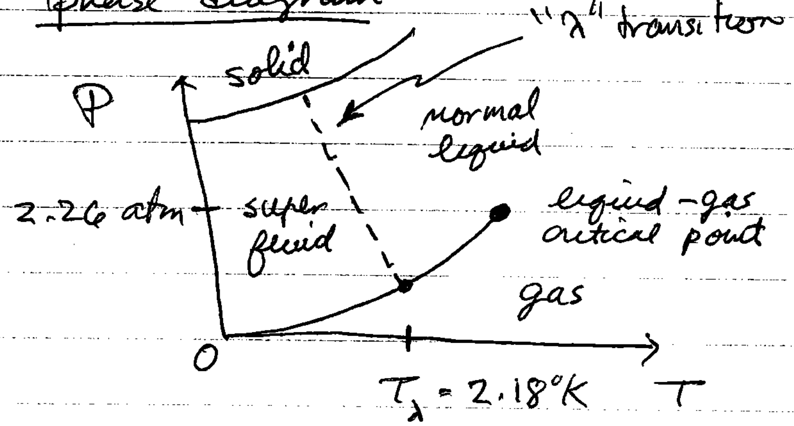
Superfluid 4He

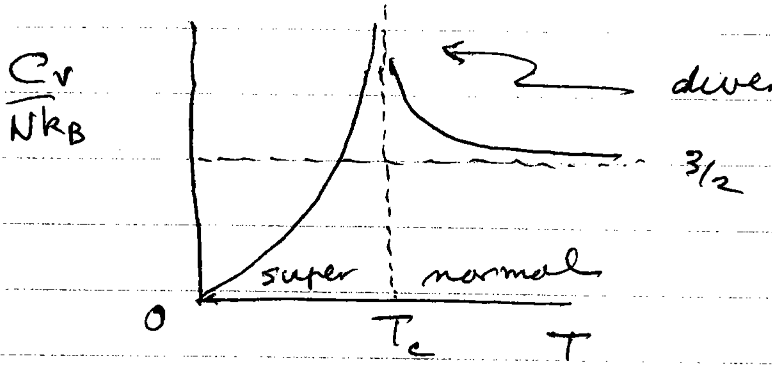
phase diagram



liquid-gas transition is 1st order – there is a latent heat

normal-superfluid transition is 2nd order - no latent heat

specific heat



diverges at T_c where "λ" line is crossed.

① Shape of C_V reminds one of the cusp in C_V for Bose-Einstein condensation in ideal bose gas, although here C_V diverges at T_c

② In superfluid phase, some fraction $\rho_s(T)/\rho$ [ρ_s = superfluid density, ρ = total density] of the fluid flows without any dissipation and carries no entropy – reminds one of the condensate of Bose-Einstein condensation.

③ for ^4He mass $m = 6.65 \times 10^{-24}$ g, and ^4He fluid specific volume $v = 27.6$ cm^3/mole, one finds a Bose-Einstein condensation temperature of $T_c \simeq 3.13$ °K not far from $T_\lambda = 2.18$ °K.

These observations suggested that superfluidity in 4He was related to Bose-Einstein condensation (BEC) of an ideal gas.

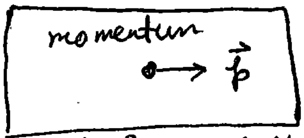
<u>However</u>

① BEC transition line in P-T plane, $P_c \propto T^{5/2}$ has a positive slope, whereas λ-line of ^4He has a negative slope

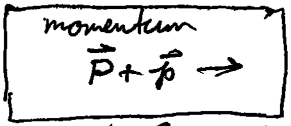
② As demonstrated by <u>Landau</u> the condensate of BEC in an idea bose gas is <u>NOT</u> a superfluid.

<u>Landaus arguement</u>

Consider a condensate (all particles in same state) of total mass M, flowing with velocity $\vec{v}$ down a pipe. It has total momentum $\vec{P} = M\vec{v}$. [illegible] rest frame of this fluid, consider an excitation that is created with momentum $\vec{p}$ and energy $\epsilon(\vec{p})$.



rest frame of fluid



rest frame of pipe

Back in the rest frame of the pipe, the change in energy due to the creation of this excitation is (in the limit of large total mass $M \to \infty$)

$$\Delta E = \frac{(\vec{P}+\vec{p})^2}{2M} + \epsilon(\vec{p}) - \frac{P^2}{2M}$$

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

$$\Delta E = \epsilon(\vec{p}) + \vec{p}\cdot\vec{v}$$ since $\frac{\vec{P}}{M} = \vec{v}$, and

$\frac{p^2}{2M} \to 0$ for large M

If $\Delta E < 0$, then it will be energetically favorable to create such excitations of momentum $\vec{p}$ - the motion of the fluid will therefore excite particles out of the condensate and degrade the flow, ie the system will <u>not</u> display superfluidity.

$$\Delta E < 0 \Rightarrow \epsilon(p) < -\vec{p}\cdot\vec{v}$$

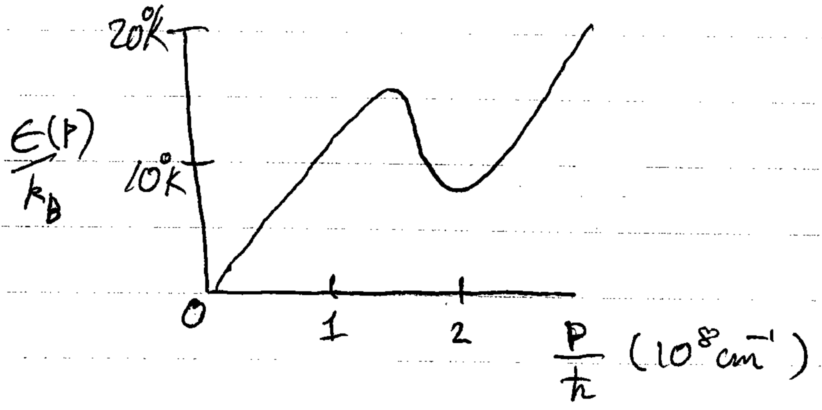
for $\vec{p} \parallel -\vec{v}$, $\Rightarrow \frac{\epsilon(p)}{p} < v$

For an ideal bose gas, $\epsilon(p) = \frac{p^2}{2m}$, so

$\frac{\epsilon(p)}{p} = \frac{p}{2m}$ will always be less than flow velocity v, for sufficiently small p.

So the condensate of an ideal Bose gas, flowing with any velocity v no matter how small, will always excite particles out of the condensate into low lying excited states, and hence will not be a superfluid.

However, from expt'l measurement such as neutron scattering and specific heat, it was known that the low lying excitation spectrum of ^4He was not free particle like, but rather as shown below



at small p, the spectrum is linear

$$\epsilon(p) \simeq cp$$

at higher p there is a dip

$$\epsilon(p) \simeq \Delta + \frac{(p-p_0)^2}{2m^*}$$

excitations in the low p linear region are phonons, or sound modes. excitations near the dip were called "rotons"

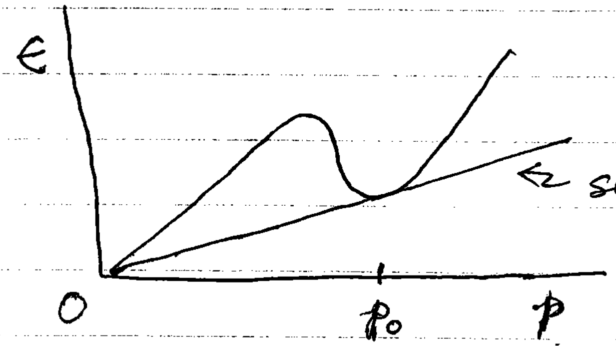
$$\frac{\Delta}{k_B} \simeq 8.7\,°K$$

$$c \simeq 2.4 \times 10^4 \text{ cm/s}$$

$$m^* \simeq 0.16\, m_{He}$$

$p_0/\hbar \simeq 1.9$ Å^{-1}

As the fluid flow velocity v is increased from zero, the condition $\frac{\epsilon(p)}{p} = v$ will first be reached at the velocity v^* shown below



$\leftarrow$ slope is $v^* = \frac{\epsilon(p_0)}{p_0} = \frac{\Delta}{p_0}$

$v^* \simeq 60$ m/s

for $v < v^*$ $\frac{\epsilon(p)}{p} > v$ for all values of p,

and so no particles will be excited out of the condensate by the flow. The fluid is now a superfluid!

Experimentally, while superfluidity does ex in 4 He at low flow velocities, the critical velocity v_{crit}, above which the flow becomes dissipative, is much lower than the v^* above, and is strongly dependent on the size and shape of the container. This is due to the onset of turbulence accompanied by the proliferation of quantized vortices in the condensate flow.

The fact that the spectrum $\epsilon(p)$ is linear at small p, and not free particle-like, is due to the fact that the ^{4}He atoms are NOT an ideal gas - in fact, the ^{4}He atoms are strongly interacting. This should not be surprising - the ^{4}He is a liquid and not a gas, particles collide with other giving rise to sound modes as the low lying excitations, rather than free "ballistic" motion of individual atoms.

One can show that for an interacting Bose gas, even for weak interactions, the small p part of the excitation spectrum always is phonon-like, ie linear, (see Pathria §10.3 or ~~take~~ PHY 509!). Superfluidity can only exist for interacting bose systems.

Because interactions between ^{4}He atoms are not weak, there is no good microscopic theory of superfluidity in ^{4}He. Calculations can, however, be performed for weak interactions. This has lead people to look for superfluidity or BEC in weakly interacting bose gases. This search was finally ~~a~~ successful with the observation of BEC in magnetically trapped, laser cooled, dilute atomic gases (produced two Nobel prizes!)

Bose-Einstein Condensation in laser cooled gases

gases of alkali atoms Li, Na, K, Rb, Cs

- all have a single s-electron in outermost shell.
  - important for efficiency of laser cooling
- use isotopes such that total intrinsic spin of all electrons and nucleons add up to an integer $\hbar$
  $\Rightarrow$ atoms are <u>bosons</u>
- all have a net magnetic moment - used to confine dilute gas of atoms in a "magnetic trap"
- use "laser cooling" to get <u>very</u> low temperatures in low density gases, to try and see <u>BEC</u>

magnetic trap $\rightarrow$ effective harmonic potential for atoms

$$V(r) = \tfrac{1}{2} m\omega_0^2 r^2 \qquad \omega_0 \simeq 2\pi \times 100\,\text{Hz}$$

1995 - 10^3 atoms with $T_c \sim 100\,\text{nK}$

1999 - 10^8 atoms with $T_c \sim \mu\text{K}$ gas size ~ many microns

How was BEC in these systems observed?

energy levels of ideal (non-interacting) bosons in harmonic trap

$$\epsilon(n_x, n_y, n_z) = (n_x + n_y + n_z + 3/2)\hbar\omega_0$$

n_x, n_y, n_z integers

ground state condensate wavefunction

$$\psi_0(r) \sim e^{-r^2/2a^2} \quad \text{with} \quad a = \left(\frac{\hbar}{m\omega_0}\right)^{1/2}$$

$a \sim 1\,\mu\text{m}$ for current traps

$\Rightarrow$ Condensate has spatial extent $\sim a$

The spatial extent of the n^{th} excited energy level is roughly

$$m\omega_0^2 \langle r^2\rangle \sim \epsilon(n) \simeq n\hbar\omega_0$$

$$\Rightarrow \langle r^2\rangle \sim \frac{n\hbar}{m\omega_0} \quad \text{or} \quad \sqrt{\langle r^2\rangle} = \left(\frac{n\hbar}{m\omega_0}\right)^{1/2}$$

For $k_BT \gg \hbar\omega_0$, the atoms are excited up to level $n \sim \dfrac{k_BT}{\hbar\omega_0}$

$\Rightarrow$ spatial extent of the normal component of the gas is

$$R \sim \left(\frac{n\hbar}{m\omega_0}\right)^{1/2} \sim \left(\frac{\hbar k_BT}{\hbar m\omega_0^2}\right)^{1/2} = \left(\frac{k_BT}{m\omega_0}\right)$$

$$R \sim a\left(\frac{k_BT}{\hbar\omega_0}\right)^{1/2} \gg a$$

If T_c is the BEC transition temperature, then for $T > T_c$ one sees a more or less uniform cloud of atoms with radius $R \sim a\,(k_BT/\hbar\omega_0)^{1/2} \gg a$. But when one cools to $T < T_c$, one now has a finite fraction of the atoms condensed in the ground state. $\rightarrow$ superimposed on the atomic cloud of radius R one sees the growth of a sharp peak in density at the center of cloud – this peak has a radius $a \ll R$.

To find T_c, (use $z=1$ at $T \le T_c$)

for $T \le T_c$

$$n = n_0 + \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \, \frac{1}{e^{(n_x+n_y+n_z)\hbar\omega_0/k_BT} - 1}$$

$$= n_0 + \left(\frac{k_BT}{\hbar\omega_0}\right)^3 \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz \, \frac{1}{e^{(x+y+z)} - 1}$$

$$= n_0 + \left(\frac{k_BT}{\hbar\omega_0}\right)^3 \zeta(3)$$

at T_c, $n_0 = 0 \Rightarrow k_BT_c = \hbar\omega_0 \left(\frac{n}{\zeta(3)}\right)^{1/3}$

condensate density $n_0(T) = n\left(1 - \left(\frac{T}{T_c}\right)^3\right)$

↑

different from ideal free gas due to presence of magnetic trapping potential

Classical ideal gas with internal degrees of freedom

assume $n\lambda^3 \ll 1$ so molecules are classical as far as their translational motion is concerned

$$\Rightarrow \quad Q_N = \frac{1}{N!}\left[Q_1\right]^N$$

Q_1 is single molecule partition function

Suppose molecule has internal degrees of freedom, so that its energy is

$$\frac{p^2}{2m} + \epsilon_i$$

where ϵ_i are the internal energy levels

Then

$$Q_1 = \int \frac{d^3r}{h^3}\int d^3p \sum_i e^{-\beta(p^2/2m + \epsilon_i)}$$

$$= \frac{V}{\lambda^3}\sum_i e^{-\beta\epsilon_i} \qquad \lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$$

sum over all internal states of molecule

let $q = \sum_i e^{-\beta\epsilon_i}$

then $Q_1 = \frac{V}{\lambda^3}\, q$

$$Q_N = \frac{1}{N!}\left[\frac{V}{\lambda^3}\, q\right]^N = Q_N^{(0)}\, q^N \qquad Q_N^{(0)} = \frac{1}{N!}\Big[\frac{V}{\lambda^3}$$

partition function for point particle

Helmholtz free energy

$$A(T,V,N) = -k_BT \ln Q_N$$

$$= -k_BT \ln Q_N^{(0)} - k_BT \ln q^N$$

$$= \underset{\substack{\uparrow \\ \text{free energy for point particles}}}{A^{(0)}} - \underset{\substack{\uparrow \\ \text{free energy of internal degrees of freedom}}}{k_BTN \ln q}$$

effect of internal degrees of freedom are additive to free energy

$$A = A^{(0)} + A_{int} \qquad A_{int} = -k_BTN \ln q$$

Note: q has no dependence on N or V; only depends on T.

$\Rightarrow$ pressure $p = -\frac{\partial A}{\partial V} = \frac{\partial A^{(0)}}{\partial V}$ uneffected by internal degrees of freedom

chemical potential

$$\mu = +\frac{\partial A}{\partial N} = \frac{\partial A^{(0)}}{\partial N} - k_BT \ln q$$

$$= \mu^{(0)} + \mu_{int} \qquad \mu_{int} = -k_BT \ln q$$

internal degrees of freedom add T-dependent constant to μ

entropy

$$S = \frac{-\partial A}{\partial T} = \frac{-\partial A^{(0)}}{\partial T} + \frac{\partial}{\partial T}\left(k_BTN \ln q\right)$$

$$S = S^{(0)} + Nk_B \ln q + Nk_BT \frac{\partial}{\partial T} \ln q$$

$$= S^{(0)} + S_{int}$$

energy

$$A = E - TS$$

$$\Rightarrow \quad E = A + TS$$

$$= E^{(0)} + A_{int} + T S_{int}$$

$$= E^{(0)} + E_{int}$$

$$E_{int} = -k_B T N \ln q + T N k_B \ln q + N k_B T^2 \frac{\partial}{\partial T} \ln q$$

$$= N k_B T^2 \frac{\partial}{\partial T} \ln q$$

specific heat

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = C_V^{(0)} + C_{V\,int}$$

$$C_{V\,int} = \frac{\partial}{\partial T}\left(N k_B T^2 \frac{\partial}{\partial T} \ln q\right)$$

$$= 2 N k_B T \frac{\partial}{\partial T} \ln q + N k_B T^2 \frac{\partial^2}{\partial T^2} \ln q$$

The internal degrees of freedom can often be separated into different physical sources

1) electronic excitation
2) vibrational excitation of bonds
3) rotational motion of molecule

In many cases these different modes of excitation are only weakly interacting so one can write

$$\epsilon_i = \epsilon_{elec} + \epsilon_{vib} + \epsilon_{rot}$$

$$q = \sum_i e^{-\beta(\epsilon_{elec} + \epsilon_{vib} + \epsilon_{rot})} = \left(\sum_{i_{elec}} e^{-\beta \epsilon_{elec}}\right)\left(\sum_{i_{vib}} e^{-\beta \epsilon_{vib}}\right) \times \left(\sum_{i_{rot}} e^{-\beta \epsilon_{rot}}\right)$$

where i_{elec}, i_{vib}, i_{rot} stand for the quantum numbers associated with the electronic, vibrational, and rotational degrees of freedom

$$q = q_{elec}\, q_{vib}\, q_{rot}$$

$$A_{int} = A_{elec} + A_{vib} + A_{rot}$$

example

A mono atomic gas - particles are single atoms. internal degrees of freedom are excitations to higher electron levels. Electronic excitation energies are $O(1\,eV) \sim O(10^4\,°K)$ so at room temperatures, only the lowest excited states can be populated.

$$q \simeq g_0 e^{-\beta\epsilon_0} + g_1 e^{-\beta\epsilon_1}$$

where ϵ_0 and ϵ_1 are energies of ground + 1st excited states, and g_0 and g_1 are their degeneracies

$$q = g_0 e^{-\beta\epsilon_0}\left(1 + \frac{g_1}{g_0} e^{-\beta\Delta\epsilon}\right) \qquad \Delta\epsilon = \epsilon_1 - \epsilon_0$$

$$A_{int} = -k_B T N \ln\left(1 + \frac{g_1}{g_0} e^{-\beta\Delta\epsilon}\right) + N\epsilon_0 - k_B T N \ln g_0$$

$$C_{V\,\mathrm{int}} = \frac{\partial}{\partial T}\left(N k_B T^2 \frac{\partial}{\partial T} \ln q\right)$$

$$= \frac{\partial}{\partial T}\left(N k_B T^2 \frac{\partial}{\partial T}\left(\ln g_0 - \frac{\epsilon_0}{k_B T} + \ln\left(1 + g_1/g_0\, e^{-\beta\Delta\epsilon}\right)\right)\right)$$

$$= \frac{\partial}{\partial T}\left(N k_B T^2 \left[\frac{\epsilon_0}{k_B T^2} + \frac{g_1/g_0\, e^{-\beta\Delta\epsilon}\left(\frac{\Delta\epsilon}{k_B T^2}\right)}{1 + \frac{g_1}{g_0} e^{-\beta\Delta\epsilon}}\right]\right.$$

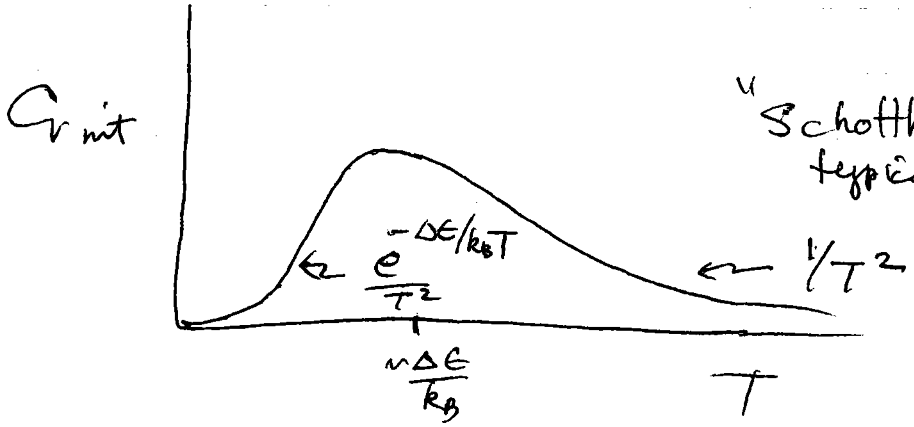
$$= N \frac{\partial}{\partial T}\left[\epsilon_0 + \frac{\Delta\epsilon\,(g_1/g_0)\, e^{-\beta\Delta\epsilon}}{1 + g_1/g_0\, e^{-\beta\Delta\epsilon}}\right]$$

$$= N\Delta\epsilon\,(g_1/g_0)\, \frac{\left[1 + g_1/g_0\, e^{-\beta\Delta\epsilon}\right] e^{-\beta\Delta\epsilon}\left(\frac{\Delta\epsilon}{k_B T^2}\right) - e^{-\beta\Delta\epsilon}}{\left[1 + g_1/g_0\, e^{-\beta\Delta\epsilon}\right]^2}$$

$$\uparrow\ \times\left(\frac{g_1}{g_0} e^{-\beta\Delta\epsilon} \frac{\Delta}{k_B T}\right.$$

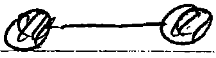
$$\cancel{= N\Delta\epsilon}$$

$$\boxed{C_{V\,\mathrm{int}} = N k_B \left(\frac{\Delta\epsilon}{k_B T}\right)^2 \left(\frac{g_1}{g_0}\right) \frac{e^{-\beta\Delta\epsilon}}{\left[1 + \frac{g_1}{g_0} e^{-\beta\Delta\epsilon}\right]^2}}$$



"Schottky anomaly"
typical of excitation of one energy level

Diatomic molecules



vibrational excitations

$$\epsilon_{vib} = (n+1/2)\hbar\omega_0$$

ω_0 is vibrational frequency related to stiffness of bond + mass of atoms. $\omega_0 = \sqrt{K/2M}$

$$q_{vib} = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega_0} = e^{-\beta\hbar\omega_0/2} \sum_{n=0}^{\infty} \left[e^{-\beta\hbar\omega_0}\right]^n$$

$$q_{vib} = \frac{e^{-\beta\hbar\omega_0/2}}{1-e^{-\beta\hbar\omega_0}} = \frac{1}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}}$$

$$= \frac{1}{2\sinh(\beta\hbar\omega_0/2)}$$

$$C_{V\,vib} = \frac{\partial}{\partial T}\left(Nk_BT^2 \frac{\partial}{\partial T} \ln q_{vib}\right)$$

$$= \frac{\partial}{\partial T}\left(Nk_BT^2 \frac{\partial}{\partial T}\left[-\ln\left(e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}\right)\right]\right)$$

$$= \frac{\partial}{\partial T}\left(Nk_BT^2(-1)\frac{\left(-\frac{\hbar\omega_0}{2k_BT^2}\right)e^{\beta\hbar\omega_0/2} - \left(\frac{\hbar\omega_0}{2k_BT^2}\right)e^{-\beta\hbar\omega_0/2}}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}}\right.$$

$$= \frac{\partial}{\partial T}\left(Nk_BT^2 \frac{\hbar\omega_0}{2k_BT^2} \frac{e^{\beta\hbar\omega_0/2} + e^{-\beta\hbar\omega_0/2}}{e^{\beta\hbar\omega_0/2} - e^{-\beta\hbar\omega_0/2}}\right)$$

$$= \frac{N\hbar\omega_0}{2}\frac{\partial}{\partial T}\left(\coth\left(\beta\frac{\hbar\omega_0}{2}\right)\right)$$

$$C_{v\,vib} = \frac{N\hbar\omega_0}{2}\,\frac{\left[\sinh^2\left(\beta\frac{\hbar\omega_0}{2}\right) - \cosh^2\left(\beta\frac{\hbar\omega_0}{2}\right)\right]}{\sinh^2\left(\beta\frac{\hbar\omega_0}{2}\right)}\left(-\frac{\hbar\omega_0}{2k_BT^2}\right)$$

$$= Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2\frac{1}{4}\,\frac{1}{\sinh^2\left(\beta\frac{\hbar\omega_0}{2}\right)}$$

$$C_{v\,vib} = Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2\frac{e^{\beta\hbar\omega_0}}{\left[e^{\beta\hbar\omega_0}-1\right]^2}$$

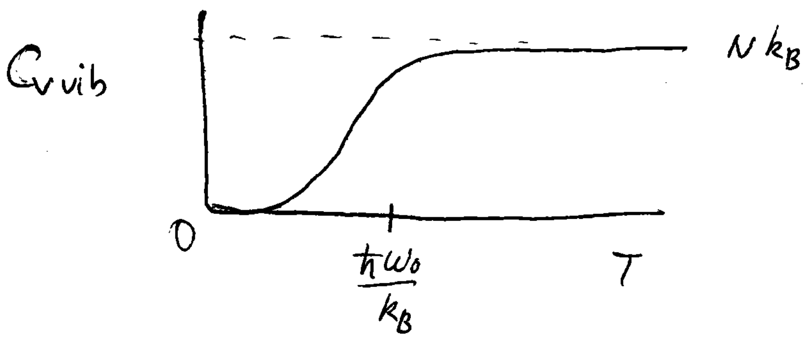
For ~~[illegible]~~ $\beta\hbar\omega_0 = \frac{\hbar\omega_0}{k_BT} \ll 1$ ie high temp

$$C_{v\,vib} \simeq Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2\frac{1}{\left(\frac{\hbar\omega_0}{k_BT}\right)^2} = Nk_B$$

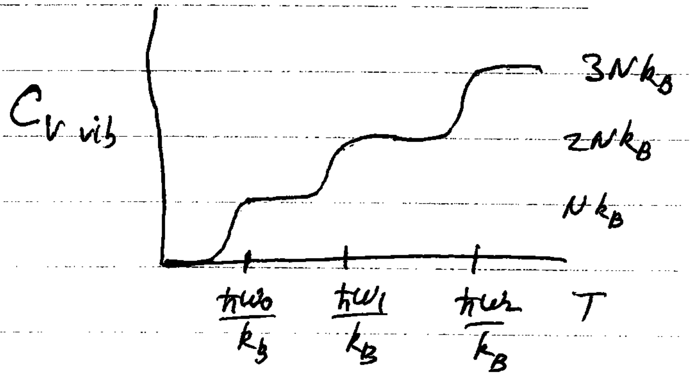
classical equipartition result

At low T, $\beta\hbar\omega_0 \gg 1$

$$C_{v\,vib} \simeq Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 e^{-\hbar\omega_0/k_BT}$$



for a polyatomic molecule with many bonds of freq $\omega_0 < \omega_1 < \omega_2$, $C_{V\,vib}$ is just sum of terms for each bond



Rotational degree of freedom

$$H_{rot} = \frac{\hbar^2 L^2}{2I}$$

$\vec{L}$ = angular momentum

I = moment of inertia

for diatomic molecule

$I = \mu R^2$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$ reduced mass

$$\epsilon_{rot} = \frac{l(l+1)\hbar^2}{2I}$$

$$\zeta_{rot} = \sum_{l=0}^{\infty} (2l+1)\, e^{-\beta l(l+1)\hbar^2/2I}$$

degeneracy of angular momentum eigenvalue l

$$\simeq \int_0^\infty dl\,(2l+1)\, e^{-\beta l(l+1)\hbar^2/2I}$$

let $x = l(l+1)$

$dx = (2l+1)\,dl$

good when

$\frac{\beta\hbar^2}{2I} \ll 1$ ie $k_B T$ larger than level spacing

$$q_{rot} = \int_0^\infty dx\; e^{-\beta\hbar^2 x/2I} = \frac{2I}{\beta\hbar^2} = \frac{2Ik_BT}{\hbar^2} = \frac{T}{\Theta_R}$$

where $\Theta_R = \dfrac{\hbar^2}{2Ik_B}$

$$C_{v\,rot} = \frac{\partial}{\partial T}\left(Nk_BT^2\frac{\partial}{\partial T}\ln q_{rot}\right)$$

$$= \frac{\partial}{\partial T}\left(Nk_BT^2\frac{\partial}{\partial T}\ln(T/\Theta_R)\right)$$

$$= \frac{\partial}{\partial T}\left(Nk_BT^2\frac{1}{T}\right) = Nk_B$$ classical equipartition result.

To do better than approx sum by integral use Euler - Maclaurin series

$$\sum_{n=0}^\infty f(n) = \int_0^\infty f(x)\,dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) + \cdots$$

↑ used a version of this when did Landau diamagnetism

using $f(x) = (2x+1)\exp(-x(x+1)\Theta_R/T)$

$$\Rightarrow\; q_{rot} = \frac{T}{\Theta_R} + \frac{1}{3} + \frac{1}{15}\frac{\Theta_R}{T} + \frac{4}{315}\left(\frac{\Theta_R}{T}\right)^2 + \cdots$$

$$C_{v\,rot} = Nk_B\left\{1 + \frac{1}{45}\left(\frac{\Theta_R}{T}\right)^2 + \frac{16}{945}\left(\frac{\Theta_R}{T}\right)^3 + \cdots\right\}$$

For low T, ~~then first~~ $\frac{\beta\hbar^2}{2I} \gg k_BT$ or $\Theta_R \gg T$ the first few terms of $\sum_\ell$ give

$$q_{rot} \doteq 1 + 3e^{-2\Theta_R/T} + 5e^{-6\Theta_R/T} + \cdots$$

$$C_{v\,rot} \simeq 12 N k_B \left(\frac{\theta_R}{T}\right)^2 e^{-2\theta_R/T}$$