibrium at each stage in the compression. Presumably for liquid helium, the quantities involved aren't that great, so a quick compression wouldn't be that hard to do.]

For temperatures above 0.3 K, the slope $\frac{dP}{dT}$ is positive, so in this region, the solid has a lower entropy than the liquid, so an adiabatic compression of the liquid produces a solid with a higher temperature.