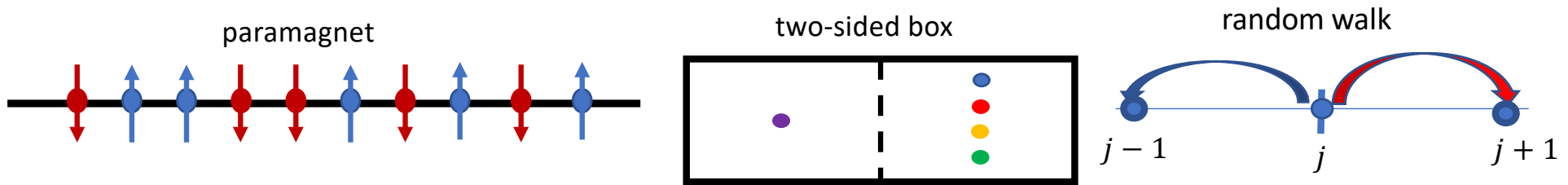


Lecture 7

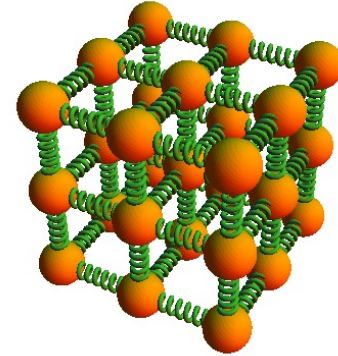
Large systems, multiplicity, entropy,

Recap: Two-state models



- System: N spins, particles or steps
 - Independent (no interaction between spins/particles, no correlation between successive steps)
 - Distinguishable (the order matters)
 - Equal probability of states $s_i = \pm 1$ (up/down, left/right)
- Microstates:
 - All possible combinations of ordering the N particles/steps
 - Fundamental assumption of statistical mechanics: In an isolated system in thermal equilibrium, all accessible microstates are equally probable.
 - Total number = 2^N
- Macrostates:
 - $k = \sum_{i=1}^N s_i$ (net magnetization, excess of particles on left side, distance walked to the left)
 - multiplicity of macrostate $\Omega(N, k) = \frac{N!}{k!(N-k)!}$
 - probability of macrostate $P(N, k) = \frac{2^{-N} N!}{k!(N-k)!}$

Recap: Einstein crystal



- N independent and localized (distinguishable) quantum harmonic oscillators
- Each quantum oscillator has a discrete spectrum of energy levels, $n = 0, 1, 2, \dots$ (not two-state)

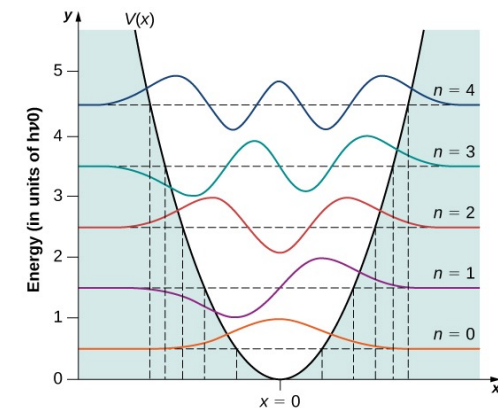
$$\epsilon_n = \left(n + \frac{1}{2}\right) \hbar\omega$$

- Microstates: $\{n_1, n_2, \dots, n_{N-1}, n_N\}$
- Macrostate = total energy:

- $U_N = \sum_{i=1}^N \epsilon_{n_i} = \sum_{i=1}^N n_i \hbar\omega + \frac{N}{2} \hbar\omega$

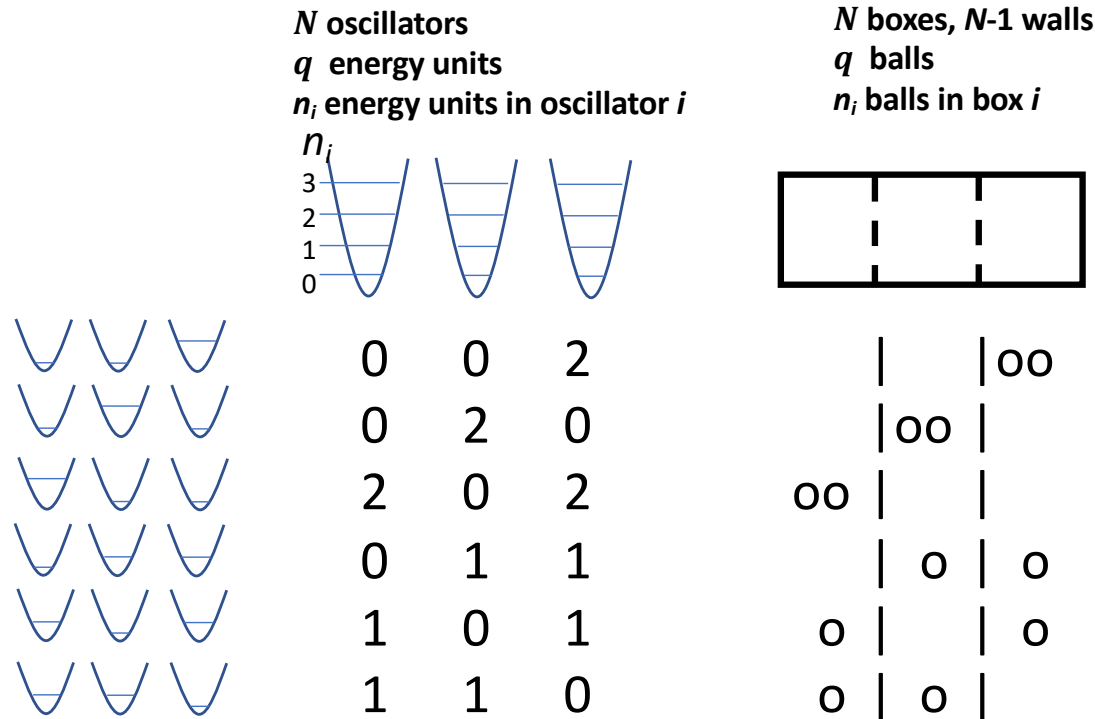
- $q = \frac{U_N - \frac{N}{2} \hbar\omega}{\hbar\omega} = \sum_{i=1}^N n_i$

- defined by (N, q)



Recap: Einstein crystal

Multiplicity $\Omega(N, q)$ of a macrostate with N oscillators and q units of energy distributed between them. Trick: map to two-state system.



Two-state model:

$$\Omega(N, k) = \frac{N!}{k! (N - k)!}$$

Number of digits: $N' = N - 1 + q$ (= wall + balls)

Number of states: $k' = q$

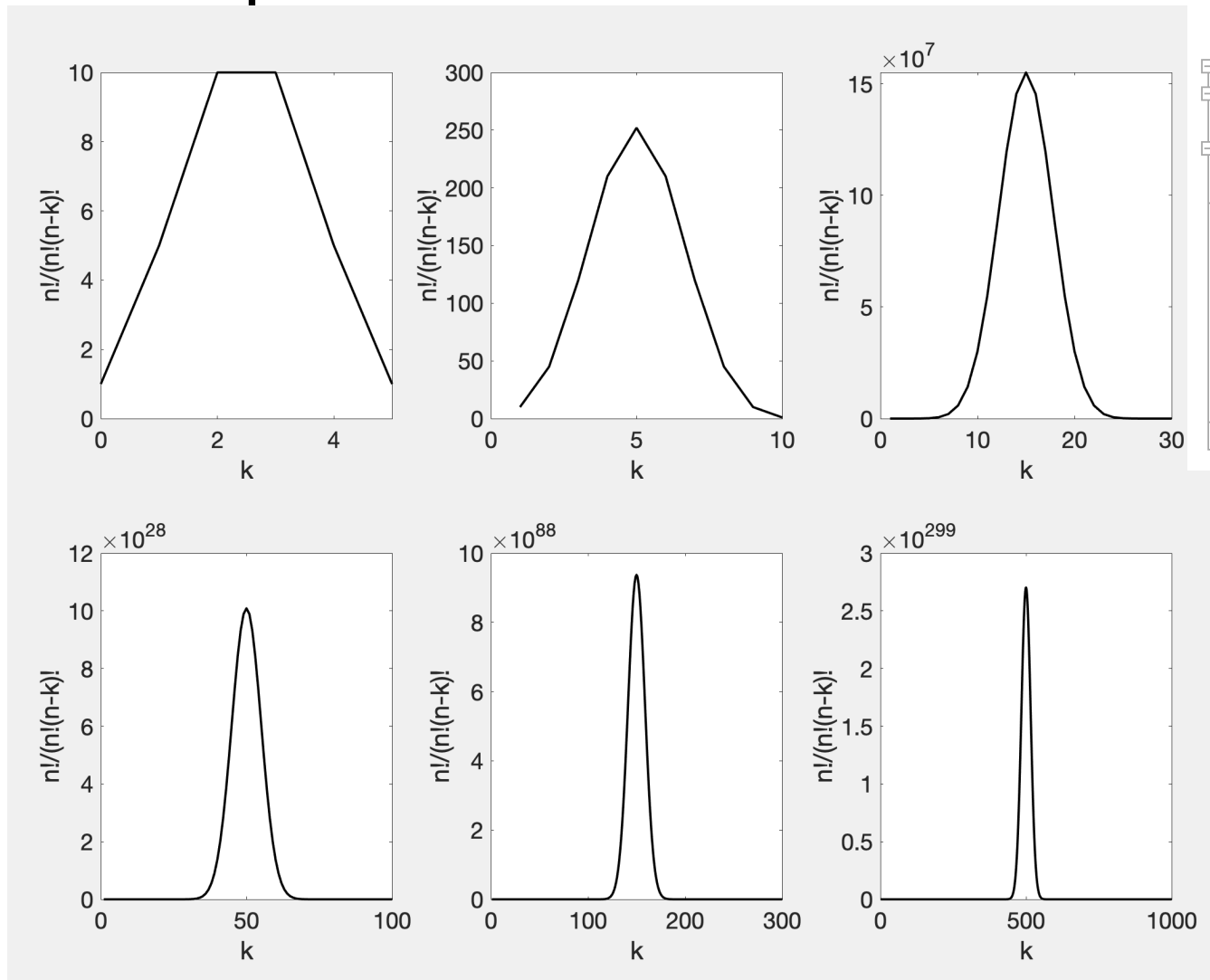
$$N' - k' = N - 1 + q - q = N - 1$$

Number of ways of combining $(N-1)$ -walls and q

balls:

$$\Omega(N, q) = \frac{(N - 1 + q)!}{q! (N - 1)!}$$

Sharpness of distribution



```
n=[5 10 30 100 300 1000];
l=1;
for i=1:2
    for j=1:3
        nk=1;
        for k=1:n(l)
            nk(k)=nchoosek(n(l),k);
        end
        subplot(2,3,l)
        plot(nk, 'k', 'LineWidth',2)
        xlabel('k', 'FontSize',20)
        ylabel('n!/(n!(n-k)!', 'FontSize',20)
        ax1 = gca; % current axes
        ax1.FontSize = 20;
        l=l+1;
    end
end
```

What happens when $q \rightarrow 10^{23}$?

$$\Omega(N, n) = \frac{N!}{n!(N-n)!}$$

We need an approximation for $N!$ when $N \gg 1$

Stirling's approximation for $N!$ when $N \gg 1$

$$N! = 1 \cdot 2 \cdot 3 \cdot 4 \dots (N - 1) \cdot N$$

$$N! \approx \sqrt{2\pi N} N^N e^{-N}$$

$$\ln N! \approx N \ln N - N + \frac{1}{2} \ln 2\pi N \approx N \ln N - N$$

Large Einstein crystal

$$\Omega(q, N) = \frac{(N-1+q)!}{q!(N-1)!} \approx \frac{(N+q)!}{q!N!}, \quad N, q \gg 1$$

$$\ln n! = n \ln n - n$$

Low T: $q \ll N$

High T: $q \gg N$

$$\ln \Omega = (N+q) \ln(N+q) - (N+q) - q \ln q + q - N \ln N + N$$

$$\ln \Omega = (N+q) \ln N \left(1 + \frac{q}{N}\right) - q \ln q - N \ln N$$

$$\ln \Omega = N \ln N + q \ln N + (N+q) \ln \left(1 + \frac{q}{N}\right) - q \ln q - N \ln N$$

$$\ln \Omega = q \ln \frac{N}{q} + (N+q) \ln \left(1 + \frac{q}{N}\right)$$

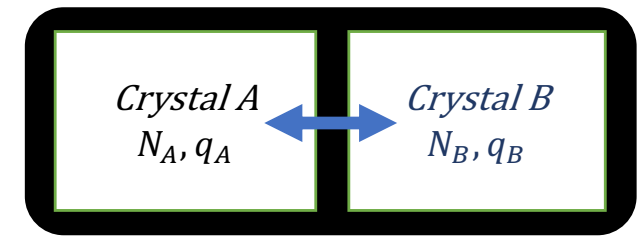
$$q \ll N, \ln(1+\epsilon) \approx \epsilon \quad \ln \Omega \approx q \ln \frac{N}{q} + (N+q) \frac{q}{N}, \quad q = \ln e^q$$

$$\ln \Omega \approx q \ln \frac{N}{q} + q + \frac{q^2}{N} \approx \ln \left(\frac{Ne}{q}\right)^q$$

$$\text{Low T: } q \ll N \quad \Omega_{\text{low } T}(q, N) \approx \left(\frac{Ne}{q}\right)^q$$

$$\text{High T: } q \gg N \quad \Omega_{\text{high } T}(q, N) \approx \left(\frac{qe}{N}\right)^N$$

Two large Einstein crystals



$$\Omega_t = \Omega_A \cdot \Omega_B \approx \frac{(N_A + q_A)!}{q_A! N_A!} \cdot \frac{(N_B + q_B)!}{q_B! N_B!}, \quad N_A, q_A, N_B, q_B \gg 1$$

High T: $q \gg N$ $\Omega_{\text{high T}}(q, N) \approx \left(\frac{qe}{N}\right)^N$

$$N_A = N_B = N$$

$$q_A + q_B = q$$

$$\Omega_t \approx \left(\frac{q_A e}{N}\right)^N \left(\frac{q_B e}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N$$

Ω_t is max:

$$q_A = q_B = \frac{q}{2}$$

$$\Omega_t^{\text{max}} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N}$$

Expand around
the peak:

$$q_A = \frac{q}{2} + x, \quad q_B = \frac{q}{2} - x$$

$$\Omega_t \approx \left(\frac{e}{N}\right)^{2N} \left[\left(\frac{q}{2}\right)^2 - x^2\right]^N$$

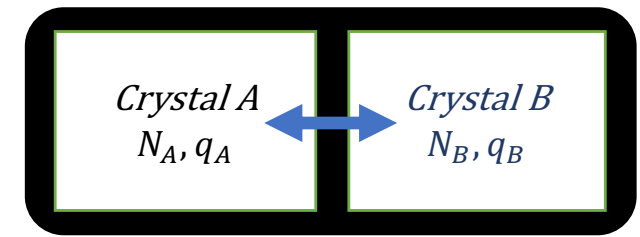
$$\ln \Omega_t \approx 2N \ln \frac{e}{N} + N \ln \left[\left(\frac{q}{2}\right)^2 - x^2\right] = 2N \ln \frac{e}{N} + 2N \ln \frac{q}{2} + N \ln \left[1 - \left(\frac{2x}{q}\right)^2\right]$$

$\ln(1 + \epsilon) \approx \epsilon$ $\ln \Omega_t \approx \ln \left(\frac{eq}{2N}\right)^{2N} - N \left(\frac{2x}{q}\right)^2$

$$\ln \Omega_t \approx \ln \Omega_t^{\text{max}} - N \left(\frac{2x}{q}\right)^2, \quad \Omega_t^{\text{max}} = \left(\frac{eq}{2N}\right)^{2N}$$

$$\Omega_t = \Omega_t^{\text{max}} \cdot e^{-N \left(\frac{2x}{q}\right)^2}$$

Two large Einstein crystals



High T: $q \gg N$ $\Omega_{\text{high T}}(q, N) \approx \left(\frac{qe}{N}\right)^N$

$$N_A = N_B = N \gg \gg 1$$

$$q_A + q_B = q \gg 1$$

$$q_A = \frac{q}{2} + x, \quad q_B = \frac{q}{2} - x$$

$$\Omega_t = \Omega_t^{\text{max}} \cdot e^{-N\left(\frac{2x}{q}\right)^2}, \quad \Omega_t^{\text{max}} = \left(\frac{eq}{2N}\right)^{2N}$$

Ω_t falls off to $e^{-1/2}$ of its maximum when

$$N \left(\frac{2x}{q}\right)^2 = \frac{1}{2} \quad \Rightarrow \quad x = \frac{q}{2\sqrt{2N}} \quad \Rightarrow \quad \sigma = \frac{q}{\sqrt{2N}} \approx \frac{q}{\sqrt{N}}$$

Fluctuations around the mean

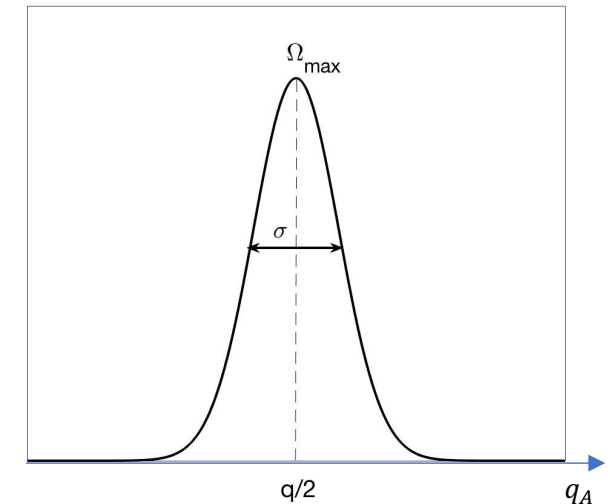
$$\frac{\sigma}{\langle q \rangle} = \frac{q/\sqrt{2N}}{q/2} \approx \frac{1}{\sqrt{N}} \rightarrow 0$$

Normalization: $\int_{-\infty}^{+\infty} \Omega_t = \Omega_t^{\text{max}} \int_{-\infty}^{+\infty} dx e^{-\frac{4N}{q^2} x^2} = \Omega_t^{\text{max}} \frac{q}{2} \sqrt{\frac{\pi}{N}}$

$$x = q_A - \frac{q}{2} \quad \Omega_t(q_A) = \Omega_t^{\text{max}} \cdot e^{-\frac{4N}{q^2} \left(q_A - \frac{q}{2}\right)^2}$$

Probability of having q_A energy units

$$P(q_A) = \frac{\Omega_t}{\Omega_t^{\text{max}} \frac{q}{2} \sqrt{\frac{\pi}{N}}} = \frac{2}{q} \sqrt{\frac{N}{\pi}} e^{-\frac{4N}{q^2} \left(q_A - \frac{q}{2}\right)^2}$$

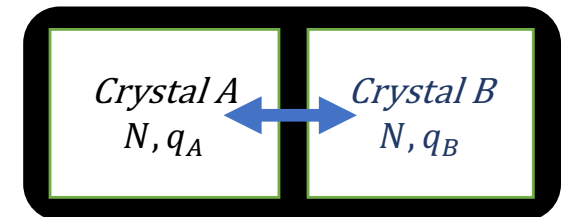


Large systems

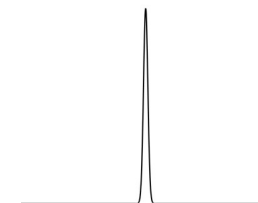
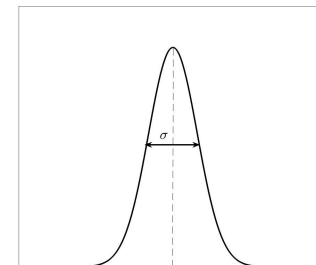
- Stirling approximation for large systems $N! \approx N^N e^{-N} \sqrt{2\pi N} \approx N^N e^{-N}$, for $N \gg 1$

- Interacting Einstein crystals: Multiplicity near its maximum

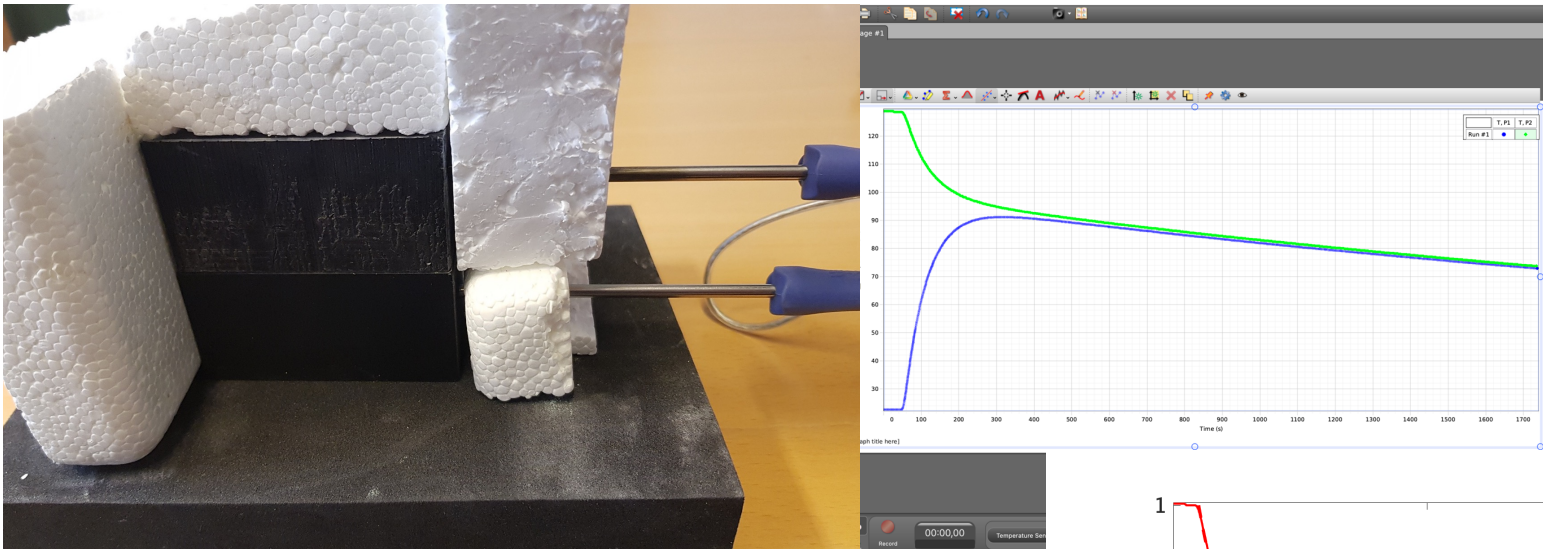
$$\Omega_t(q_A) \approx \Omega_{t,max} e^{-\frac{4N}{q^2} \left(q_A - \frac{q}{2}\right)^2}$$



- In the thermodynamic limit $N \rightarrow \infty$, any random fluctuation away from the most likely states is extremely unlikely

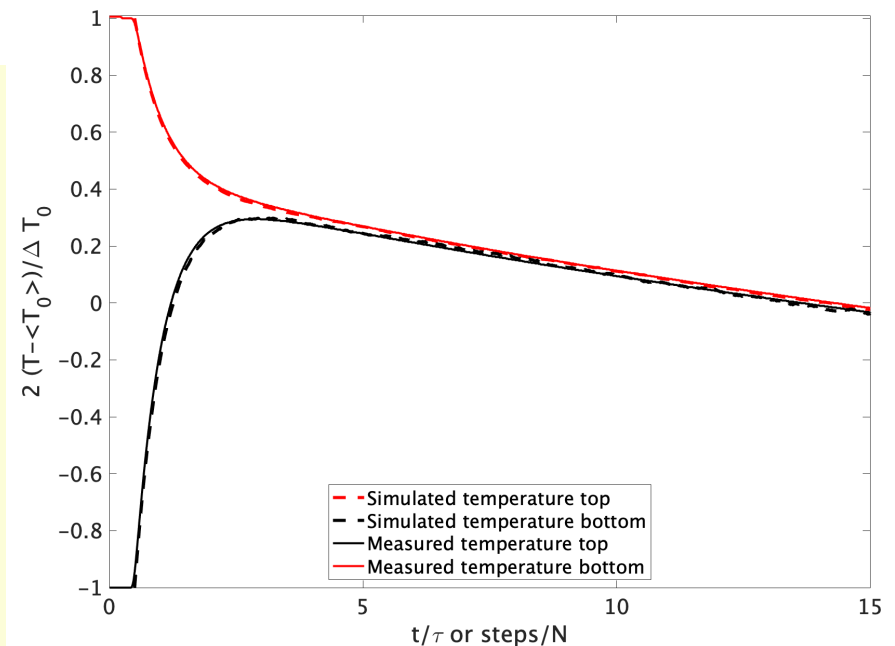


Recap: Thermal conduction



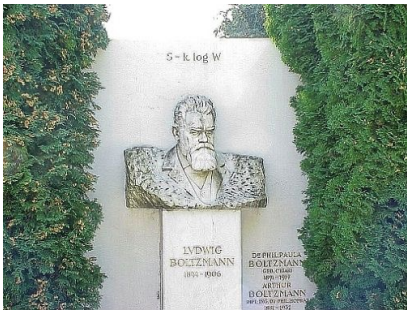
```

for i = 2:nstep
    r = 4*rand(1,1)-2; % Random number between 2 and -2
    DT=Tt(i-1)-Tb(i-1); % temperature difference top to bottom
    if (r<DT)
        Tt(i) = Tt(i-1) - 1/N; % Move heat quanta from top to bottom
        Tb(i) = Tb(i-1) + Ctb/N;
    else
        Tt(i) = Tt(i-1) + 1/N; % Move heat quanta from bottom to top
        Tb(i) = Tb(i-1) - Ctb/N;
    end
    if environment
        % heat loss from top to environment
        r = 4*rand(1,1)-2; % Random number between 2 and -2
        DTt=Tt(i)-Tr; % temperature difference to room
        if (r<DTt)
            Tt(i) = Tt(i) - Closs/N; % Remove heat quanta from top
        else
            Tt(i) = Tt(i) + Closs/N; % Add heat quanta to top
        end
    end
end
    
```



Recap: Thermal equilibrium

- $N, q = q_A + q_B, (N, q)$ constant
- Most likely state = equilibrium state
- Multiplicity $\Omega_{tot} = \Omega_A \Omega_B$ is maximum in equilibrium

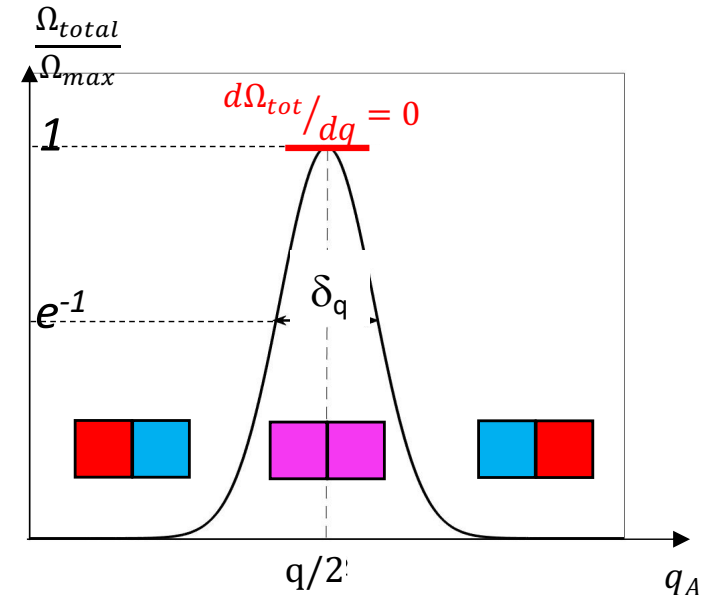


$$\frac{\partial \Omega_{tot}}{\partial q_A} = 0$$

$$\frac{\partial (\Omega_A \Omega_B)}{\partial q_A} = \Omega_A \frac{\partial \Omega_B}{\partial q_A} + \Omega_B \frac{\partial \Omega_A}{\partial q_A} = 0$$

$$\frac{-1}{\Omega_B} \frac{\partial \Omega_B}{\partial q_B} + \frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial q_A} = 0$$

$$\frac{\partial \ln \Omega_B}{\partial q_B} = \frac{\partial \ln \Omega_A}{\partial q_A}$$



Thermal equilibrium:

$$\frac{q_A}{N_A} = \frac{q_B}{N_B}$$

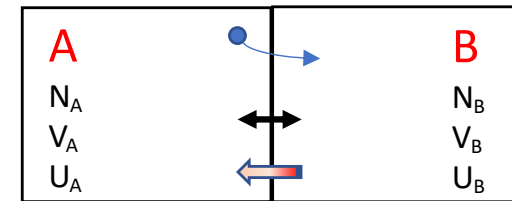
$$T_A = T_B$$

Entropy: $S = k \ln \Omega(N, V, U)$

$$\frac{\partial S_A}{\partial q_A} = \frac{\partial S_B}{\partial q_B}, \quad \frac{1}{T_A} \equiv \left(\frac{\partial S}{\partial U_A} \right)_N$$

Equilibrium between two systems

- $N=N_A+N_B$, $V=V_A+V_B$, $U=U_A+U_B$, all (N,V,U) constant
- Can vary one of the three $\alpha \in (N, V, U)$,
 - keeping the other 2 constant
 - keep total constant: $\alpha = \alpha_A + \alpha_B = \text{const.}$
- Multiplicity $\Omega_{tot} = \Omega_A \Omega_B$ is maximum
 - = most likely state
 - = equilibrium state



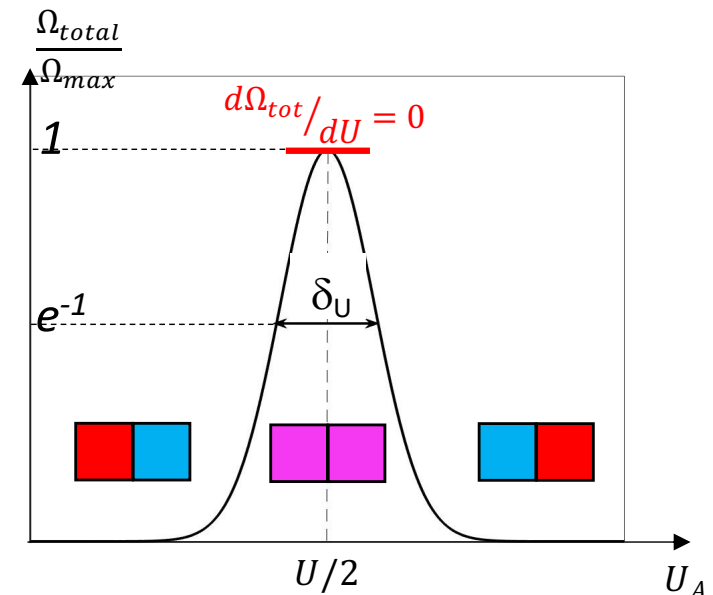
System: can contain "anything"

maximum when $\frac{\partial \Omega_{tot}}{\partial \alpha_A} = 0$

$$\frac{\partial(\Omega_A \Omega_B)}{\partial \alpha_A} = \Omega_A \frac{\partial \Omega_B}{\partial \alpha_A} + \Omega_B \frac{\partial \Omega_A}{\partial \alpha_A} = 0$$

$$d\alpha_A = -d\alpha_B \quad \frac{-1}{\Omega_B} \frac{\partial \Omega_B}{\partial \alpha_B} + \frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial \alpha_A} = 0$$

Equilibrium condition:
$$\frac{\partial \ln \Omega_B}{\partial \alpha_B} = \frac{\partial \ln \Omega_A}{\partial \alpha_A}$$

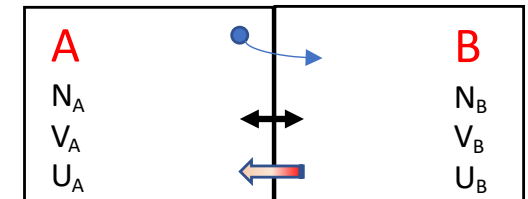


Equilibrium between two systems

- $N=N_A+N_B$, $V=V_A+V_B$, $U=U_A+U_B$, all (N,V,U) constant
- Can vary one of the three $\alpha \in (N, V, U)$,
 - keeping the other 2 constant
 - keep total constant: $\alpha = \alpha_A + \alpha_B = \text{const.}$
- $S_{tot} = S_A + S_B$ is maximum in equilibrium

Equilibrium criterium:

$$\frac{\partial S_B}{\partial \alpha_B} = \frac{\partial S_A}{\partial \alpha_A}$$



Entropy: $S = k \ln \Omega(N, V, U)$

Thermal equilibrium: $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}$, $\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}$, $\frac{[S]}{[U]} = \frac{J K^{-1}}{J}$

Mechanical equilibrium: $\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}$, $P \equiv T \left(\frac{\partial S}{\partial V}\right)_{N,U}$, $\frac{[P]}{[T]} = \frac{J}{m^3 K}$

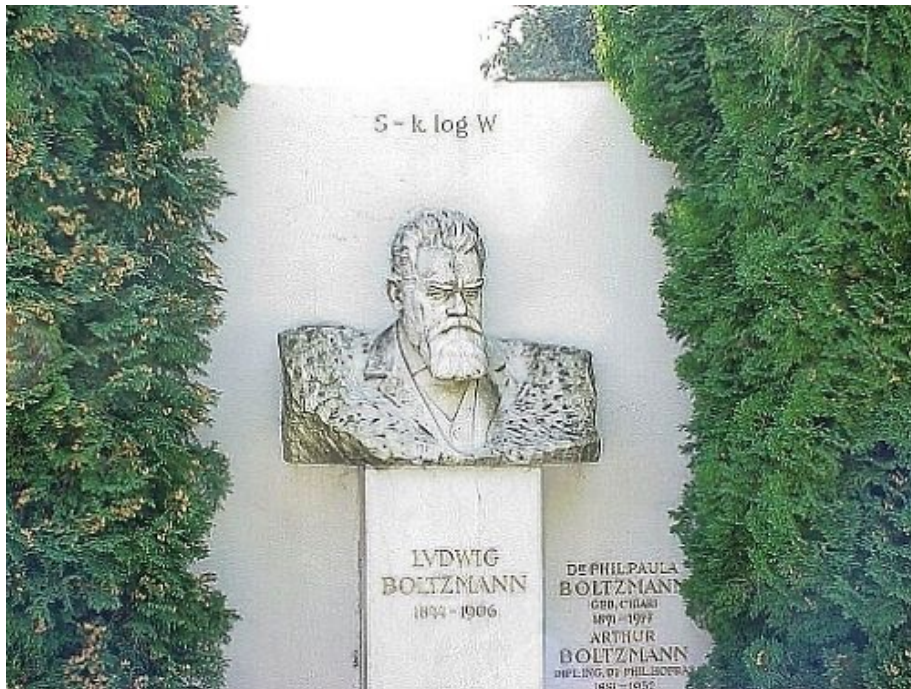
Chemical equilibrium: $\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}$, $\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$, $\frac{[\mu]}{[T]} = \frac{J}{K}$

Boltzmann's Entropy

$$S = k \ln \Omega$$

Relates

- the number of **microstates** (multiplicity) and
- the thermodynamic (**macroscopic**) state of the system



Equilibrium condition:

$$\frac{\partial \ln \Omega_B}{\partial \alpha_B} = \frac{\partial \ln \Omega_A}{\partial \alpha_A}$$
$$\frac{\partial S_A}{\partial \alpha_A} = \frac{\partial S_B}{\partial \alpha_B}$$

All systems move towards most probable states = equilibrium

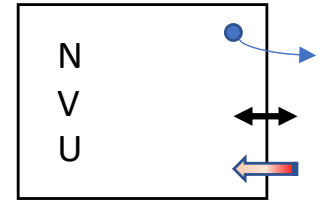
$$\Delta S = k \ln \frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}}$$

Second law of thermodynamics:

$$\Delta S_{\text{tot}} \geq 0$$

All real processes are irreversible

Thermodynamic identity



- Change in entropy due to *energy, volume, particle number*

has a total differential:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

- Use definitions: $\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}$, $P \equiv T\left(\frac{\partial S}{\partial V}\right)_{N,U}$, $\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

- => Thermodynamic identity for $U(S, V, N)$

$$dU = TdS - PdV + \mu dN$$

- The *thermodynamic identity* holds *true* for any infinitesimal change in a system

Heat, work and the 1st & 3rd law

Heat, Q: Energy transfer to a system that is not work or matter:
Conduction, radiation, friction, Joule heat.

Work, W: Energy transfer to a system through measurable forces and corresponding changes in state variables of the system: Pressure – volume; magnetic flux density – magnetization;

First law: $\Delta U = Q + W$

Thermodynamic identity for $U(S, V)$: $dU = TdS - PdV$ (N const)

\Rightarrow Heat: $Q = TdS$, Work: $W = -PdV$

Third law: The entropy of a system approaches a constant as the temperature approaches zero.

Second law before Boltzmann

- Original definition of entropy from heat: $Q = TdS$
- Entropy is the thing which increases by $\frac{Q}{T}$ when heat Q enters the system at temperature T
- Solid (N, V constant): $T = \frac{dQ}{dS} \quad \left(\frac{1}{T_A} \equiv \left(\frac{\partial S}{\partial U_A} \right)_N \right)$
- Thermodynamics is an axiomatic theory of heat and work.
- Axioms of thermodynamics: First and Second laws.
- Second law is a generalization of empirical observations:
 - Clausius (1854): Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.
 - + many, many other formulations
- Boltzmann's entropy gave a theoretical basis for the second law.

$$\Delta S = k \ln \frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}} \geq 0$$

- For an **isolated system**, the entropy can never decrease, $\Delta S \geq 0$
- In all processes, the **total entropy** of system and surroundings increases.

$$\Delta S_{\text{tot}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$