Statistical physics (microcanonical ensemble)

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Introduction

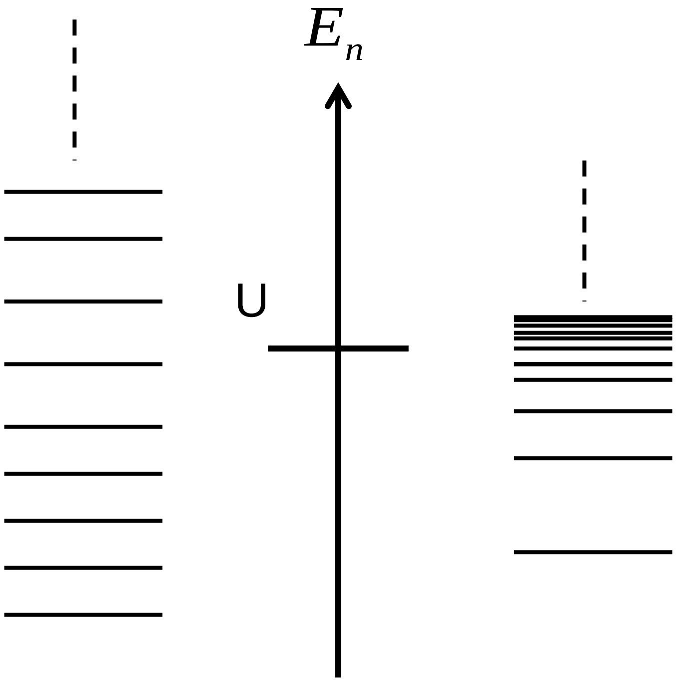
How do we tell one molecule from another ?

They have different energy spectra !

I. Entropy

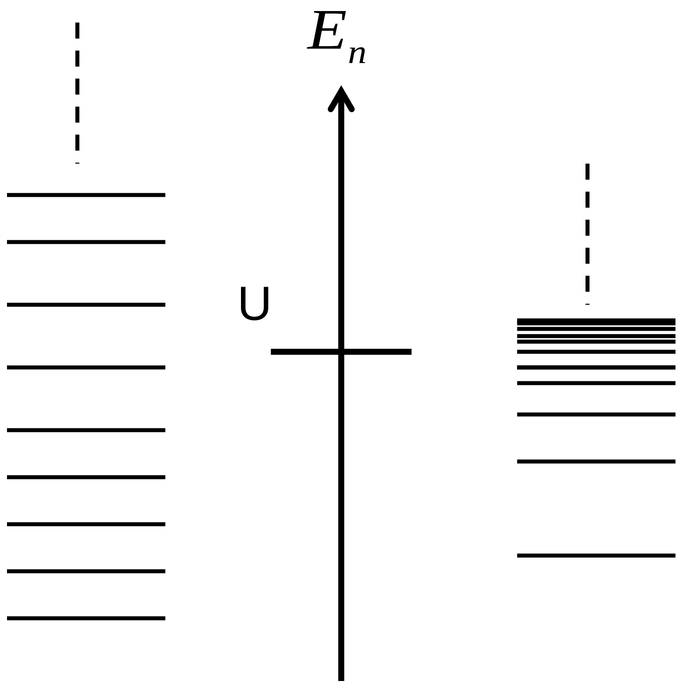
How do we tell one **macroscopic system** from another ?

They have different energy spectra !



I. Entropy

How do we characterize spectra?



Order states according to increasing energies and give

$$n \to E_n$$

I. Entropy

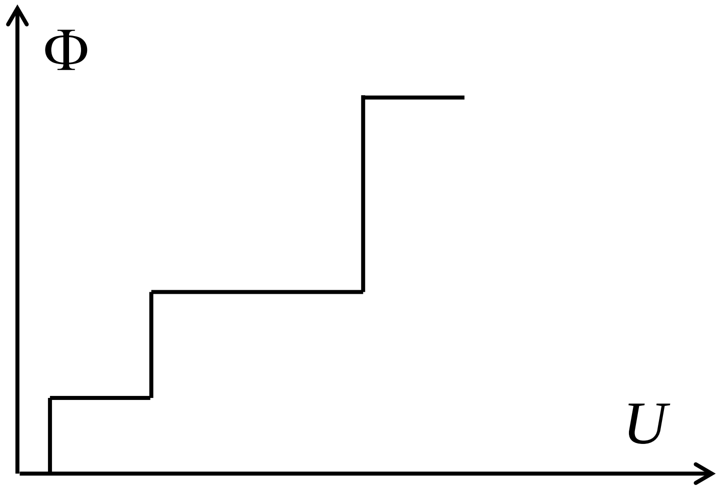
How do we characterize spectra?

$$E = E_n = E(n, V)$$

Define

$$\Phi(U) = \sum_n \Theta(U - E_n)$$

$$\Phi(U) = \sum_{E_m \le U} \Omega(E_m)$$



I. Entropy

Examples

- **Einstein crystal**

$$\Phi(U) = \left[\left(\frac{e}{3\hbar\omega} \frac{U}{N} \right)^3 \right]^N \frac{1}{\sqrt{6\pi N}}$$

- **Ideal gas**

$$\Phi(U) = \left[\left(\frac{me}{3\pi\hbar^2} \frac{U}{N} \right)^{3/2} \frac{V}{N} e \right]^N \frac{1}{\sqrt{6\pi N}}$$

I. Entropy

Define entropy

$$S = k_B \ln \Phi$$

Examples

- **Einstein crystal** $$S = N k_B \ln\left[\left(\frac{e}{3\hbar\omega}\frac{U}{N}\right)^3\right] + \cancel{k_B \ln\frac{1}{\sqrt{6\pi N}}}$$
- **Ideal gas** $$S = N k_B \ln\left[\left(\frac{me}{3\pi\hbar^2}\frac{U}{N}\right)^{3/2}\frac{V}{N}e\right] + \cancel{k_B \ln\frac{1}{\sqrt{6\pi N}}}$$

II. Thermodynamics

Pretend you have never heard about thermodynamics

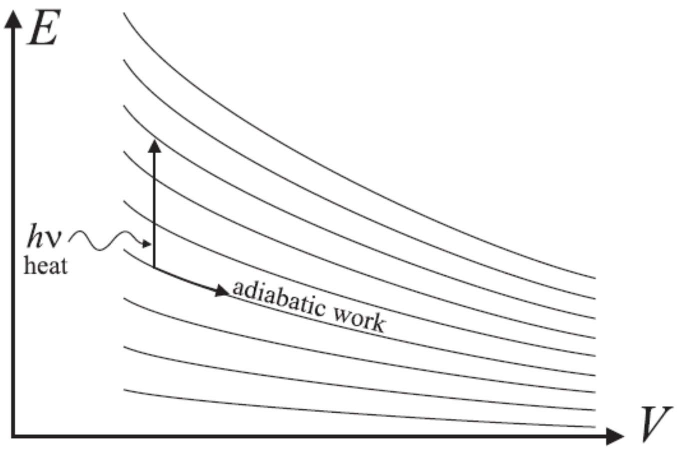
How does energy change with
entropy, volume or number of particles?

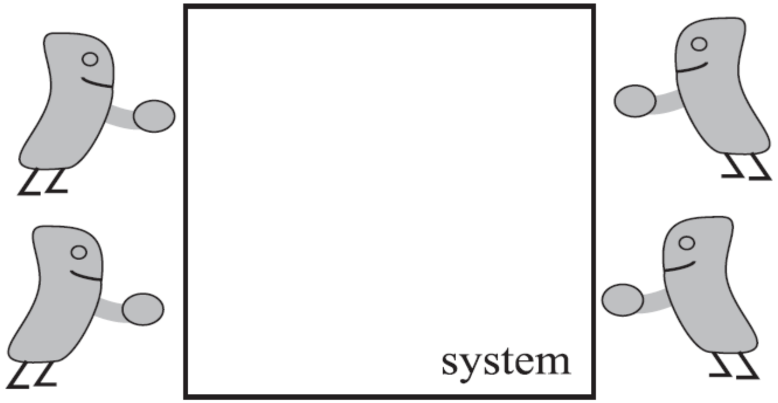
$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

What does it mean?

II. Thermodynamics

Energy changes at constant number of particles (closed system)





‘adiabatic’ means: only change volume, not the state.
‘adiabatic’ means: ‘at constant entropy’.

II. Thermodynamics

Energy change at constant number of particles

$$dU_N = -p^{ext} dV$$

Energy change at constant number of particles and constant entropy; only a particular p_S^{ext} will do

Define $p = p_S^{ext}$

Then $dU_{S,N} = -p dV \longrightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_{S,N} = -p}$

II. Thermodynamics

Energy change at constant number of particles and constant volume

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \Big/ \left(\frac{\partial S}{\partial V}\right)_{U,N}$$

Ideal gas

$$S = Nk_B \ln\left[\left(\frac{me}{3\pi\hbar^2}\frac{U}{N}\right)^{3/2}\frac{V}{N}e\right]$$

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{pV}{Nk_B} = \frac{R}{N_{Av}k_B}T$$

Choose

$$k_B = \frac{R}{N_{Av}} \quad \longrightarrow \quad p = \frac{nR}{V}\left(\frac{\partial U}{\partial S}\right)_{V,N} \quad \longrightarrow \quad \left(\frac{\partial U}{\partial S}\right)_{V,N} = T$$

II. Thermodynamics

Yes, you say, only for ideal gas !!

Ideal gas thermometer:
Bring system in thermal contact with small body of ideal gas and measure temperature of ideal gas

Later:
For two systems A and B in thermal contact

$$\left(\frac{\partial U}{\partial S}\right)_{V,N}^{(A)} = \left(\frac{\partial U}{\partial S}\right)_{V,N}^{(B)} \qquad \rightarrow \qquad \boxed{\left(\frac{\partial U}{\partial S}\right)_{V,N} = T}$$

II. Thermodynamics

Define: $$\boxed{\left(\frac{\partial U}{\partial N}\right)_{S,N} = \mu}$$

Final result

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

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

II. Thermodynamics

Entropy is extensive

$$S(xU, xV, xN) = xS(U, V, N)$$

Temperature, pressure and chemical potential are intensive

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

II. Thermodynamics

Extensivity

$$S(xU, xV, xN) = xS(U, V, N)$$

$$\frac{d}{dx} S(xU, xV, xN) = \frac{d}{dx} xS(U, V, N)$$

$$\frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}N = S$$

$$U = TS - pV + \mu N$$

II. Thermodynamics

Gibbs-Duhem

$$U = TS - pV + \mu N$$

$$dU = SdT + TdS - Vdp - pdV + Nd\mu + Nd\mu$$

$$\rightarrow$$

$$SdT - Vdp + Nd\mu = 0$$

No three intensive variables are independent

III. Irreversible processes and equilibrium

Intermezzo

$$\Phi(U) = \sum_n \Theta(U - E_n) \quad \leftrightarrow \quad \Phi(U) = \sum_{E_m \le U} \Omega(E_m)$$

In the logarithm only the last term contributes

$$\ln \Phi(U) \approx \ln \Omega(U)$$

Example, harmonic crystal

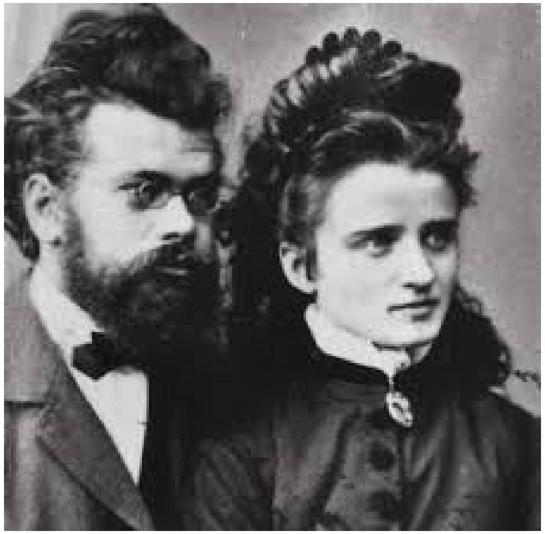
$$\Omega(U) = \frac{(M+3N-1)!}{M!(3N-1)!} \qquad \Phi(U) = \frac{(M+3N)!}{M!(3N)!}$$

$$M = \frac{U}{\hbar\omega} - \frac{3N}{2}$$

III. Irreversible processes and equilibrium

Intermezzo

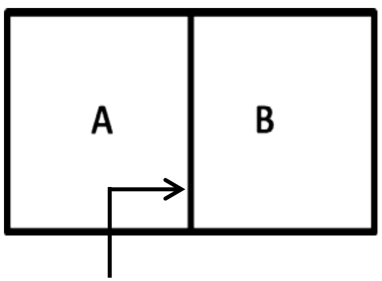
$$S(U,V,N) = k_B \ln \Omega(U,V,N)$$

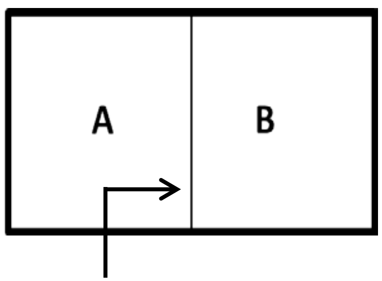
III. Irreversible processes and equilibrium

Spontaneous processes are induced by removing constraints

Constrained **Unconstrained**



Thermally insulating

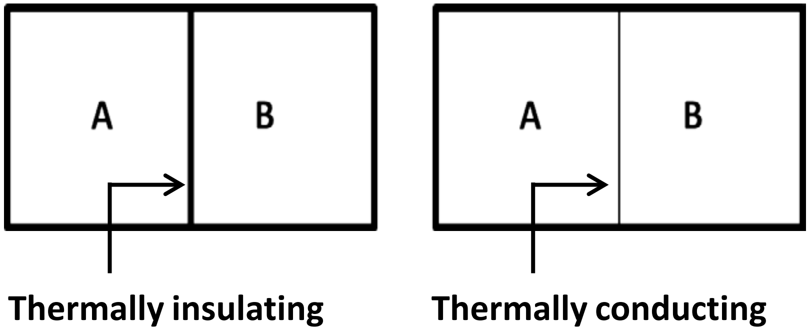


Thermally conducting

III. Irreversible processes and equilibrium

Spontaneous processes are induced by removing constraints

Constrained **Unconstrained**



$$\Omega^c \to \Omega^u$$

$$\Omega^u \geq \Omega^c$$

$$S^u \geq S^c$$

Entropy increases with spontaneous processes

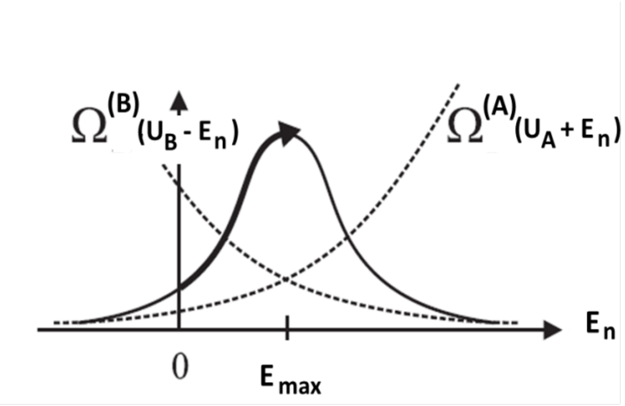
$$\Delta S = S^u - S^c \geq 0$$

III. Irreversible processes and equilibrium

Analysis and operational criterion

$$\Omega^{c} = \Omega^{(A)}(U_A^c) \cdot \Omega^{(B)}(U_B^c)$$

$$\Omega^{u} = \sum_n \Omega^{(A)}(U_A^c + E_n) \cdot \Omega^{(B)}(U_B^c - E_n)$$



Sum over possible exchange energies

$$\Omega^{(A)}(U_A^c + E_n) \cdot \Omega^{(B)}(U_B^c - E_n)$$
$$= \Omega^{(A)}(U_A^c + E_{\max}) \cdot \Omega^{(B)}(U_B^c - E_{\max}) \cdot \exp\left[-\frac{(E_n - E_{\max})^2}{2\sigma_{AB}^2} \right]$$

III. Irreversible processes and equilibrium

Analysis and operational criterion

$$\Omega^{u} = \Omega^{(A)}(U_A^c + E_{\max}) \cdot \Omega^{(B)}(U_B^c - E_{\max}) \cdot \underbrace{\sum_n \exp\left[-\frac{(E_n - E_{\max})^2}{2\sigma_{AB}^2} \right]}_{\rho_{L,AB}\sqrt{2\pi\sigma_{AB}^2}}$$

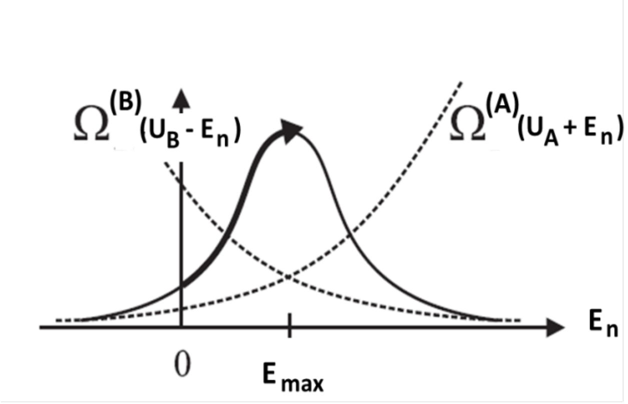
$$S^{u} = k_B \ln \Omega^{(A)}(U_A^c + E_{\max}) + k_B \ln \Omega^{(B)}(U_B^c - E_{\max}) + k_B \ln \cancel{\left(\rho_{L,AB}\sqrt{2\pi\sigma_{AB}^2} \right)}$$

III. Irreversible processes and equilibrium

Analysis and operational criterion

$$S^c = S^{(A)}(U_A^c) + S^{(B)}(U_B^c)$$

$$S^u = S^{(A)}(U_A^c + E_{\max}) + S^{(B)}(U_B^c - E_{\max})$$



Exchange energy untill entropy is maximal

$$\frac{dS^u}{dE_{\max}} = \left.\frac{dS^{(A)}}{dU}\right|_{U=U_A^c+E_{\max}} - \left.\frac{dS^{(B)}}{dU}\right|_{U=U_B^c-E_{\max}} = 0$$

$$\rightarrow \quad \left(\frac{\partial S}{\partial U}\right)_{V,N}^{(A)} = \left(\frac{\partial S}{\partial U}\right)_{V,N}^{(B)}$$ **(as promised)**

III. Irreversible processes and equilibrium

Equilibrium criterion:
additional redistribution of energy, volume and particles won't change entropy

$$dS = dS^{(A)} + dS^{(B)} = 0$$

$$dS = \frac{1}{T^{(A)}} dU^{(A)} + \frac{p^{(A)}}{T^{(A)}} dV^{(A)} - \frac{\mu^{(A)}}{T^{(A)}} dN^{(A)} + \frac{1}{T^{(B)}} dU^{(B)} + \frac{p^{(B)}}{T^{(B)}} dV^{(A)} - \frac{\mu^{(B)}}{T^{(B)}} dN^{(B)} = 0$$

Isolated system: $dU^{(A)} = -dU^{(B)}$**,** $dV^{(A)} = -dV^{(B)}$**,** $dN^{(A)} = -dN^{(B)}$

$$dS = \left(\frac{1}{T^{(A)}} - \frac{1}{T^{(B)}} \right) dU^{(A)} + \left(\frac{p^{(A)}}{T^{(A)}} - \frac{p^{(B)}}{T^{(B)}} \right) dV^{(A)} - \left(\frac{\mu^{(A)}}{T^{(A)}} - \frac{\mu^{(B)}}{T^{(B)}} \right) dN^{(A)} = 0$$

III. Irreversible processes and equilibrium

Equilibrium criterion:
additional redistribution of energy, volume and particles won’t change entropy

$$dS = \left(\frac{1}{T^{(A)}} - \frac{1}{T^{(B)}}\right) dU^{(A)} + \left(\frac{p^{(A)}}{T^{(A)}} - \frac{p^{(B)}}{T^{(B)}}\right) dV^{(A)} - \left(\frac{\mu^{(A)}}{T^{(A)}} - \frac{\mu^{(B)}}{T^{(B)}}\right) dN^{(A)} = 0$$

$$\rightarrow \quad \begin{aligned} T^{(A)} &= T^{(B)} \\ p^{(A)} &= p^{(B)} \\ \mu^{(A)} &= \mu^{(B)} \end{aligned}$$

III. Irreversible processes and equilibrium

Alternative criterion for constant temperature:

Put system plus thermostat in isolation

$$\Delta S + \Delta S^{Th} \geq 0$$

$$\Delta S^{Th} = \Delta U^{Th} / T$$

$$\Delta U^{Th} = -\Delta U$$

$$\Delta S - \frac{\Delta U}{T} \geq 0 \qquad \rightarrow \qquad \Delta A \leq 0 \qquad (\, A = U - TS \,)$$

IV. Probabilities

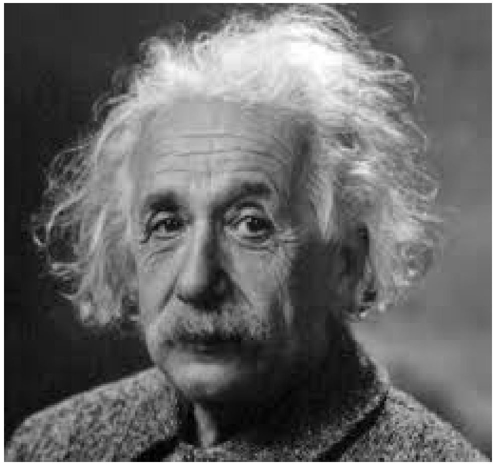
Reminder: we still discuss isolated systems

All of the $\Omega(U)$ **states may be observed with equal probability**

$$P_n = \frac{1}{\Omega(U)}$$

For observable A**, define** $\Omega_A(a) = \# states(A_n = a)$

$$P_A(a) = \frac{\Omega_A(a)}{\Omega} \qquad \rightarrow \qquad P_A(a) = \exp\left(\left(S_A(a) - S\right)/k_B\right)$$



IV. Probabilities

Reminder: we still discuss isolated systems

ergodic hypothesis:
measurement of observable A yields

$$\langle A \rangle = \sum_n P_n A_n = \sum_n \frac{1}{\Omega} A_n$$

$$\langle A \rangle = \sum_a a P_A(a)$$

Thank you

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