

Notes for today

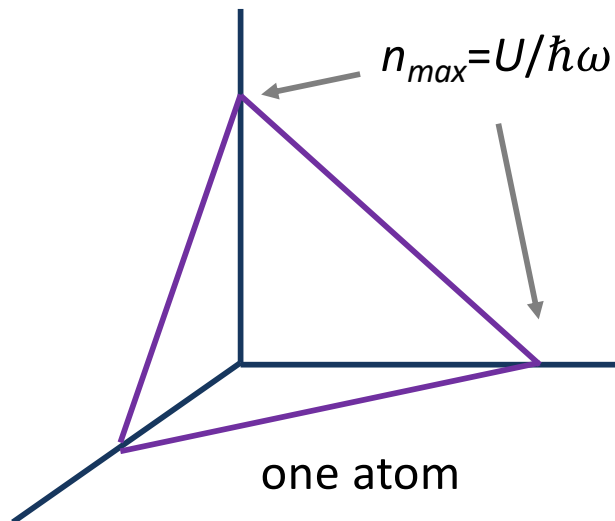
- Reading: This week finishing chapter 15, then we continue with (the remainder of) chapter 2. Soon: ch. 3

Hypersphere counting argument (text)

- **Solution:** choose a range of energies, between $(U-\Delta U)$ and U rather than fixed U .

For large N : find that for arbitrarily small ΔU , result includes same number of states as for $\Delta U=U$!

Einstein solid



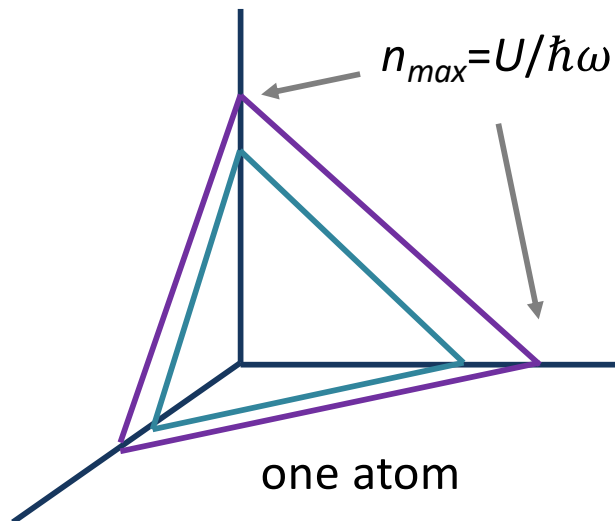
$$\Omega = \frac{1}{6} (U/\hbar\omega)^3$$

Hypersphere counting argument (text)

- **Solution:** choose a range of energies, between $(U-\Delta U)$ and U rather than fixed U .

For large N : find that for arbitrarily small ΔU , result includes same number of states as for $\Delta U=U$!

Einstein solid



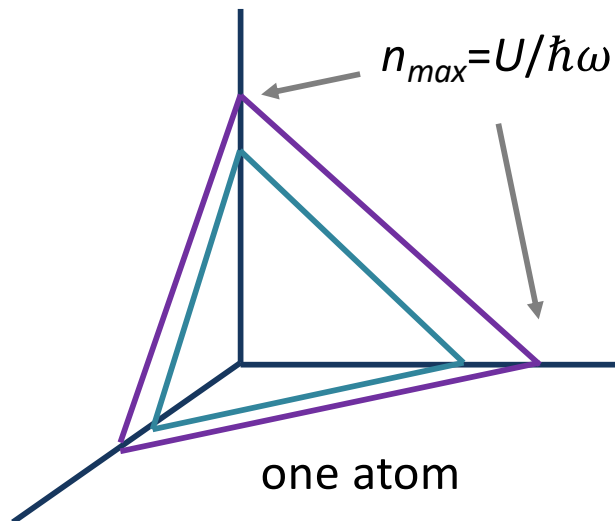
$$\Omega = \frac{1}{6} (U/\hbar\omega)^3 \quad \Rightarrow \quad \frac{1}{(3N)!} (U/\hbar\omega)^{3N}$$

Hypersphere counting argument (text)

- **Solution:** choose a range of energies, between $(U-\Delta U)$ and U rather than fixed U .

For large N : find that for arbitrarily small ΔU , result includes same number of states as for $\Delta U=U$!

Einstein solid



$$\Omega = \frac{1}{6} (U/\hbar\omega)^3 \quad \Rightarrow \quad \frac{1}{(3N)!} (U/\hbar\omega)^{3N}$$

Smaller shell contains zero!

actually :
$$\Omega(U) \left(\frac{U - \Delta U}{U} \right)^{3N}$$

Fixed energy in microcanonical ensemble:

Find: range of allowed U can be *immeasurably small*, however Ω can nevertheless be *immense* for a macroscopic system.

(We need to assure that ΔU is not so small that counting statistics no longer work— not a problem for large systems.)

Or, can even define all energies less than U to be included rather than a thin shell (e.g. for computational convenience), result will be the same.

For small systems, a probabilistic treatment might be preferable (e.g. canonical ensemble)

Fixed energy in microcanonical ensemble:

$$U, V, N$$

Statistical mechanics version of microcanonical ensemble: fixed U formally considered to include small energy spread, for large systems leads to well-defined, continuous behavior.

- Then use $S = k_B \ln \Omega$, from which all thermal properties can be derived (assuming Ω can be obtained for given U, V, N).

Thermodynamics version: U & S are continuous properties; no conflict with microscopic view for large N .

- Then $S(U, V, N)$ determined e.g. from calorimetry, allows all properties of the system to be derived.

Fundamental behavior:

Thermodynamics: U & S continuous properties; $S(U, V, N)$ once determined, allows all properties of the system to be derived.



Or: Once $U(S, V, N)$ is determined, *also* allows all properties to be derived. U -centered fundamental relation always* (in principle) can invert to S -centered form.

* 3rd postulate, S increases as U increases.
(Requires $T > 0$).

Fundamental behavior:

Thermodynamics: U & S continuous properties; $S(U, V, N)$ or $U(S, V, N)$ once determined, allow all properties to be derived.

Fundamental equation: $S(U, V, N)$ or $U(S, V, N)$

$$S = Nk_B \ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right] + \frac{5}{2} Nk_B$$

$$U = C(VNS)^{1/3}$$

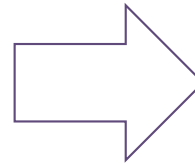
Fundamental behavior:

Fundamental equation: $S(U, V, N)$ or $U(S, V, N)$

First law:

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

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



Connect to
physical properties

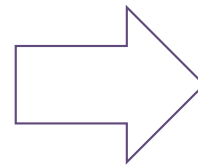
Fundamental behavior:

Fundamental equation: $S(U, V, N_1, N_2 \dots)$ or $U(S, V, N_1, N_2 \dots)$

First law:

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

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



Connect to
physical properties

$$T = \left(\frac{\partial U}{\partial S} \right)_{VN}$$

$$-P = \left(\frac{\partial U}{\partial V} \right)_{SN}$$

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{SV}$$

**Equations of
state**

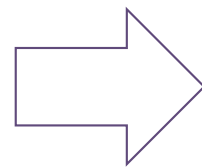
Fundamental behavior:

Fundamental equation: $S(U, V, N_1, N_2 \dots)$ or $U(S, V, N_1, N_2 \dots)$

First law:

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

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



Connect to
physical properties

$$T = \left(\frac{\partial U}{\partial S} \right)_{VN}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{VN}$$

$$-P = \left(\frac{\partial U}{\partial V} \right)_{SN}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{UN}$$

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{SV}$$

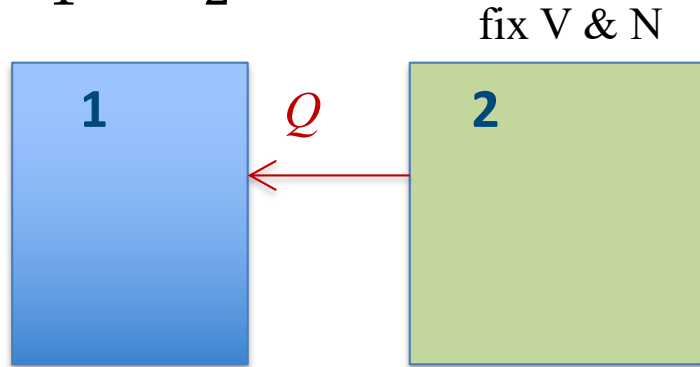
$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N} \right)_{UV}$$

**Equations of
state**

Note T, P, μ not
fundamental equations
in microcanonical; single
equation of state can't
determine all behavior
(constants of integration)

Thermal equilibrium we have seen:

$$T_1 < T_2$$



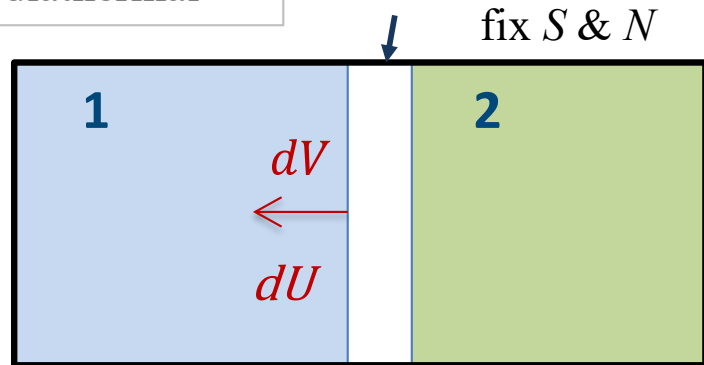
$$\text{Overall } dS = +\frac{dU}{T_1} - \frac{dU}{T_2} > 0$$

- *Entropy maximum principle* assures heat flow from high to low temperature.
2nd law corollary
- Individual S can decrease; overall always increases toward equilibrium = maximum.
- Universe entropy thus always increasing.
- At equilibrium, $T_1 = T_2$ since $dS_1 = -dS_2$ for fluctuations at *extremum*, where $dS = 0$.

Mechanical equilibrium:

Note thermally
conducting =
“diathermal”

Thermally
conducting
piston



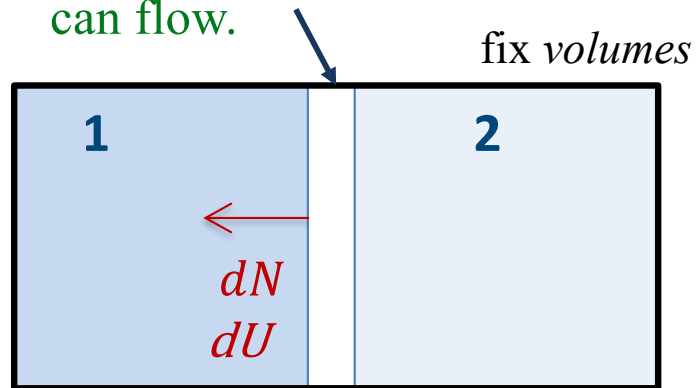
- Again use additive property of entropy.
- Also $dU_1 = -dU_2 = dU$
- Once in equilibrium dU -exchange terms cancel.
- Also at equilibrium, $P_1 = P_2$ since $dS_1 = -dS_2$ for fluctuations at *extremum*, where $dS = 0$.

$$\text{Overall } dS = \cancel{\frac{dU}{T_1}} + \frac{P_1 dV}{T_1} - \cancel{\frac{dU}{T_2}} - \frac{P_2 dV}{T_2} = 0$$

Chemical equilibrium:

Conductive barrier.

Also *one particle type*
can flow.



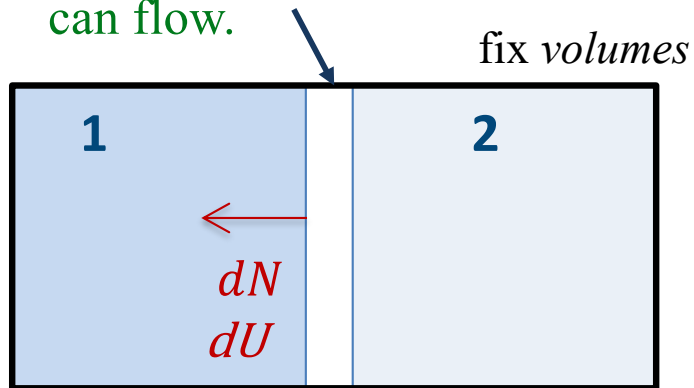
- Use additive property of entropy.
- Also $dU_1 = -dU_2 = dU$

$$\text{Overall } dS = \frac{dU}{T_1} - \frac{\mu_1 dN}{T_1} - \frac{dU}{T_2} + \frac{\mu_2 dN}{T_2} = 0$$

Chemical equilibrium:

Conductive barrier.

Also *one particle type*
can flow.



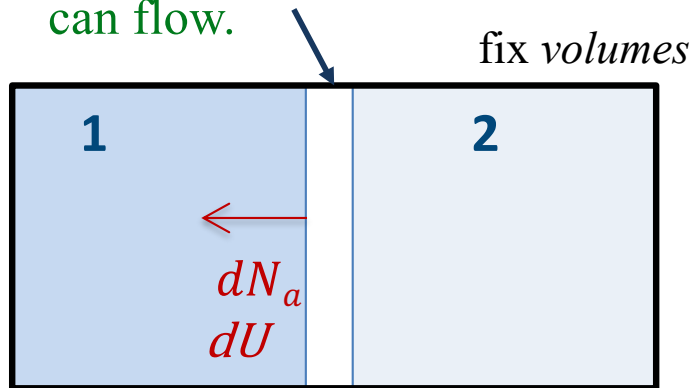
- Use additive property of entropy.
- Also $dU_1 = -dU_2 = dU$
- At equilibrium, $\mu_1 = \mu_2$ since $dS_1 = -dS_2$ for fluctuations at *extremum*, where $dS = 0$.

$$\text{Overall } dS = \cancel{\frac{dU}{T_1}} - \frac{\mu_1 dN}{T_1} - \cancel{\frac{dU}{T_2}} + \frac{\mu_2 dN}{T_2} = 0$$

Chemical equilibrium:

Conductive barrier.

Also *one particle type*
can flow.



- Use additive property of entropy.
- Also $dU_1 = -dU_2 = dU$
- At equilibrium, $\mu_1 = \mu_2$ since $dS_1 = -dS_2$ for fluctuations at *extremum*, where $dS = 0$.

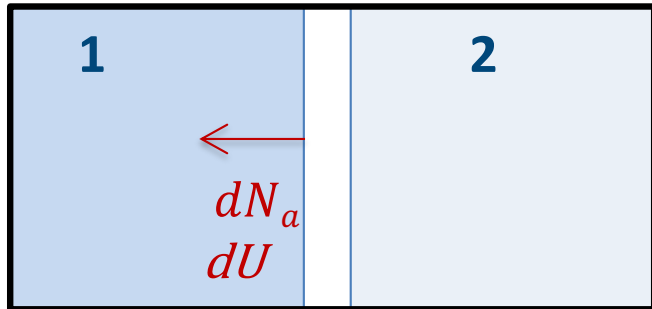
$$\text{Overall } dS = \cancel{\frac{dU}{T_1}} - \frac{\mu_{1a}dN_a}{T_1} - \cancel{\frac{dU}{T_2}} + \frac{\mu_{2a}dN_a}{T_2} = 0$$

Generalize to multiple particle types: Find chemical potentials for each particle type equal at equilibrium:

μ_{O_2} same both sides, μ_{N_2} same both sides, μ_{NO_2} same both sides...

Different values for
each constituent

Chemical equilibrium:



Chemical potential: Important feature for chemical reactions (or particle dissociation, etc.), also electron interchange (computer devices, electronic phase transitions), Bose condensation and quantum fluids, etc.