3.F. The Helium Liquids

	^{3}He	^{4}He
composition	$2p+1n+2e$	$2p+2n+2e$
nuclear spin	$\frac{1}{2}\oplus\frac{1}{2}\oplus\frac{1}{2}=\frac{1}{2},\ \frac{3}{2},\ \ldots$	$\frac{1}{2}\oplus\frac{1}{2}\oplus\frac{1}{2}\oplus\frac{1}{2}=0,1,2,\ \ldots$
electron spin	$\frac{1}{2}\oplus\frac{1}{2}=0,1,2,\ \ldots$	$\frac{1}{2}\oplus\frac{1}{2}=0,1,2,\ \ldots$
statistics	Fermi – Dirac	Bose – Einstein
bosons in superfluid	bound pairs of ^{3}He ($S=1, L=1$)	^{4}He atoms
T_C	$2.7\times10^{-3}\,K$	$2.19\,K$

where $\oplus$ denotes the quantum mechanical addition of angular momenta.

Liquid mixture of ^{3}He & ^{4}He is endowed with the additional behavior of binary mixtures.

3.F.1. Liquid ^{4}He

The phase diagram of ^{4}He is shown in Fig.3.15.

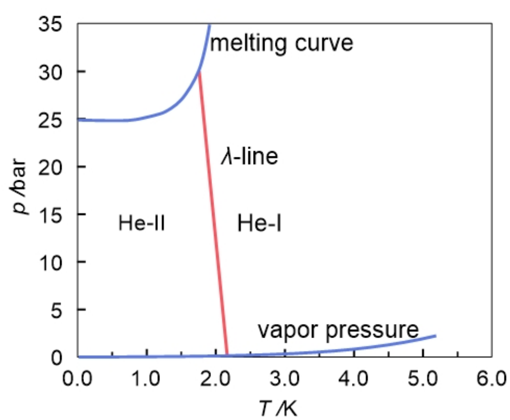

Fig.3.15. 1 bar ≈ 0.987 atm.

Two features that distinguish ^{4}He from other ordinary substances are

1. For $P \lesssim 25$ atm, ^{4}He remains in liquid form down to $T=0$.
2. There are two liquid phases, called He I and He II, for ^{4}He.
   He I behaves like normal liquid while He II is a superfluid.

The superfluid component is a Bose-Einstein condensate that has neither viscosity nor entropy.

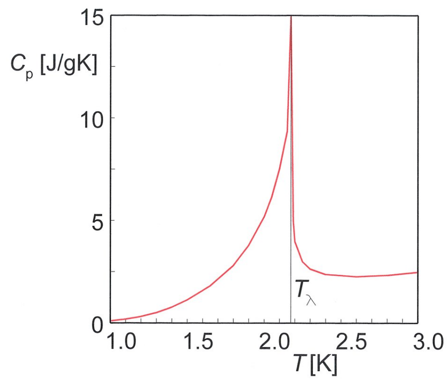

Fig.3.16. Constant pressure heat capacity. For a long time, it was thought that $C_P(T) \propto -\ln(T_\lambda - T)$ so that the critical exponent is $\alpha = 0$. However, recent experiments showed that $\alpha \approx -0.01285$ so that C_P remains finite at T_λ. See J. A. Lipa et al, Phys. Rev. Lett. 76, 944–947 (1996).

The coexistence curve between He *I* & He II is made up of a line of λ-points called the λ-line, so named because the plot of the constant pressure specific heat $C_P(T)$ looks like the letter λ in the vicinity of T_λ [see Fig.3.16]. Here, T_λ is the temperature at the intersection of the horizontal $P = \text{constant}$ line and the λ-line in Fig.3.15, i.e.,

$$P = P_{\text{coex}}(T_\lambda) = \text{saturation vapor pressure at } T_\lambda.$$

However, unlike the vaporization curve, phase transition at each λ-point is continuous with $\Delta h = 0$. Thus, each λ-point is a critical point and the Clausius-Clapeyron equation does not apply.

The zero viscosity of the superfluid gives rise to some interesting phenomena including

1. As T drops below T_λ, the newly formed He II component can leak through the container that held He *I*.
2. Due to the capillary effect, He II can climb up the inside, and then down the outside, wall of an open container.
3. Fountain effect [see §S3.B].

Finally, combining the 3rd law result (2.54) of §2.D.4 with the Maxwell relation (2.100) of §2.F.3, we have

$$\frac{d P_{\text{coex}}}{d T} = \left(\frac{\partial S}{\partial V}\right)_T \to 0 \qquad \text{as } T \to 0 \qquad [\text{ 3rd law. }]$$

This behavior can be observed in both fusion and vaporization curves in Fig.3.15.

3.F.2. Liquid ^{3}He

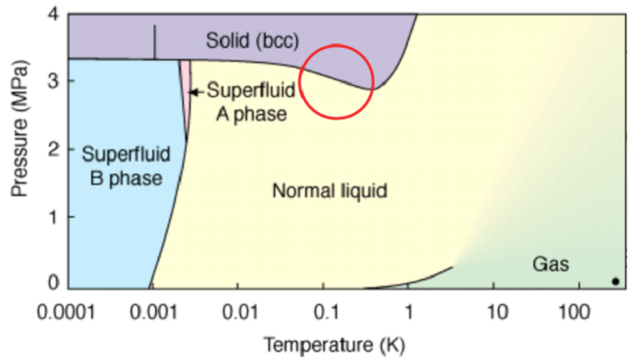

Fig.3.17a. Semi-log plot of the phase diagram of ^{3}He with $\boldsymbol{H} = 0$. [1 MPa ≈ 10 atm].

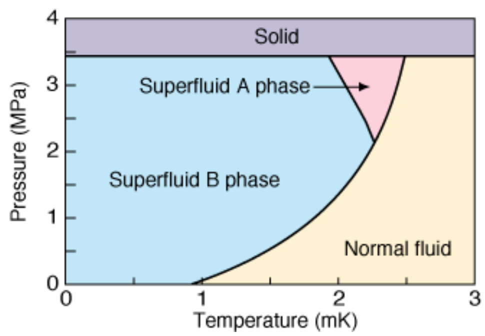

Fig.3.18. Phase diagram of ^{3}He with $\boldsymbol{H} = 0$.

The phase diagrams of ^{3}He are shown in Fig.3.17a and Fig.3.18. Like ^{4}He , ^{3}He remains liquid down to $T = 0$ for $P \lesssim 34$ atm. For $T \lesssim 2.5$ mK, it becomes a superfluid, with two superfluid phases A and B. Phase A is anisotropic (with axial symmetry) while phase B is isotropic.

Another interesting feature of the fusion curve is its negative slope in the region around $T = .1\,K$ and marked with a red circle in Fig.3.17a. Since $v_{\text{liquid}} > v_{\text{solid}}$, the Clausius-Clapeyron equation indicates the unusual result $s_{\text{liquid}} < s_{\text{solid}}$, which is due to the spin degrees of freedom. Nevertheless, the slope of the fusion curve levels out as $T \to 0$, in agreement of the 3rd law.

3.F.3. Liquid ^{3}He – ^{4}He Mixture

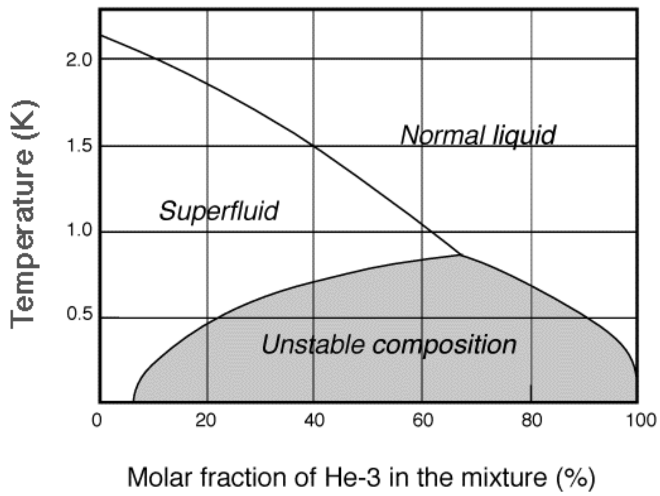

Fig.3.19.

Mixing ^{3}He with ^{4}He introduces an extra degrees of freedom, which can be chosen as the fraction x_3 of ^{3}He. Properties of the coexistence region (marked as unstable in Fig.3.19) can be described by the general theory of binary mixtures [see §S.3.E].

The coexistence curve between normal and superfluid is a λ-line. However, phase transitions on the boundary of the unstable region are 1st order. The end of the λ-line therefore represents the coincidence of 3 critical points (1 from the λ-line, and 1 each from the x_3- rich and x_3-poor coexistence curves on the border of the unstable region). It is therefore called the tricritical point.