10/10

Last time:

Classical case:

$$Z_N = \left(\frac{kT}{\hbar\omega}\right)^N$$

Quantum case:

$$Z_N = \left[2 \sinh \frac{\hbar\omega}{2kT}\right]^{-N} =$$

$$= \left[e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}\right]^{-N}$$

Density of States for the quantum harmonic oscillator:

$$Z_N(\beta) = e^{-(\frac{N}{2}\beta\hbar\omega)}(1-e^{-\beta\hbar\omega})^{-N}$$

Notice that

$$(1-x)^{-n} = \sum_{r=0}^{\infty}\binom{n+r-1}{r}x^r$$

$$Z_N(\beta) = e^{-\frac{N}{2}\beta\hbar\omega}\sum_{r=0}^{\infty}\binom{N+r-1}{r}e^{-\beta r\hbar\omega} =$$

$$= \sum_{r=0}^{\infty}\binom{N+r-1}{r}e^{-\beta\left[\frac{N}{2}\hbar\omega + r\hbar\omega\right]} \qquad (1)$$

but

$$Z_N(\beta) = \int_0^{\infty} g(\epsilon)\, e^{-\beta\epsilon}\, d\epsilon \qquad (2)$$

we see that

$$Z_N(\beta) = \int_0^\infty g(\epsilon)\, e^{-\beta\epsilon}\, d\epsilon = \sum_{r=0}^{\infty} \binom{N+r-1}{r} e^{-\beta\left(\frac{N}{2}\hbar\omega + r\hbar\omega\right)}$$

if

$$g(\epsilon) = \sum_{r=0}^{\infty} \binom{N+r-1}{r} \delta\left(\epsilon - \left[r+\frac{N}{2}\right]\hbar\omega\right)$$

So we see that if $\epsilon_r = \left(r+\frac{N}{2}\right)\hbar\omega$ then the # of allowed microstates is given by

$$\binom{N+r-1}{r} = \frac{(N+r-1)!}{r!\,(N-1)!} = \binom{N+r-1}{N-1}$$

Microcanonical Ensemble:

Consider energy E distributed among N identical harmonic oscillators with

$$\varepsilon_r = (r + \tfrac{1}{2}) \hbar \omega \qquad r = 0, 1, 2, \ldots$$

Since each oscillator will have $\frac{1}{2} \hbar \omega$ energy at least, the energy left to be distributed is

$$E_R = E - \frac{N}{2} \hbar \omega \qquad \text{fixed.}$$

$$R = \frac{E_R}{\hbar \omega} = \frac{E - \frac{N}{2} \hbar \omega}{\hbar \omega} \qquad \text{integer}$$

$$\therefore\ E = R \hbar \omega + \frac{N}{2} \hbar \omega$$

To find in how many ways we can distribute the R quanta of energy among the N distinguishable oscillators we need to find out in how many ways R indistinguishable objects can be placed in N distinguishable boxes!

$$\frac{(R+N-1)!}{R!\,(N-1)!} = \binom{R+N-1}{R} = \binom{R+N-1}{N-1}$$

identical to the # of ways that appeared in $g(E)$ [obtained in the canonical].

Now since $S = k \ln \Omega$ and we know Ω:

$$S = k \ln \left(\frac{(N+R-1)!}{R!\,(N-1)!} \right) \approx k \left[\ln (R+N)! - \ln R! - \ln N! \right]$$

$$\approx k \left[(R+N) \ln (R+N) - R \ln R - N \ln N \right]$$

R : integer

Stirling

But

$$R = \frac{E - \frac{1}{2} N \hbar \omega}{\hbar \omega} \quad (*) \quad \Rightarrow \quad \frac{\partial R}{\partial E} = \frac{1}{\hbar \omega}$$

and

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = \frac{\partial S}{\partial R} \frac{\partial R}{\partial E} = \frac{k}{\hbar \omega} \left[\ln (R+N) + \frac{(R+N)}{R+N} - \ln R - \frac{R}{R} \right] = \frac{k}{\hbar \omega} \ln \left(\frac{R+N}{R} \right) \overset{(*)}{=} \frac{k}{\hbar \omega} \ln \left[\frac{E + \frac{1}{2} N \hbar \omega}{E - \frac{1}{2} N \hbar \omega} \right]$$

$$\therefore \quad \frac{\hbar\omega}{kT} = \ln\left[\frac{E + \frac{1}{2}N\hbar\omega}{E - \frac{1}{2}N\hbar\omega}\right] \qquad \text{here } T = T(E)$$

Now we solve to get $E = E(T)$. ∴

$$e^{\frac{\hbar\omega}{kT}} = \frac{E + \frac{1}{2}N\hbar\omega}{E - \frac{1}{2}N\hbar\omega}$$

then

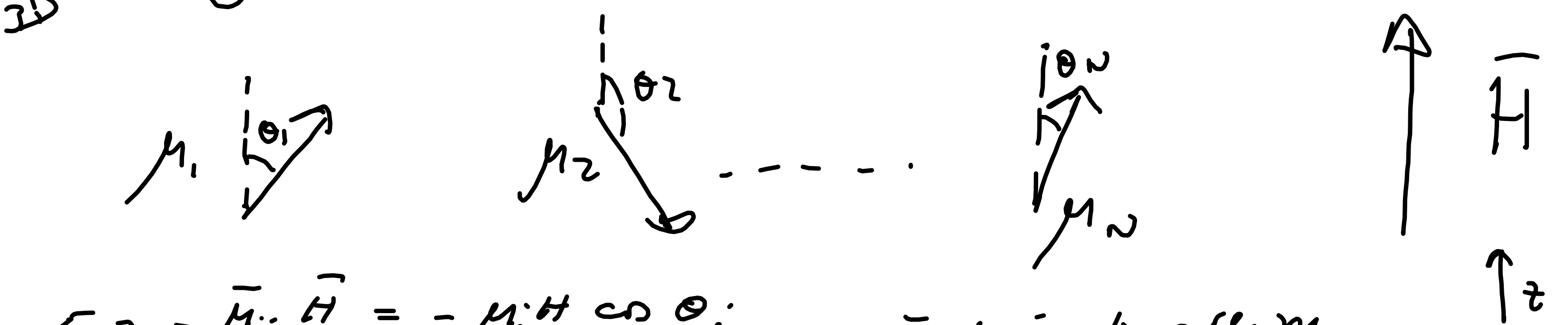
$$\frac{E}{N} = \frac{\hbar\omega}{2}\,\frac{\left(e^{\frac{\hbar\omega}{kT}} + 1\right)}{\left(e^{\frac{\hbar\omega}{kT}} - 1\right)}$$

which is identical to the expression that we obtained from $E = -\frac{\partial \ln Z}{\partial \beta}$.

Paramagnetism (derivation in canonical formalism).

Classical picture:

N non-interacting magnetic dipoles with magnetic moment $\bar{\mu}$. Distinguishable because they are localized.



$E_i = -\bar{\mu}_i \cdot \bar{H} = -\mu_i H \cos\theta_i$ $\qquad$ $\bar{\mu}$ tries to align with $\bar{H}$.

You see that at $T \to 0$ the dipoles are going to be alligned with $\vec{H}$. But if T increases and $kT >> \mu H$ then H will be negligible and the dipoles will be randomly ordered.

Classically:

$$Z_N(\beta) = (Z_1(\beta))^N = \left[\sum_{\theta} e^{\beta\mu H\cos\theta}\right]^N \longrightarrow$$

$\theta \to$ all possible values of θ and φ in 3D

$$\to \left[\underbrace{\int_0^{2\pi} d\varphi}_{2\pi} \int_0^{\pi} e^{\beta\mu H\cos\theta} \underbrace{\sin\theta\, d\theta}_{-d(\cos\theta)}\right]^N =$$

$\cos\theta = x$

$$= \left[2\pi \int_{-1}^{1} e^{\beta\mu H x} dx\right]^N = \left[2\pi \left.\frac{e^{\beta\mu H x}}{\beta\mu H}\right|_{-1}^{1}\right]^N =$$

$$= \left[\frac{2\pi}{\beta\mu H}\underbrace{\left(e^{\beta\mu H} - e^{-\beta\mu H}\right)}_{2\sinh\beta\mu H}\right]^N = \left[\frac{4\pi}{\beta\mu H}\sinh\beta\mu H\right]^N$$

Magnetization:

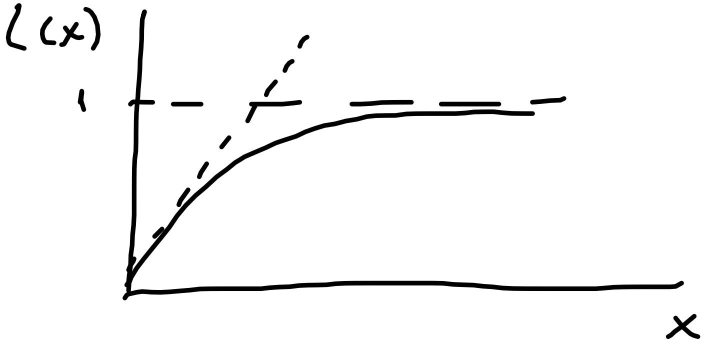
$$\bar{\mu}_z = \frac{M_z}{N} = \langle \mu\cos\theta\rangle \overset{1\text{ dipole}}{=} \frac{\sum_\theta \mu\cos\theta\, e^{\beta\mu H\cos\theta}}{\sum_\theta e^{\beta\mu H\cos\theta}} =$$

$$= \frac{1}{\beta}\frac{\partial \ln Z_1}{\partial H} = \frac{kT}{N}\frac{\partial \ln Z_N}{\partial H} = -\frac{1}{N}\frac{\partial F}{\partial H}\Big|_T =$$

$$= \frac{kT}{N}\frac{\partial \ln\left(\frac{4\pi}{\beta\mu H}\sinh\beta\mu H\right)^N}{\partial H}\Bigg|_\beta = kT\left(\beta\mu\coth\beta\mu H - \frac{1}{H}\right) \Rightarrow$$

$$\Rightarrow \bar{\mu}_z = \mu \left(\coth \beta\mu H - \frac{1}{\beta\mu H} \right) = \mu L(\beta\mu H)$$

$$L(x) = \coth x - \frac{1}{x}$$ Langevin function.



Define $N_0 = \frac{N}{V}$ density of dipoles.

$$M_{z0} = N_0 \bar{\mu}_z = N_0 \mu L(x)$$ magnetization per unit volume.

Here $x = \beta \mu H = \dfrac{\mu H}{kT}$ $\qquad M_{z0} = N_0 \mu L(x)$

For $x \gg 1 \Rightarrow kT \ll \mu H$ (low T limit)

$\dfrac{\mu H}{kT} \gg 1 \Rightarrow \mu H \gg kT \quad L(x) \to 1$

$\therefore M_{z0} = N_0 \mu$ (saturation) all dipoles are parallel to H.

For $x \ll 1 \Rightarrow kT \gg \mu H$ (high T limit)

$L(x) \approx \dfrac{x}{3} - \dfrac{x^3}{45} + \cdots$ (linear at lowest order)

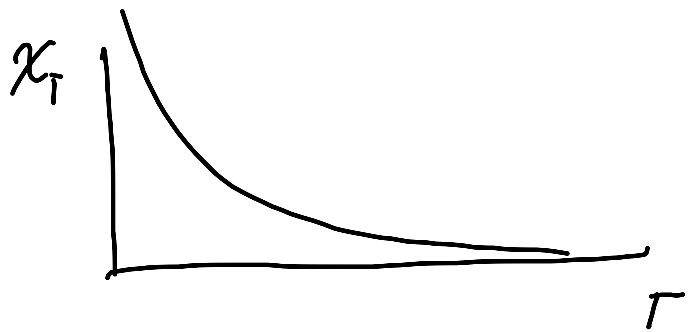
$M_{z0} \cong N_0 \mu \dfrac{x}{3} \approx \dfrac{N_0 \mu^2 H}{3kT} \propto H$

goes to 0 if $H \to 0$ and if $T \to \infty$ as expected.

Magnetic susceptibility:

$$\chi_T = \lim_{H \to 0} \left(\frac{\partial M_{z0}}{\partial H} \right)_T \simeq \frac{N_0 \mu^2}{3kT} = \frac{C}{T}$$

Curie's law



isothermal magnetic susceptibility.

Works well at high T or for molecules with high magnetic moments.

Quantum treatment:

$$\bar{\mu} = \overbrace{g \frac{e}{2mc}}^{\text{gyromagnetic ratio}} \bar{\ell}$$

angular momentum

$$\ell^2 = J(J+1)\hbar^2$$

$J = \frac{1}{2}, \frac{3}{2}, \dots$

or $J = 0, 1, \dots$

Landé's factor

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

S: spin

L: angular momentum

$\bar{J} = \bar{L} + \bar{S}$

for pure spins $L = 0$ $S = J$

$\therefore g = \frac{3}{2} + \frac{1}{2} = 2$

for atoms with $L \neq 0$ but $S = 0$

$g = \frac{3}{2} - \frac{1}{2} = 1$

Then

$$\mu^2 = g^2 \frac{e^2}{4m^2c^2} J(J+1)\hbar^2 = g^2 \mu_B^2 J(J+1)$$

Bohr's magneton

$$\mu_B = \frac{e\hbar}{2mc}$$

and $\mu_z = g\mu_B m$ $m = -J, -J-1, \ldots J-1, J$

$2J+1$ possible values of m.

$$\therefore Z_1(\beta) = \sum_{m=-J}^{J} e^{\beta g \mu_0 m H} = \sum_{m=-J}^{J} e^{\frac{mx}{J}} =$$

if $x = \beta (g\mu_B J) H$

geometric series

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

$$M_z = N\bar{\mu}_z = \frac{N}{\beta}\frac{\partial \ln Z_1}{\partial H} =$$

$$\bar{\mu}_z = \frac{1}{\beta}\frac{\partial \ln Z_1}{\partial H} \qquad x = x(H)$$

(found before)

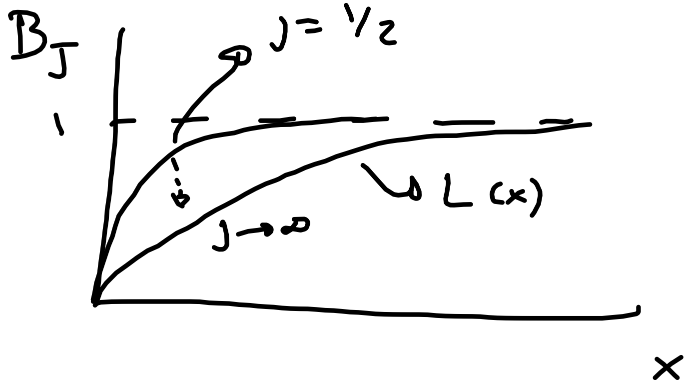
$$= N(g\mu_B J)\left[\left(1+\frac{1}{2J}\right)\coth\left(1+\frac{1}{2J}\right)x - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)\right]$$

$$\bar{\mu}_z = g\mu_B J\, B_J(x)$$

Brillouin function

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

$$\lim_{J\to\infty} B_J(x) = \coth x - \frac{1}{x} \equiv L(x)$$



$\bar{\mu}_z = g\mu_B J$ instead of just μ for $x \to \infty$

$$\bar{\mu}_z \cong \frac{g^2\mu_B^2 J(J+1)H}{3kT} \quad \therefore \quad \frac{\chi_T}{N} = \lim_{H\to 0} \left.\frac{\partial \bar{\mu}_{z0}}{\partial H}\right)_T \propto \frac{1}{T}$$

$\chi \propto \frac{1}{T}$ with $C_J = \frac{N_0\mu^2}{3k}$ if $\mu^2 = g^2\mu_B^2 J(J+1)$

We also obtain Curie's law.