

Ideal quantum gases

(1)

- identical $\longleftrightarrow$ indistinguishable
- thermal wavelength large $\rightarrow$ statistics can be expected to play a crucial role in determining behaviour
- in chapter 5 we saw that the criterion for "classical" ~~quantum~~ behavior is: $n\lambda^3 \ll 1$

$$\frac{n h^3}{(2\pi m k T)^{3/2}} \ll 1$$

$\Rightarrow$ small mass, low $T \Rightarrow$ quantum behavior
large density

- use grand-canonical ensemble: $Z = \text{Tr} e^{-\beta(\hat{H} - \mu\hat{N})}$
- no need to fix N
- consider ideal gas in box $V = L^3$



momentum operator: $\vec{p}_{\vec{m}} = \hbar \left(\frac{2\pi}{L} \right) (m_x \hat{i} + m_y \hat{j} + m_z \hat{k})$

kinetic energy operator:

$$\frac{p^2}{2m} = \epsilon_{\vec{m}} = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L} \right)^2 (m_x^2 + m_y^2 + m_z^2)$$

$\Downarrow$

in second quantization:

$$\hat{H} = \sum_{\vec{m}} \epsilon_{\vec{m}} \hat{n}_{\vec{m}}$$

$\Rightarrow$ general result also applicable to
tight-binding model

for bosons: $Z = \prod_{\vec{m}} \left[\sum_{n_{\vec{m}}=0}^{\infty} \exp[-\beta(\epsilon_{\vec{m}} - \mu)n_{\vec{m}}] \right]$

$$n_{\vec{m}} = 0, 1, 2, \dots, \infty$$

for fermions: $Z = \prod_{\vec{m}} \left[\sum_{n_{\vec{m}}=0}^1 \exp[-\beta(\epsilon_{\vec{m}} - \mu)n_{\vec{m}}] \right]$
 $n_{\vec{m}} = 0, 1$ (spin ignored)

Bose-Einstein Gases

consider case with $s = 0$

$$Z = \prod_{\vec{m}} \left(\sum_{n_{\vec{m}}=0}^{\infty} e^{-\beta(\epsilon_{\vec{m}} - \mu)n_{\vec{m}}} \right)$$

$$= \prod_{\vec{m}} \frac{1}{1 - e^{-\beta(\epsilon_{\vec{m}} - \mu)}}$$

free energy (grand potential)

$$\Omega = -k_B T \ln Z = k_B T \sum_{\vec{m}} \ln(1 - e^{-\beta(\epsilon_{\vec{m}} - \mu)})$$

average number of particles

$$\langle N \rangle = - \frac{\partial \Omega}{\partial \mu} = -k_B T \sum_{\vec{m}} \frac{1}{1 - e^{-\beta(\epsilon_{\vec{m}} - \mu)}} \left(-e^{-\beta(\epsilon_{\vec{m}} - \mu)} \right) \beta$$

$$= \sum_{\vec{m}} \frac{1}{e^{\beta(\epsilon_{\vec{m}} - \mu)} - 1} = \sum_{\vec{m}} \langle n_{\vec{m}} \rangle$$

can also write in terms of fugacity $\lambda = e^{\beta\mu}$

$$\langle N \rangle = \sum_{\vec{m}} \frac{\lambda}{e^{\beta\epsilon_{\vec{m}}} - \lambda} \quad \lambda = e^{\beta\mu}$$

can undergo a phase transition

minimum $\epsilon_{\vec{m}}$ is $\epsilon_0 = 0 \Rightarrow \lambda \leq e^{\beta\epsilon_{\vec{m}}} \leq \infty$

$\Downarrow$
 $\Downarrow$
 $\Downarrow$

it follows that $0 \leq \lambda \leq 1$, otherwise $\langle n_{\vec{m}} \rangle$

can become negative

$$\Rightarrow \mu \leq 0 \quad (\mu \leq \epsilon_{\min})$$

$$\text{at minimum: } \langle n_0 \rangle = \frac{z}{1-z}$$

$$\text{as } \mu \rightarrow 0 \quad z \rightarrow 1 \quad \langle n_0 \rangle \rightarrow \infty \Rightarrow \text{Occupation of state with } 0 \Rightarrow \underline{\text{macroscopic}}$$

to compute thermodynamic quantities $\Rightarrow$ convert sum

$\sum_{\vec{m}}$ to an integral

- since $\vec{m}=0$ is singular $\Rightarrow$ exclude it

$$\sum_{\vec{m}} \Rightarrow 0\text{-term} + \underbrace{\sum'_{\vec{m}}}_{\text{rest}}$$

$$\sum'_{\vec{m}} \approx \int d\vec{m} = \frac{V}{(2\pi\hbar)^3} \int d\vec{p} = \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty p^2 dp$$

$$\langle N \rangle = \frac{z}{1-z} + \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty p^2 dp \frac{z}{e^{\frac{\beta p^2}{2m}} - z}$$

$$-\Omega = k_B T \ln(1-z) + \frac{4\pi V k_B T}{(2\pi\hbar)^3} \int_0^\infty p^2 dp \frac{z}{\ln(1 - e^{-\frac{\beta p^2}{2m}} z)}$$

variable transformation: $x^2 = \frac{\beta p^2}{2m}$

$$\langle N \rangle = \frac{z}{1-z} + \frac{4V}{\lambda_T^3 \sqrt{\pi}} \int_{\frac{\lambda_T \sqrt{\pi}}{L}}^\infty x^2 dx \left(\frac{z}{e^{x^2} - z} \right)$$

$$-\Omega = k_B T \ln(1-z) + \frac{4V k_B T}{\lambda_T^3 \sqrt{\pi}} \int_{\frac{\lambda_T \sqrt{\pi}}{L}}^\infty x^2 dx \ln[1 - z e^{-x^2}]$$

$$\lambda_T = \left(\frac{2\pi\hbar^2}{m k_B T} \right)^{1/2}$$

in limit $L \rightarrow \infty$ ($V \rightarrow \infty$) we will have a function appearing of the form

$$g_{5/2}(z) = -\frac{4}{\sqrt{\pi}} \int_0^\infty x^2 dx \ln[1 - ze^{-x^2}]$$

evaluate integral: expand $\ln(1 - ze^{-x^2})$ in z

$$\left. \begin{aligned} f(z) &= \ln(1 - ze^{-x^2}) \\ f'(z) &= \left(\frac{1}{1 - ze^{-x^2}} \right) (-ze^{-x^2}) \\ f''(z) &= -\frac{1}{(1 - ze^{-x^2})^2} (e^{-2x^2}) \\ f'''(z) &= -\frac{2}{(1 - ze^{-x^2})^3} e^{-3x^2} \end{aligned} \right\} \begin{aligned} f(0) &= 0 \\ f'(0) &= -e^{-x^2} \\ f''(0) &= -2e^{-2x^2} \\ f'''(0) &= -2e^{-3x^2} \end{aligned}$$

$$f^{(n)}(0) = -(n-1)! e^{-nx^2}$$

Taylor expansion

$$f(z) = \sum_{n=1}^{\infty} \frac{-(n-1)! e^{-nx^2}}{n!} z^n$$

$$f(z) = \sum_{n=1}^{\infty} -\frac{e^{-nx^2}}{n} z^n$$

$$g_{5/2}(z) = +\frac{4}{\sqrt{\pi}} \int_0^\infty x^2 dx \left\{ \sum_{n=1}^{\infty} \frac{e^{-nx^2}}{n} z^n \right\}$$

$$= \sum_{n=1}^{\infty} \frac{4z^n}{n\sqrt{\pi}} \underbrace{\int_0^\infty x^2 dx e^{-nx^2}}_{\frac{\sqrt{\pi}}{2n^{3/2}}} = \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}}$$

in the expression for $\langle N \rangle$ we have

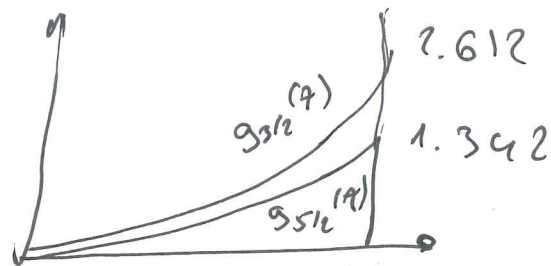
$$\langle N \rangle = \frac{Z}{1-Z} + \frac{4V}{\lambda_T^3 \sqrt{\pi}} \int_{\frac{r}{L}}^{\infty} x^2 dx \frac{Z}{e^{x^2} - Z}$$

for limit $L \rightarrow \infty$

$$g_{3/2}(Z) = \frac{4}{\sqrt{\pi}} \int_0^{\infty} x^2 dx \frac{Z}{e^{x^2} - Z} = Z \frac{d}{dZ} g_{5/2}(Z) = \sum_{n=1}^{\infty} \frac{Z^n}{n^{3/2}}$$

functions $g_{5/2}(Z)$, $g_{3/2}(Z)$ are well-behaved on interval

$$0 \leq Z < 1 \Rightarrow \cancel{g_{3/2}}$$



- in taking the limit $V \rightarrow \infty$ need to also understand

how $\epsilon_f = 0$ terms behave

pressure:
$$P = -\frac{\Omega}{V} = -\frac{k_B T}{V} \ln(1-Z) + \frac{k_B T}{\lambda_T^3} g_{5/2}(Z) + \dots$$

$\bar{\Omega}$ term:
$$-\frac{\ln(1-Z)}{V}$$

average particle number:

$$\frac{\langle N \rangle}{V} = \frac{\langle N \rangle}{V} = \frac{1}{V} \frac{Z}{1-Z} + \frac{4V}{\lambda_T^3 \sqrt{\pi}} \frac{1}{\lambda_T^3} g_{3/2}(Z)$$

$$\frac{N_0}{V} = \frac{1}{V} \frac{Z}{1-Z} \Rightarrow N_0(1-Z) = Z \Rightarrow Z = \frac{N_0}{N_0+1}$$

$\Downarrow$

$$-\frac{\ln(1-Z)}{V} = -\frac{\ln\left(\frac{N_0+1-N_0}{N_0+1}\right)}{V} = +\frac{\ln N_0+1}{V}$$

$\Rightarrow V \rightarrow \infty$ ($N_0 \rightarrow \infty$) but $\frac{N_0}{V}$ fixed

$$\Rightarrow \frac{\ln(N_0+1)}{V} \rightarrow 0$$

$$\frac{1}{V} \frac{n}{1-n} \rightarrow \frac{n_0}{V}$$

pressure:

$$P = \begin{cases} \frac{n_B T}{\lambda_T^3} g_{5/2}(\eta) & \eta < 1 \\ \frac{n_B T}{\lambda_T^3} g_{5/2}(1) & \eta = 1 \end{cases}$$

average particle number

$$\langle n \rangle = \frac{\langle N \rangle}{V} = \begin{cases} \frac{1}{\lambda_T^3} g_{3/2}(\eta) & \eta < 1 \\ \frac{1}{\lambda_T^3} g_{3/2}(1) + n_0 & \eta = 1 \end{cases}$$

to determine phase diagram:

BEC occurs when fugacity $\eta \rightarrow 1$ ($\mu = 0$)

$$\langle n \rangle \lambda_T^3 = g_{3/2}(1)$$

One can obtain critical density $\langle n \rangle_c$ for a particular temperature, and vice versa

$$\langle n \rangle_c = \frac{1}{\lambda_T^3} = \frac{g_{3/2}(1)}{\lambda_T^3} \sim T^{3/2}$$

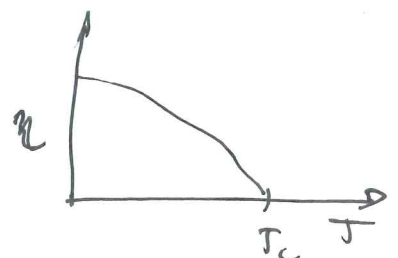
$$\lambda_{T_c}^3 = \frac{g_{3/2}(1)}{\langle n \rangle} \Rightarrow T_c \sim \langle n \rangle^{2/3}$$

order parameter

$$\eta = \frac{n_0}{\langle n \rangle} - \text{condensate fraction}$$

$$n_0 = \langle n \rangle - \frac{g_{3/2}(1)}{\lambda_T^{3/2}}$$

$$\eta = 1 - \frac{g_{3/2}(1)}{\langle n \rangle \lambda_T^{3/2}} = 1 - \frac{\lambda_{T_c}^3}{\lambda_T^3} = 1 - \left(\frac{T}{T_c} \right)^{3/2}$$



coexistence curve:

for $z=1$
$$P = \frac{k_B T}{\lambda_T^3} g_{5/2}(1) \Rightarrow \text{independent of } \langle n \rangle \text{ or } \langle V \rangle$$

(in this range $\langle V \rangle < \langle V_c \rangle$)

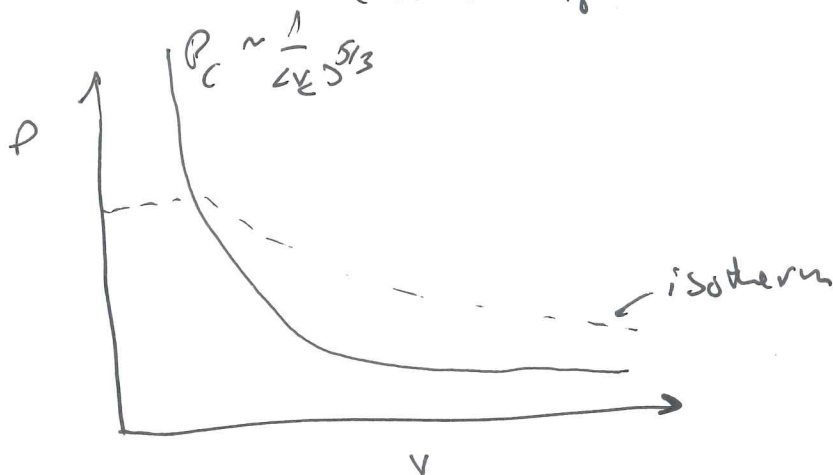
can write:
$$P_c = \frac{k_B T_c}{\lambda_{T_c}^3} g_{5/2}(1)$$

$$P_c \sim T_c^{5/2} \quad T_c \sim \langle n \rangle_c^{2/3} \sim \frac{1}{\langle V \rangle_c^{2/3}}$$

$$P_c \sim \frac{1}{\langle V \rangle_c^{5/3}}$$

(exact expression:

$$P_c = \frac{2\pi k_B^2 g_{5/2}(1)}{m (g_{3/2}(1))^{5/3}} \frac{1}{\langle V \rangle_c^{5/3}})$$



to calculate latent heat:

- either calculate entropy

$$S = \left(\frac{\partial(PV)}{\partial T} \right)_{n, V}$$

or
$$\frac{dP_c}{dT_c} = \frac{L}{\Delta V T}$$

(Clausius-Clapeyron equation)

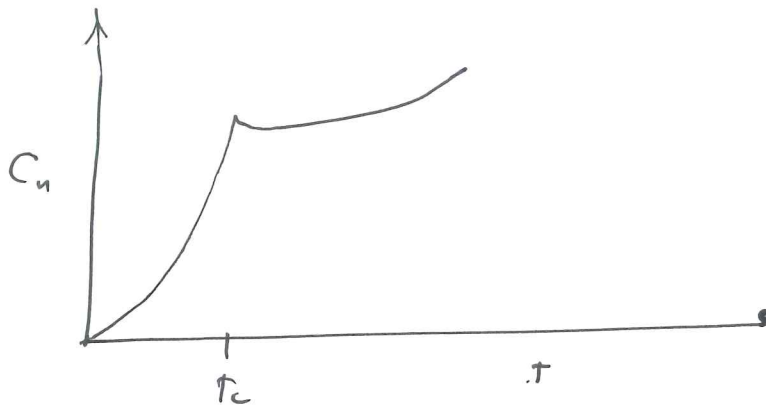
$$\frac{dP_c}{dT_c} \sim \frac{5}{2} T_c^{3/2} = \frac{5}{2 \langle V \rangle_c}$$

$\Rightarrow$ finite latent heat

- can also calculate $c_n = T \left(\frac{\partial S}{\partial T} \right)_n$

$$S = \left(\frac{\partial S}{\partial V} \right)_{T,n} = \left(\frac{\partial P}{\partial T} \right)_{V,n} \Rightarrow S = \begin{cases} k_B \frac{5}{2} \frac{1}{\lambda_T^3} g_{5/2}(z) - k_B \ln Z \\ k_B \frac{5}{2} \frac{1}{\lambda_T^3} g_{5/2}(1) \end{cases}$$

$$c_n = T \left(\frac{\partial S}{\partial T} \right)_n \Rightarrow c_n = \begin{cases} k_B \frac{15}{4} \frac{1}{\lambda_T^3} g_{5/2}(z) - \langle n \rangle k_B \frac{g_{5/2}(z)}{g_{3/2}(z)} \\ k_B \frac{15}{4} \frac{g_{5/2}(1)}{\lambda_T^3} \end{cases}$$



- BEC is sometimes called 1st order (latent heat)
sometimes second order (discontinuous slope of $c_{v,n}$)

- Bose condensate order parameter

$$\psi = |\psi| e^{i\phi} \quad |\psi|^2 \text{ gives the density in the superfluid phase}$$

- off-diagonal long-range order

density matrix:

$$g(\vec{r}, \vec{r}') = \langle \psi^\dagger(\vec{r}) \psi(\vec{r}') \rangle$$

$\psi, \psi^\dagger$ - annihilation/
creation operators

$$g(\vec{r}, \vec{r}') \sim \frac{1}{V} \sum_{\vec{n}, \vec{n}'} \langle c_{\vec{n}}^\dagger c_{\vec{n}'} \rangle e^{i\vec{k} \cdot \vec{r}} e^{-i\vec{k}' \cdot \vec{r}'}$$

for a non-interacting system (ideal gas)

$$g(\vec{r}, \vec{r}') \sim \frac{1}{V} \sum_{\vec{n}} \langle c_{\vec{n}}^\dagger c_{\vec{n}} \rangle e^{i\vec{k} \cdot (\vec{r} - \vec{r}')} = \frac{1}{V} \sum_{\vec{n}} \langle n_{\vec{n}} \rangle e^{i\vec{k} \cdot (\vec{r} - \vec{r}')}$$

- since system is condensing into state with $n=0$

$$g(\vec{r}, \vec{r}') \rightarrow n_0$$

$g(\vec{r}, \vec{r}')$ will be independent of distance $\Rightarrow$ "long-range order"

$\Rightarrow$ usually correlation functions are used as a test for long range order $\rightarrow$ if a correlation function decays to zero $\Rightarrow$ no long range order; if it decays to a finite value $\Rightarrow$ long range order

- for BEC $\Rightarrow$ density matrix "decays" to a finite value: i. e. $\lim_{|\vec{r}-\vec{r}'| \rightarrow \infty} g(\vec{r}, \vec{r}') \neq n_0$

- in general: $g(\vec{r}, \vec{r}') \rightarrow n_0 \psi^*(\vec{r}) \psi(\vec{r}')$

- dimensionality:

$$\frac{N}{V} = \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{d/2} g_{d/2}(\xi)$$

$$g_\nu(\xi) = \sum_{j=1}^{\infty} \frac{\xi^j}{j^\nu}$$

$$\text{for } \nu \leq 1 \quad g_\nu(1) \rightarrow \infty$$

$\Rightarrow$ for 2D and 1D $\Rightarrow$ no BEC at finite temperature

Fermi - Dirac Ideal Gases

- particles in a box $V = L^3$

- assume $s = 1/2$ (spin)

$$Z_{FD} = \prod_{\vec{m}=0}^{\infty} \left(\sum_{\vec{m}=0}^1 e^{-\beta \epsilon_{\vec{m}} (\epsilon_{\vec{m}} - \mu)} \right)^2$$

$$= \prod_{\vec{m}=0}^{\infty} (1 + e^{-\beta (\epsilon_{\vec{m}} - \mu)})^2$$

$$\Omega = -2k_B T \sum_{\vec{m}} \ln (1 + e^{-\beta (\epsilon_{\vec{m}} - \mu)})$$

$$\langle N \rangle = - \frac{\partial \Omega}{\partial \mu} = +2k_B T \sum_{\vec{m}} \frac{e^{-\beta (\epsilon_{\vec{m}} - \mu)}}{1 + e^{-\beta (\epsilon_{\vec{m}} - \mu)}}$$

$$= 2 \sum_{\vec{m}} \langle n_{\vec{m}} \rangle$$

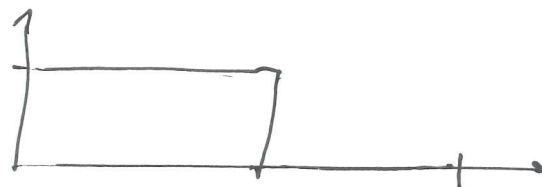
- in this case $\Rightarrow$ no possibility of divergence

$\langle n_{\vec{m}} \rangle$ is well defined for all values of energy

$$0 \leq \langle n_{\vec{m}} \rangle \leq 1$$

- $\langle n_{\vec{m}} \rangle$ can only take values $0 \leq \langle n_{\vec{m}} \rangle \leq 1$

- as $T \rightarrow 0$



Fermi sea

E_F - Fermi energy

$$\frac{p_F}{\hbar} = E_F \Rightarrow \text{Fermi momentum}$$

-replace sum by integral - straight forward in most cases

$$\sum_{\vec{m}} \sim \frac{4\pi V}{(2\pi\hbar)^3} \int_0^\infty p^2 dp$$

↓

$$\Omega = - \frac{2h_b T V}{\lambda_T^3} f_{5/2}(\beta)$$

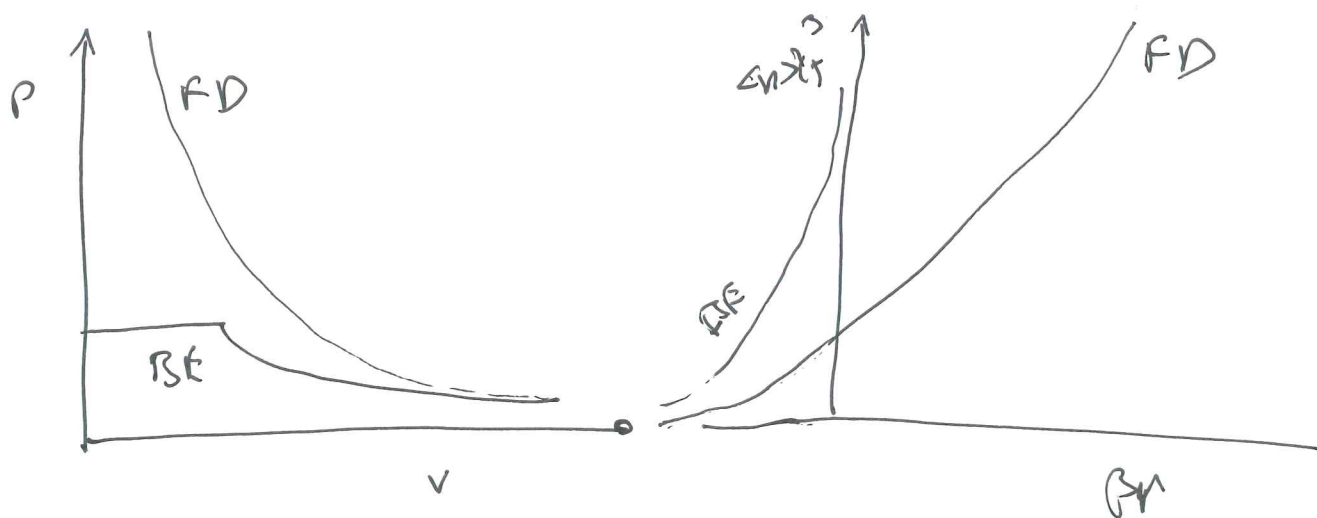
$$\langle N \rangle = \frac{2}{\lambda_T^3} f_{3/2}(\beta)$$

$$f_{5/2}(\beta) = \frac{4}{\sqrt{\pi}} \int_0^\infty x^2 dx \ln [1 + \beta e^{-x^2}] = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\beta^n}{n^{5/2}}$$

$$f_{3/2}(\beta) = \beta \frac{d}{d\beta} f_{5/2}(\beta)$$

$f_{5/2}, f_{3/2}$ - well-behaved
for $\beta \geq 0$

$$P = \frac{2h_b T}{\lambda_T^3} f_{5/2}(\beta)$$



Super fluidity

- similar to BEC, but superfluidity involves interactions between particles

Qualitative features

- superfluid: able to flow through capillaries, etc. without dissipation
- ideal Bose gas: does not have this property
 - consider a fluid flowing with relative velocity $\vec{v}$ compared to container wall
 - in ideal gas BEC, excitations are "single-particle" like
 - through interaction with wall (moving relative to fluid), single-particle excitations can occur, and dissipate energy

$$E_L = (N-1) \frac{m v^2}{2} + \frac{(\vec{p} + m \vec{v})^2}{2m}$$

$$\Rightarrow E_L < 0 \text{ if } \frac{p^2}{2m} + m \vec{v} \cdot \vec{p} < 0$$

example $\vec{p}$ anti-parallel to $\vec{v}$

$\Downarrow$ $\Downarrow$
BEC is not a superfluid

^4He - superfluid $\Rightarrow$ low-lying excitations are sound quanta

- sound wave: cooperative displacement (Landau, Pita, Pines)

- excitation spectra can be obtained by inelastic neutron scattering

- excitation spectrum: 1.) as $p \rightarrow 0$ $\epsilon \sim cp$ $c \sim$ sound velocity

2.) there is a local minimum in $\epsilon(\vec{p})$ @ p_0



$$\Rightarrow \text{around minimum: } \epsilon(\vec{p}) = \Delta + \frac{(p-p_0)^2}{2m^*}$$

$$m^* \sim 0.16 m_{\text{He}}$$

- consider fluid moving in container

container moves with velocity $\vec{v}$ with respect to fluid $\Rightarrow$ container, a classical object with mass M

$$\frac{p^2}{2M} - \frac{(\vec{p} - \vec{p}')^2}{2M} = \epsilon(\vec{p}')$$

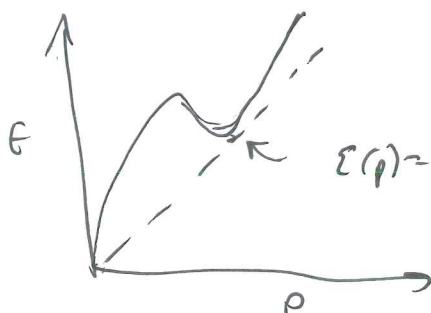
if $M \rightarrow \infty$ dissipation is possible only if

$$\vec{v} > \frac{\epsilon(p)}{p}$$

$$\frac{p^2}{2M} - \frac{p'^2}{2M} + \frac{\vec{p} \cdot \vec{p}'}{M} - \frac{p'^2}{2M} = \epsilon(p')$$

$$\vec{v} \cdot \vec{p} - \frac{p^2}{2M} = \epsilon(p) \rightarrow \vec{v} \cdot \vec{p} = \epsilon(p)$$

$$v > \frac{\epsilon(p)}{p}$$



$\epsilon(p) = vp$ (critical condition)

below $v_c \Rightarrow$ not possible to dissipate energy

- two-fluid model for Bose condensation / superfluidity

$$g = g_s + g_n$$

order parameter:

$$\psi(\vec{r}) = a(\vec{r}) e^{i\delta(\vec{r})}$$

$$g_s \sim |a(\vec{r})|^2$$

- current density of superflow

$$\vec{j}_s = \frac{i\hbar}{2} [\psi \vec{\nabla} \psi^* - \psi^* \vec{\nabla} \psi] = \hbar a^2 \vec{\nabla} \delta$$

velocity field: $\vec{u}_s = \frac{\hbar}{m} \nabla \delta(\vec{r})$

potential flow: $\vec{\nabla} \times \vec{u}_s = 0$ (irrotational)

rotating bucket experiment:

for normal fluid expect meniscus

of form: $\varphi(r) = \frac{\omega^2 r^2}{2g}$

for superfluid, expect $\varphi(r) = \frac{g_n}{g} \frac{\omega^2 r^2}{2g}$

Osborne $\Rightarrow \varphi(r)$ is always $\frac{\omega^2 r^2}{2g}$

- issue: $\delta(\vec{r})$ defined only modulo 2π

$$\psi(\vec{r}) = a(r) e^{i(\delta(\vec{r}) + 2\pi)} = a(r) e^{i\delta(\vec{r})}$$

- $\vec{u}_s = \frac{\hbar}{m} \nabla \delta(\vec{r})$ still true, but if the superfluid

density is zero at $\vec{r}=0$, where phase is

singular $\Rightarrow \oint \vec{u}_s \cdot d\vec{l} \neq 0$

$\Rightarrow$ vortex

- excitations in super fluids: vortices (quantized)

- at center $\Rightarrow S_s = 0$ $\Phi_n = S$, around the center

we can have

$$\oint \vec{\nabla} \chi \cdot d\vec{l} = 2\pi n \quad n - \text{integer}$$

$$\oint \vec{u}_s \cdot d\vec{l} = \frac{n h}{m}$$

$\Rightarrow$ breakdown of superfluidity believed to be due to quantised vortices, when critical velocity is exceeded