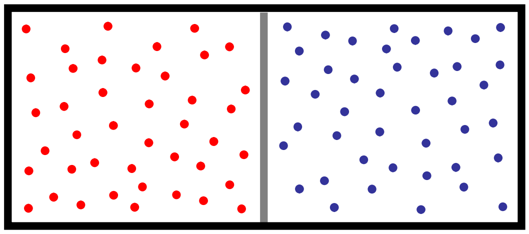
# Review

- Entropy of Mixing



For different gases with same *N*, *U* and *V* before mixing

$$\Delta S = \Delta S_A + \Delta S_B = 2Nk \ln 2$$

If same gas, entropy does not increase (significantly)

→ small changes for fluctuations in number in each volume

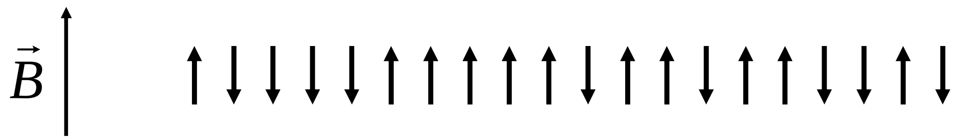
→ small impact on multiplicity

# More on Multiplicity of Ideal Gas

$$\Omega_N \approx \underbrace{\frac{1}{N!}}_{\text{for indistinguishable particles}} \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} \left(\sqrt{2mU}\right)^{3N}$$

for other notes on this eq, see lec06

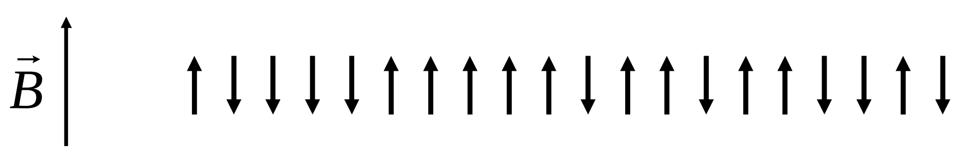
# Two-state Paramagnet



- Arrows represent microscopic magnetic dipole moments or "spins" of particles
  - Each has a dipole moment: $\mu$

- Consider an ideal paramagnet
  - No interaction between the spins
  - For real ferromagnet, interactions between spins important

# Two-state Paramagnet



- Up or down spins (parallel or antiparallel to field)
  - Quantized - only two states allowed for spin-1/2 particles

$$\Omega(N, N_{\uparrow}) = \frac{N!}{N_{\uparrow}!\,N_{\downarrow}!} \equiv \binom{N}{N_{\uparrow}}$$

- When magnetic field ($B$) direction is pointing "up" (+z)
  - Spin "up" state will have lower energy: $-\mu B$

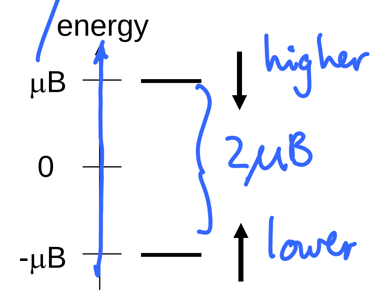
# Energy Levels and Magnetism (1)

magnitude

- Energy levels of single dipole (particle)

vector dipole moment => μ=+μ ↑ ↓ dipole moment => μ=-μ

with field against field




- Total energy

$$U = \sum -(\boldsymbol{\mu} \cdot \mathbf{B}) = \mu B(N_{\downarrow} - N_{\uparrow}) = \mu B(N - 2N_{\uparrow})$$

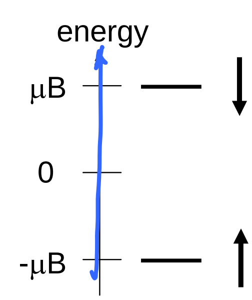
vector quantities

$U = -\mu B + \mu B + \mu B - \mu B \ldots$

# Energy Levels and Magnetism (2)

- Energy levels of single dipole (particle)

dipole moment => μ=+μ ↑ ↓ dipole moment => μ=-μ




- Magnetization (M) - Total magnetic moment of the system

$$M = \sum \boldsymbol{\mu} = \mu(N_{\uparrow} - N_{\downarrow}) = -\frac{U}{B}$$

# Calculation of Entropy

- Using $\Omega(N, N_\uparrow) = \dfrac{N!}{N_\uparrow! N_\downarrow!} \equiv \dbinom{N}{N_\uparrow}$

$$\frac{S}{k} = \ln \Omega = \ln N! - \ln N_\uparrow! - \ln N_\downarrow!$$

$$\cong N \ln N - \cancel{N} - N_\uparrow \ln N_\uparrow + \cancel{N_\uparrow} - N_\downarrow \ln N_\downarrow + \cancel{N_\downarrow}$$

$$= N \ln N - N_\uparrow \ln N_\uparrow - N_\downarrow \ln N_\downarrow$$

$$= N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln (N - N_\uparrow)$$

$$\frac{1}{k} \frac{\partial S}{\partial N_\uparrow} = -\ln N_\uparrow - N_\uparrow \frac{1}{N_\uparrow} + \ln (N - N_\uparrow) + (N - N_\uparrow) \cdot \frac{1}{(N - N_\uparrow)}$$

$$= \ln (N - N_\uparrow) - \ln N_\uparrow$$

$$= \ln \left( \frac{N - N_\uparrow}{N_\uparrow} \right) = \ln \left( \frac{N_\downarrow}{N_\uparrow} \right)$$

# Calculation of Inverse Temperature

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{N,B} = \left( \frac{\partial S}{\partial N_\uparrow} \cdot \frac{\partial N_\uparrow}{\partial U} \right)_{N,B}$$

$$U = \mu B (N - 2N_\uparrow)$$

rearranging

$$N_\uparrow = -\frac{U}{2\mu B} + \frac{N}{2} \quad \text{or} \quad N_\downarrow = \frac{U}{2\mu B} + \frac{N}{2}$$

$$\frac{\partial N_\uparrow}{\partial U} = -\frac{1}{2\mu B}$$

sub in

$$\frac{1}{T} = k \ln \left( \frac{N_\downarrow}{N_\uparrow} \right) \cdot \left( -\frac{1}{2\mu B} \right)$$

$$= \frac{-k}{2\mu B} \ln\left[\frac{U/2\mu B + N/2}{-U/2\mu B + N/2}\right]$$

$$= \frac{-k}{2\mu B} \ln\left[\frac{U/\mu B + N}{-U/\mu B + N}\right]$$

## Now, Calculate Total Energy

with a little rearranging

$$\ln\left[\frac{U/\mu B + N}{-U/\mu B + N}\right] = -\frac{2\mu B}{kT}$$

$$\frac{U/\mu B + N}{-U/\mu B + N} = e^{-2\mu B/kT}$$

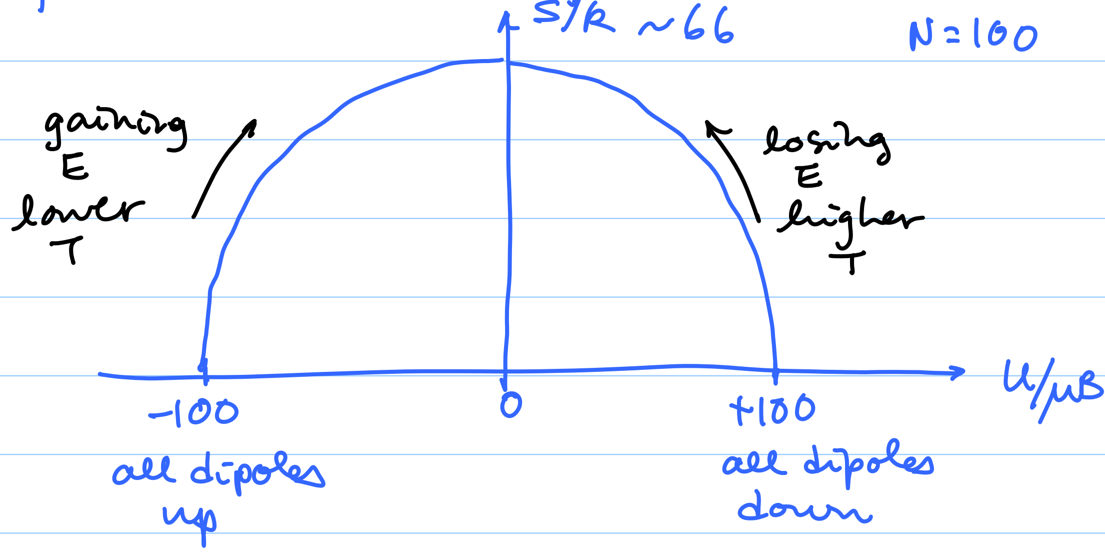
$$N\left(1 - e^{-2\mu B/kT}\right) = \frac{-U}{\mu B}\left(1 + e^{-2\mu B/kT}\right)$$

$$U = -N\mu B\left[\frac{1 - \exp(-2\mu B/kT)}{1 + \exp(-2\mu B/kT)}\right]$$

$$U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

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

plot entropy as function of total energy



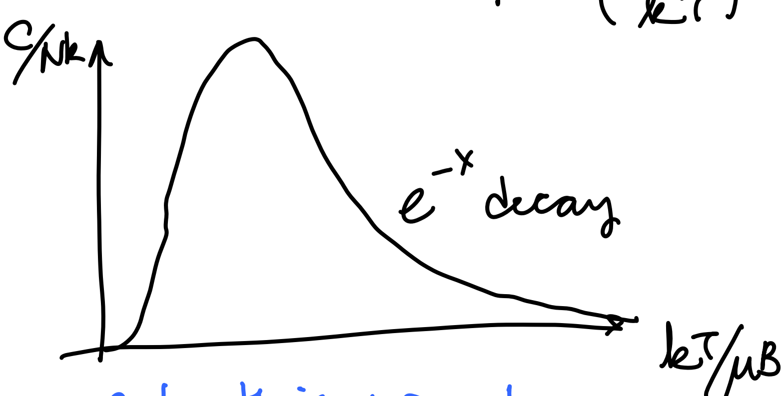

temperature behavior is unusual
→ S is more fundamental property than T

# Heat Capacity

$C_B$ at constant field

$$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = Nk\left(\frac{(\mu B/kT)^2}{\cosh^2(\mu B/kT)}\right)$$

$$= Nk\left(\frac{\mu B}{kT}\right)^2 \text{sech}^2\left(\frac{\mu B}{kT}\right)$$




$\text{sech}(x) = \frac{2}{e^{x} + e^{-x}}$

$x \to 0$

$\text{sech}(x) \approx \frac{2}{1 + x \ldots + 1 - x \ldots}$

$\approx 1$

taylor series approx.

→ plot this way to compare to earlier plots of C vs. T.

# Real-world Paramagnets

- Electronic paramagnetism
  - Dipole moments caused by “unpaired” electrons in atoms or molecules
  - For single electron in an atom with an “unpaired” spin
    - μ is called Bohr magneton

      $\mu_B = 9.274\text{x}10^{-24}$ J/T = $5.788\text{x}10^{-5}$ eV/T
  - At room temperature and with a field of ~1 Tesla

$$kT \approx \frac{1}{40}\text{eV} \qquad \mu_B \approx 5.8\text{x}10^{-5}\text{eV}$$

at room T

$$\frac{\mu B}{kT} \ll 1$$

# Curie’s Law

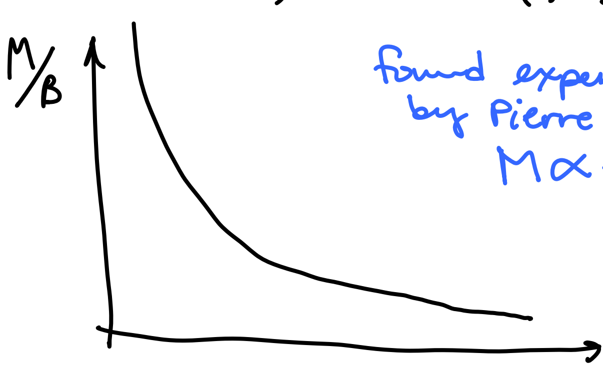
for high T limit $\quad \frac{\mu B}{kT} \to 0$

$\tan(x) \to x$

$$M = -\frac{U}{B}$$

$$= -\frac{1}{B}\left(-N\mu B \tanh\left(\frac{\mu B}{kT}\right)\right)$$

$$= N\mu \tanh\left(\frac{\mu B}{kT}\right)$$




found experimentally by Pierre Curie

$M \propto \frac{1}{T}$