Lecture 16

Need to finish calculation from last time...

Got equipartition theorem

$$\left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = kT \qquad x_i = \text{any } p \text{ or } q$$

$\Rightarrow$ each quadratic coord contributes $\frac{1}{2}kT$ to $U = \langle E \rangle$

But this is only a classical result.

Compare classical & quantum harmonic oscillators:

Classical $\quad A_{cl} = NkT \ln \frac{\hbar\omega}{kT}$

Quantum $\quad A_Q = N \left\{ \frac{\hbar\omega}{2} + kT \ln\left(1 - e^{-\beta\hbar\omega}\right) \right\}$

Saw $\quad A_Q \to A_{cl} \quad$ for $\quad kT \gg \hbar\omega$

But different if $\quad kT \lesssim \hbar\omega$

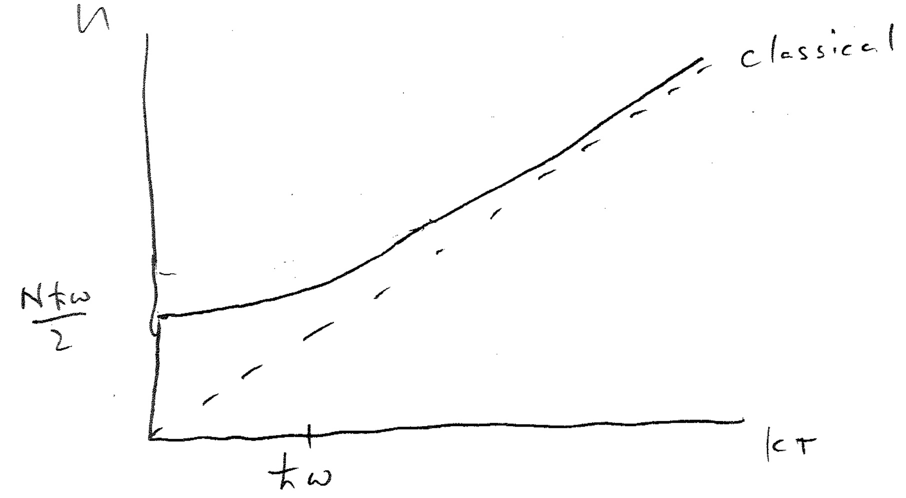
For instance

$$U_Q = \frac{\partial}{\partial\beta}(\beta A)$$

$$= \frac{\partial}{\partial\beta} N \left\{ \frac{\hbar\omega\beta}{2} + \ln\left(1 - e^{-\beta\hbar\omega}\right) \right\}$$

$$= \frac{N\hbar\omega}{2} + \frac{\hbar\omega}{1 - e^{-\beta\hbar\omega}} \neq Nk_B T$$

Plot U



More complicated T-dependence than classical

General result:

If $kT \ll$ excitation energy for quantum motion then that degree of freedom is "frozen out"

$\Rightarrow$ doesn't contribute to thermodynamics

For instance: diatomic molecule

Degrees of freedom:

$3\times$ translation (p_x, p_y, p_z)

$2\times$ rotation (p_θ, p_ϕ)

$2\times$ vibration (r, p_r)

Expect $U = \frac{7}{2} NkT$ from equipartition

But vibrational frequency pretty big

$\omega \sim 2\pi \times 10^{14}$ Hz

So $\frac{\hbar\omega}{k_B} \sim 5000\,K$

For smaller T, no vibrational excitation, $U \to \frac{5}{2} Nk_BT$

Rotational level spacing is $\sim 100\times$ smaller

Freeze out at $\sim 50K$

Gases usually liquify by then

Point: Equipartion is useful, but requires some thought

Rest of today: apply techniques to magnetic systems.

Take system = set of N magnetic dipoles
no constraint on orientation
no interactions *
(not entirely fair, but OK for now)

Ignore translation degrees of freedom

Then $\vec{\mu}$ = dipole moment of one particle
$\vec{\mathcal{H}}$ = external applied field

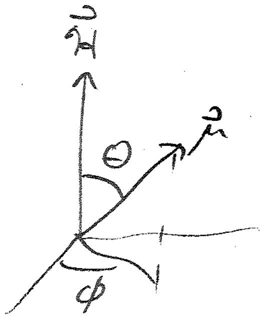
At $T = 0$, expect $\vec{\mu} \parallel \vec{\mathcal{H}}$

At large T, expect $\langle \vec{\mu} \rangle = 0$, randomized by thermal motion

Our job: calculate $\langle \vec{\mu} \rangle$ as fcn of $\mathcal{H}, T$

Gives us magnetization $\vec{M} = \rho \langle \vec{\mu} \rangle$
ρ = density

Start with classical model
Orientation of $\vec{\mu}$ set by (θ, ϕ)



Hamiltonian $H = T - \sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{\mathcal{H}}$

T = Kinetic energy
$$= \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right)$$

Moment of inertia I

If $\vec{\mathcal{H}} \propto \hat{z}$, potential energy
$$\rightarrow \mu \mathcal{H} \sum_i \cos\theta_i$$

Want to get $\langle \vec{\mu} \rangle = \langle \mu_z \rangle \hat{z} = \mu \langle \cos\theta \rangle \hat{z}$

We know

$$Q_N = (Q_1)^N$$: Dipoles at different locations, so distinguishable

$$Q_1 = \frac{1}{h^2}\int d\theta\, d\phi\, dp_\theta\, dp_\phi\; e^{-\beta H}$$

$$= \frac{1}{h^2}\int d\omega\; e^{-\beta T + \beta\mu\mathcal{H}\cos\theta}$$

and

$$\mu\langle\cos\theta\rangle = \frac{\int d\omega\, \mu\cos\theta\; e^{-\beta T + \beta\mu\mathcal{H}\cos\theta}}{Q_1}$$

$$= \frac{1}{\beta}\frac{\partial}{\partial\mathcal{H}} \ln Q_1$$

So calculate Q_1:

$$= \frac{1}{h^2}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta\, e^{\beta\mu\mathcal{H}\cos\theta} \underbrace{\int_{-\infty}^{\infty} dp_\theta\, e^{-\frac{\beta p_\theta^2}{2I}}}_{\sqrt{\frac{2\pi I}{\beta}}} \underbrace{\int_{-\infty}^{\infty} dp_\phi\, e^{-\frac{\beta p_\phi^2}{2I\sin^2\theta}}}_{\sin\theta\sqrt{\frac{2\pi I}{\beta}}}$$

$$= \frac{2\pi I}{h^2\beta} \underbrace{\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, e^{\beta\mu\mathcal{H}\cos\theta}}_{\text{Simple angular average!}} d\theta$$

$x = \cos\theta \qquad dx = -\sin\theta\, d\theta$

$$Q_1 = \frac{2\pi I}{h^2\beta}\, 2\pi \cdot \int_{-1}^{1} e^{\beta\mu\mathcal{H}x}\, dx$$

$$Q_1 = \frac{I}{\hbar^2 \beta} \frac{1}{\beta\mu\mathcal{E}} \left(e^{\beta\mu\mathcal{E}} - e^{-\beta\mu\mathcal{E}}\right)$$

$$\boxed{Q_1 = \frac{2I}{\hbar^2 \beta} \frac{\sinh \beta\mu\mathcal{E}}{\beta\mu\mathcal{E}}}$$

So $\mu\langle\cos\theta\rangle = \frac{1}{\beta}\frac{\partial}{\partial\mathcal{E}} \ln Q_1$

$$= \frac{1}{\beta}\frac{\partial}{\partial\mathcal{E}}\left[\ln \sinh \beta\mu\mathcal{E} - \ln \mathcal{E}\right]$$

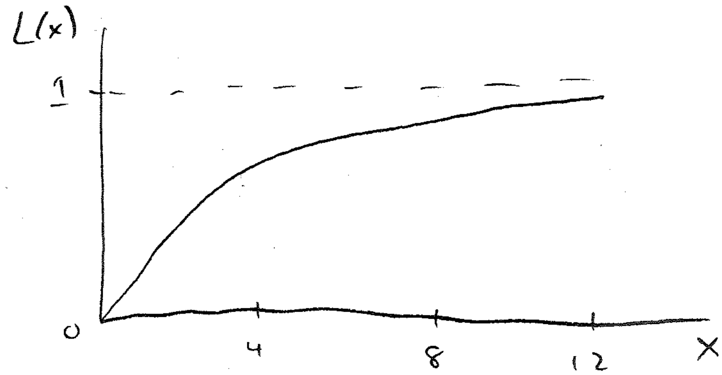
$$= \frac{1}{\beta}\left[\beta\mu \frac{\cosh \beta\mu\mathcal{E}}{\sinh \beta\mu\mathcal{E}} - \frac{1}{\mathcal{E}}\right]$$

$$= \mu\left[\coth x - \frac{1}{x}\right]$$

$$x = \beta\mu\mathcal{E} = \frac{\mu\mathcal{E}}{kT}$$

$$\equiv \mu L(x)$$

$L(x)$ = Langevin function



$L(x) \simeq \frac{x}{3}$ for small x

$\rightarrow 1$ at large x

Net magnetization $M = \rho \langle \mu_z \rangle$

$= \rho \mu L(x)$

For small x, (= small $\mathcal{H}$ or large T)

$$M \approx \frac{\rho \mu^2}{3kT} \mathcal{H}$$

Recognize Curie's Law: $\boxed{M = \frac{C}{T} \mathcal{H}}$

For large x, magnetization saturates
all dipoles aligned with field, M can't get any bigger

Systems of this type are called <u>paramagnetic</u>

Effect is generally weak (C is small)
compared to ferromagnetism
(where interactions cause neighboring spins to align)

Of course, this was classical calculation

Compare to QM
(again, we know how to do for distinguishable particles)

In quantum, have $\vec{\mu} = g \frac{\mu_B}{\hbar} \vec{J}$

$$\mu_B = \frac{e\hbar}{2mc} = \text{Bohr magneton}$$
$$= 9.27 \times 10^{-24} \text{ J/T}$$

$\vec{J}$ = angular momentum operator

g = "g-factor"

dimensionless correction factor

order 1

Angular momentum eigenstates ψ_{Jm}

have $\vec{J}^2 \psi_{Jm} = \hbar^2 J(J+1)\psi_{Jm}$

with $J = 0, 1, 2, ..$

or $J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$

Also $J_z \psi_{Jm} = \hbar m \psi_{Jm}$

$m = -J \ldots +J$ in integer steps

So here, have $\mu_z = g \frac{\mu_B}{\hbar} J_z$

$\mu_z \psi_{Jm} = g \mu_B m \psi_{Jm}$

or just $\mu_z \to g \mu_B m$

Assuming J is same for all particles, have

$$Q_1 = \sum e^{-\beta H} = \sum e^{\beta \vec{\mu} \cdot \vec{\mathcal{H}}} = \sum_{m=-J}^{J} e^{\beta g \mu_B \mathcal{H} m}$$

$$= \sum_{m=-J}^{J} (z)^m = \frac{z^{-J} - z^{J+1}}{1 - z}$$

$$z = e^{\beta g \mu_B \mathcal{H}}$$

Define $\quad X = \underbrace{\beta(g\mu_B J)}_{\text{analog of } \mu}\mathcal{H} \qquad$ So $\quad z = e^{x/J}$

$$Q_1 = \frac{z^{1/2}\left(z^{J+\frac{1}{2}} - e^{-J-\frac{1}{2}}\right)}{z^{1/2}\left(z^{1/2} - z^{-1/2}\right)}$$

$$= \frac{e^{x\left(1+\frac{1}{2J}\right)} - e^{-x\left(1+\frac{1}{2J}\right)}}{e^{x/2J} - e^{-x/2J}}$$

$$= \frac{\sinh x\left(1+\frac{1}{2J}\right)}{\sinh x/2J}$$

Then

$$M_z = \rho\langle\mu_z\rangle = \frac{\rho}{\beta}\frac{\partial}{\partial\mathcal{H}}\ln Q_1$$

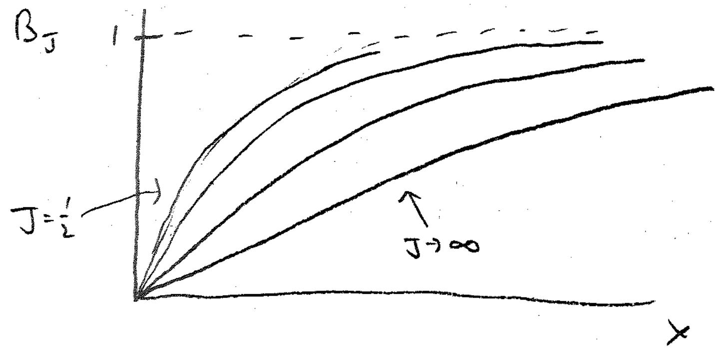
$$= \rho(g\mu_B J)\frac{\partial}{\partial x}\ln Q_1$$

$$= \rho g\mu_B J\left[\left(1+\frac{1}{2J}\right)\coth x\left(1+\frac{1}{2J}\right) - \frac{1}{2J}\coth\frac{x}{2J}\right]$$

$$\equiv \rho g\mu_B J \; B_J(x)$$

B_J = Brillouin function of order J

Similar to $L(x)$



For small x, $\quad B_J(x) \simeq \frac{1}{3}\left(1+\frac{1}{J}\right)x$

and
$$M_z \to N g \mu_B J \, \frac{1}{3}\left(1+\frac{1}{J}\right) \frac{g\mu_B J}{kT} \mathcal{H}$$
$$= N \frac{g^2 \mu_B^2 J(J+1)}{3kT} \mathcal{H}$$

Again set Curie law

$$M_z \to \frac{N \vec{\mu}^2}{3kT} \mathcal{H} \qquad \text{with } \vec{\mu}^2 = \frac{g^2 \mu_B^2}{\hbar^2} \vec{J}^2$$

Also see that $B_J(x) \to L(x)$ for small x, large J
= classical limit

In fact $B_J \to L$ as $J \to \infty$ for any x

But typically J is not large
Can get J for particles from curve of M vs $\mathcal{H}$