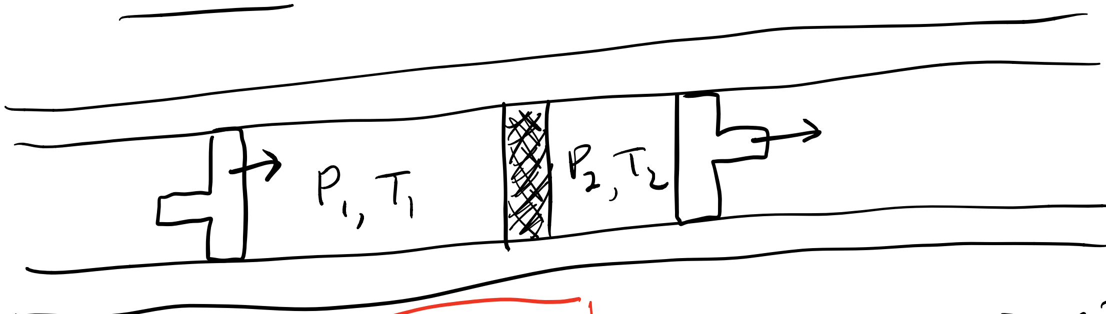
PHYS 425 - W2L1

Joule-Thomson Expansion

<u>Last Time</u>



$$\boxed{\mu_{JT} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}}$$

$\mu_{JT} > 0 \Rightarrow T_2 < T_1$ (cooling)

$\mu_{JT} < 0 \Rightarrow T_2 > T_1$ (heating)

To go further, need to model how real gasc behave $\rightarrow$ need eq'n of state.

(a) ideal gas (non-interacting)

$$PV = Nk_BT \qquad \left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk_B}{P} = \frac{V}{T}$$

$$T\left(\frac{\partial V}{\partial T}\right)_p - V = \cancel{T}\left(\frac{V}{\cancel{T}}\right) - V = 0.$$

$\therefore$ for ideal non-interacting gas $\mu_{JT} = 0$

$\therefore T_1 = T_2$

(b) Van der Waals Gas

1. Don't assume gas particles are point particles. Assume that they are hard spheres.

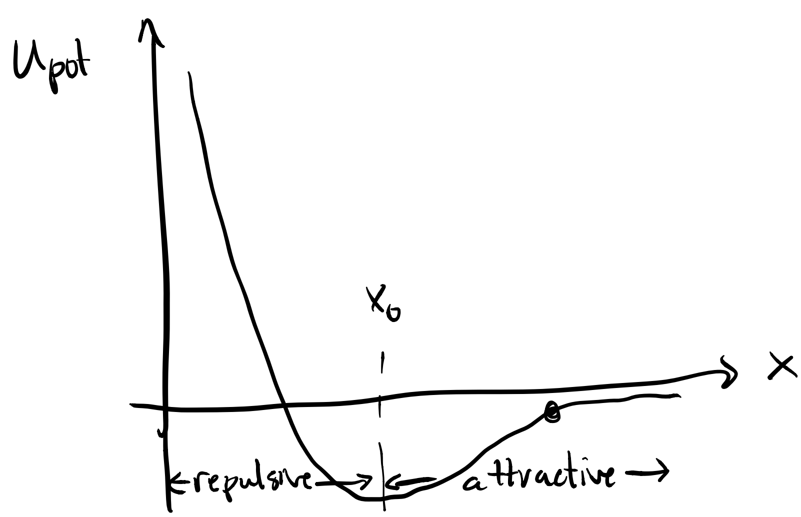
   ∴ When added to a closed volume they occupy some space

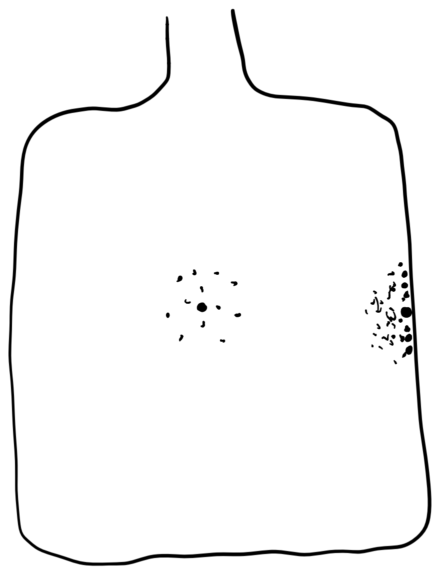
$$V \to V - Nb'$$

N: no. of particles

b' is excluded volume due to finite size of gas particle.

2. Assume that there is a short range attraction between particles.





- particles in centre don't feel net force to left or right
- particles near container wall feel net force inwards b/c of absence of particles near container wall.

- The net inward force on surface particles $\propto \frac{N}{V}$
- No. of surface particles also $\propto \frac{N}{V}$ (density)

$\therefore$ pressure on vessel walls $P \to P - a'\left(\frac{N}{V}\right)^2$

$$P = \frac{Nk_BT}{V} \quad \text{(ideal gas)}$$

$$\Downarrow$$

$$\boxed{P = \frac{Nk_BT}{V - Nb'} - a'\left(\frac{N}{V}\right)^2}$$

Van der Waal's Eq'n of state.

$$\therefore \frac{P}{k_B T} = \frac{N}{V\left(1-\frac{Nb'}{V}\right)} - \frac{a'}{k_B T}\left(\frac{N}{V}\right)^2$$

$$= \frac{N}{V}\left(1-\frac{Nb'}{V}\right)^{-1} - \frac{a'}{k_B T}\left(\frac{N}{V}\right)^2$$

If excluded volume $Nb' \ll V$

then $\left(1-\frac{N}{V}b'\right)^{-1} \approx 1-(-1)\frac{N}{V}b' = 1+\frac{N}{V}b'$

$$\therefore \frac{P}{k_B T} \approx \frac{N}{V}\left(1+\frac{N}{V}b'\right) - \frac{a'}{k_B T}\left(\frac{N}{V}\right)^2$$

or $$\frac{PV}{Nk_B T} \approx 1+\frac{N}{V}b' - \frac{a'}{k_B T}\frac{N}{V} = 1+\frac{N}{V}\underbrace{\left(b'-\frac{a'}{k_B T}\right)}_{\text{van der Waals correction.}}$$

on RHS make approx $\frac{N}{V} \approx \frac{P}{k_B T}$

$$\frac{PV}{Nk_BT} \approx 1 + \frac{P}{k_BT}\left(b' - \frac{a'}{k_BT}\right)$$

or

$$\boxed{V = \frac{Nk_BT}{P}\left[1 + \frac{1}{k_BT}\left(b' - \frac{a'}{k_BT}\right)P\right]}$$

Now evaluate $\left(\frac{\partial V}{\partial T}\right)_P$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk_B}{P}\left[1 + \frac{1}{k_BT}\left(b' - \frac{a'}{k_BT}\right)P\right]$$

$$+ \frac{Nk_BT}{P}\left[-\frac{1}{k_BT^2}\left(b' - \frac{a'}{k_BT}\right)P\right.$$

$$\left. + \frac{1}{k_BT}\left(\frac{a'}{k_BT^2}\right)P\right]$$

$$= \frac{Nk_B}{P}\left[1 + \cancel{\frac{1}{k_BT}\left(b' - \frac{a'}{k_BT}\right)P} - \cancel{\frac{1}{k_BT}\left(b' - \frac{a'}{k_BT}\right)P}\right.$$

$$\left. + \frac{a'P}{(k_BT)^2}\right]$$

$$\therefore \left(\frac{\partial V}{\partial T}\right)_p = \frac{N k_B}{p}\left[1 + \frac{a' p}{(k_B T)^2}\right]$$

Recall:

$$\mu_{JT} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}$$

$$T\left(\frac{\partial V}{\partial T}\right)_p - V = \frac{N k_B T}{p}\left[\cancel{1+}\ \frac{a' p}{(k_B T)^2}\right]$$

$$- \frac{N k_B T}{p}\left[\cancel{1} + \frac{1}{k_B T}\left(b' - \frac{a'}{k_B T}\right)p\right]$$

$$= \frac{N \cancel{k_B T}}{\cancel{p}}\left[\frac{2a' \cancel{p}}{(k_B T)^2} - \frac{b' \cancel{p}}{\cancel{k_B T}}\right]$$

$$= N\left(\frac{2a'}{k_B T} - b'\right)$$

$$\boxed{\mu_{JT} = \frac{N\left(\frac{2a'}{k_B T} - b'\right)}{C_p}}$$

low temp, $\frac{2a'}{k_B T}$ term dominates.

$$\mu_{JT} \approx \frac{2Na'}{C_p k_B T} > 0 \Rightarrow \text{get cooling}$$

high temp, b' term dominates

$$\mu_{JT} \approx -\frac{Nb'}{C_p} < 0 \Rightarrow \text{get heating}$$

At the inversion temp T_{inv}, $\mu_{JT} = 0$

$$\frac{2a'}{k_B T_{inv}} - b' = 0$$

$$\boxed{\therefore\ T_{inv} = \frac{2a'}{k_B b'}}$$

Below T_{inv}, get cooling b/c $\mu_{JT} > 0$

Above T_{inv}, get heating b/c $\mu_{JT} < 0$

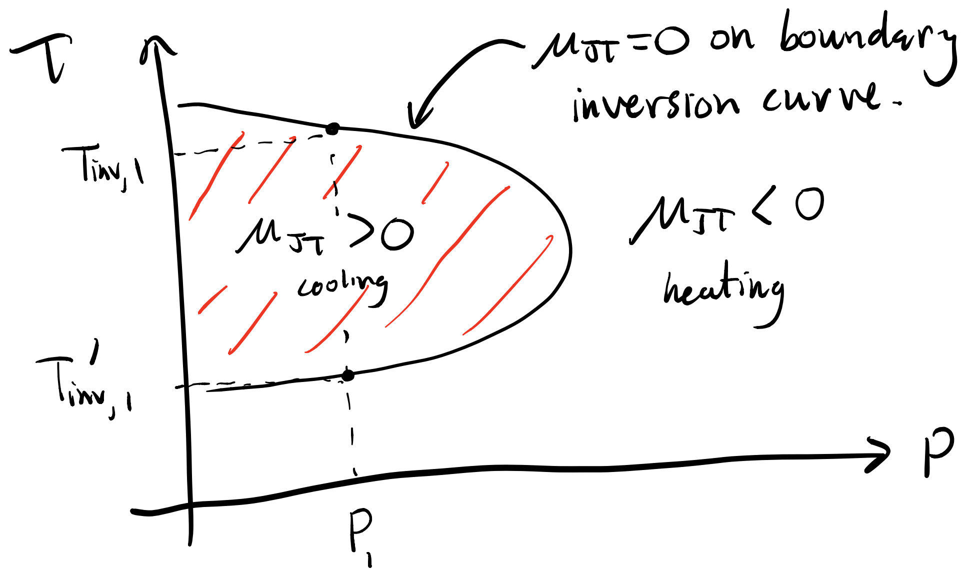
In practice μ_{JT} depends also on pressure.

In an assignment #2, you will calc μ_{JT} for van der Waals eq'n more carefully.

In your calc, won't make the approx.

$$\left(1 - \frac{N}{V} b'\right)^{-1} \approx 1 + \frac{N}{V} b'$$

& $\quad \frac{N}{V} \approx \frac{P}{k_B T}$ on RHS

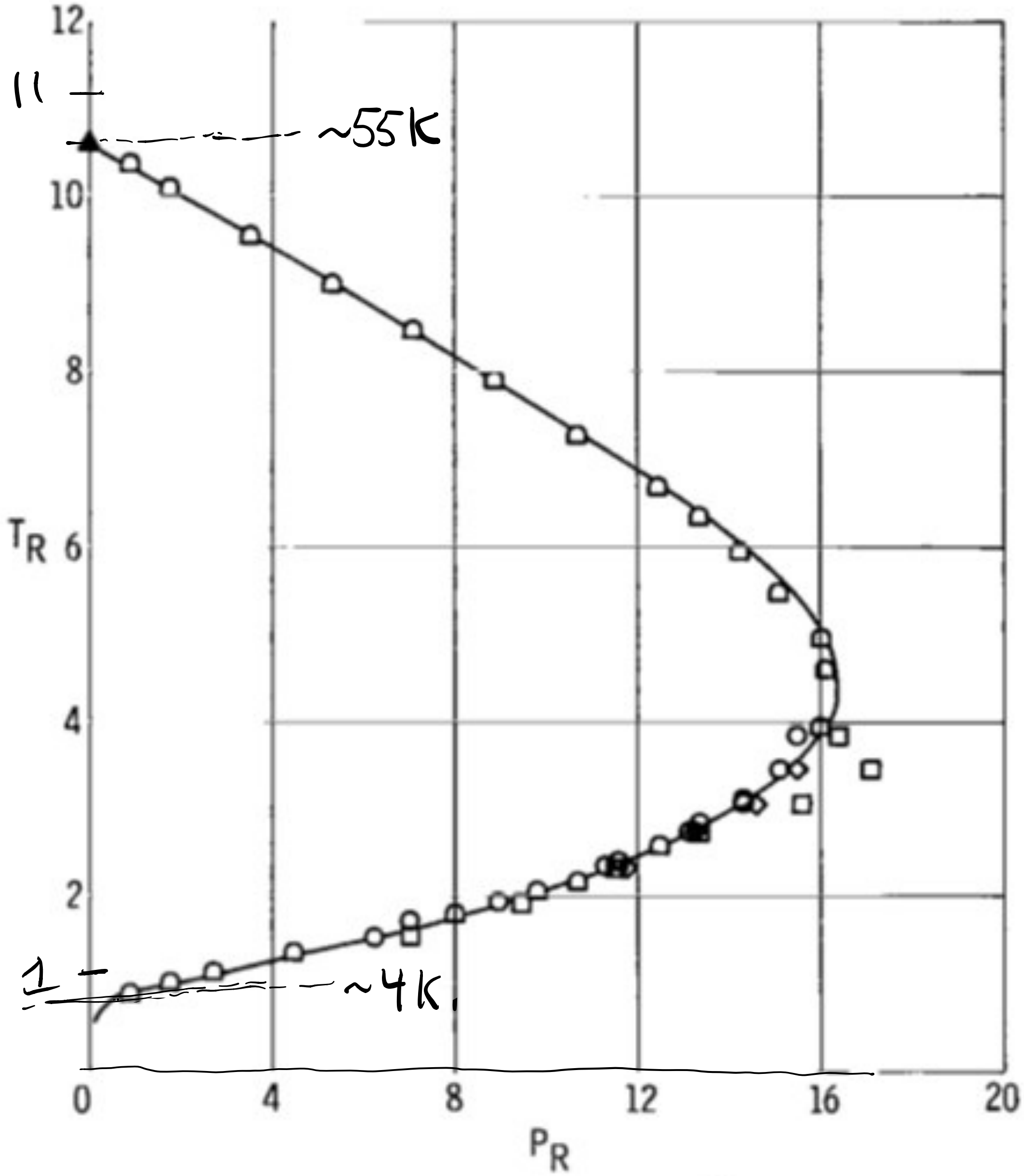


Can liquify ^4He using a Joule-Thomson expansion. At 1atm of pressure, the boiling temp. of liquid ^4He is about 4.2K.

It wasn't part of the video, but below is the actual inversion curve for ^4He. In this plot, $T_R = \frac{T}{T_c}$ where $T_c = 5.2K$

& $P_R = \frac{P}{P_c}$ where $P_c = 0.227 \frac{MN}{m^2}$

$= 0.227$ MPa



(a) Helium. P_c = 0.22746 MN/m^2; T_c = 5.2 K.