

Notes for today

- Reminder, web address: rossgroup.tamu.edu/408page.html
Has syllabus posted there. More information such as slides, HW will be posted on web as we go along.
- Reading: Ch. 1 this week, [plus added section 2.1 of chapter 2](#), followed by ch. 15.
- Lecture recordings etc.: I will record lecture for those needing to quarantine or be absent. [Update: we are now also allowed to have concurrent zoom during lecture](#), but only for those with documented Covid quarantine (or other University excuse).

Postulate 1:

System in equilibrium:

“ergodic system”: will eventually and spontaneously explore all regions of phase space (or all quantum states) accessible to it. [Not true for truly isolated quantum system]

- Postulation that equilibrium state *exists*.
- Equilibrium state is *characterized completely by quantities U , V , and the particle numbers N_1, N_2, \dots*

3-dimensional variable space needed for 1-component thermal system. (But a different set of 3 may also be chosen)

Also note, I used N for particle number, whereas text uses N for number of moles, vs \tilde{N} for particle number. I decided not to change my notation; N I will use for number of particles or atoms, etc.

Entropy postulates:

- 2) Entropy (S) *exists* as extensive quantity; Among all other initial states reachable from equilibrium state (depending on U, V, N), equilibrium state has Maximum Entropy.
- 3) Entropy is additive for subsystems (e.g. separate adjoined regions), and increases as U increases.
- 4) $S = 0$ at $T = 0$. (Also Nernst theorem, $\Delta S \rightarrow 0$)

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Known as

Second Law of Thermodynamics

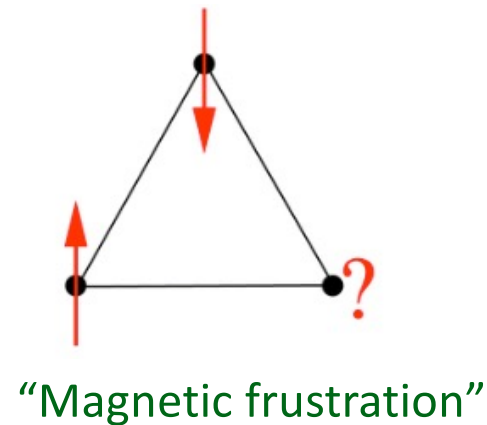
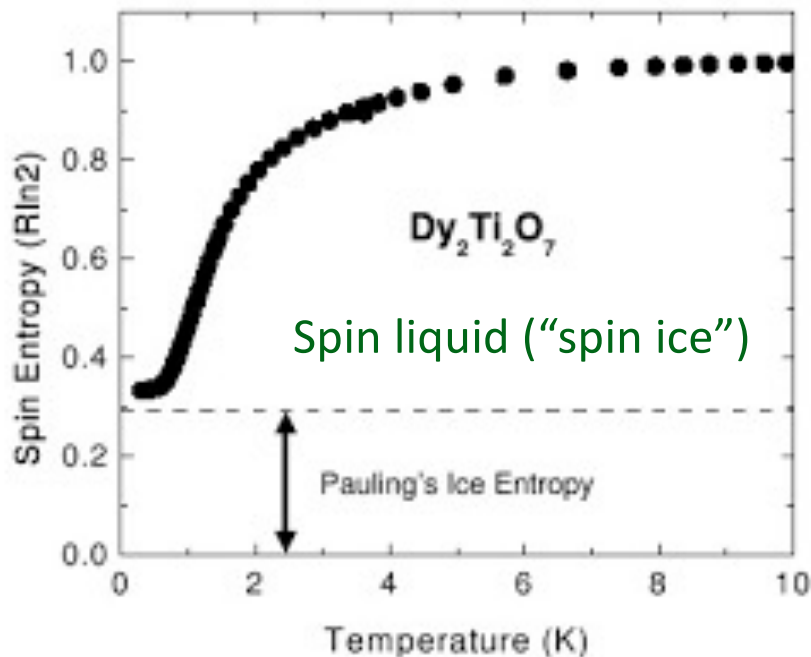
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Known as Third Law

Laws of Thermodynamics

- First law $\Delta U = Q + W$
- Second law $\Delta S \geq 0$ (& many alternative versions)
- Third law $S \rightarrow 0$ as $T \rightarrow 0$ (or in general $S \rightarrow S_0$)

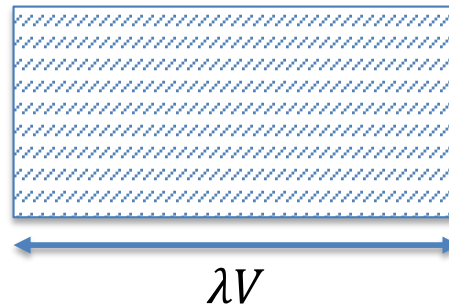
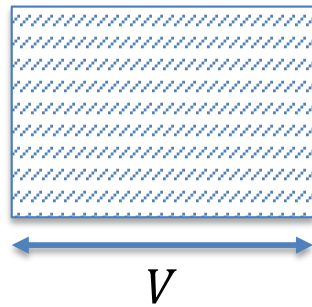


Entropy as extensive quantity & function of U, V, N :

means $S = S(U, V, N)$ (or in general N_1, N_2, \dots)

$$\lambda S = S(\lambda U, \lambda V, \lambda N) \neq \lambda^2 S, \lambda^3 S \text{ etc.}$$

Also doubling volume \neq doubling S necessarily, means also scaling all contents



(Previous slide about extensivity)

P, V : Pressure (intensive) and Volume (extensive)

Extensive: proportional to system size. e.g. depends on the *physical extent* of system.

Intensive: Independent of system size

N, H, M we have seen.

Note text notation: $I = MV$
total magnetic moment

Which are extensive/intensive?

Multi-component system: N_1, N_2, \dots e.g. $N_2 + O_2$ or nuclear matter

$T =$ Temperature. (Same as familiar quantity, formal definition to come)

$U =$ Internal energy.

$S =$ Entropy Extensive quantity

Note extensive/intensive pairs are intrinsically coupled:

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

1st law as later defined (ch. 2); maintains proper *size scaling*.

First law & differential form for U : (section 2.1)

recall, $dS = \frac{\delta Q}{T}$ defines entropy change for a controlled process.

Also recall, $dU = \delta Q + \delta W$ with mechanical work $= -PdV$, also for controlled process. (And specifically, work with no heat flow has $dS = 0$)

$$\Rightarrow dU = TdS - PdV$$

First law in terms of system variables

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

↗
Defines T

↗
Defines chemical potential μ

More general defined in a 3-dimensional parameter space

- T, P, μ we can also define in terms of S, V, N
- S, V, N as state functions, hence perfect differentials

First law & differential form for U : (section 2.1)

Thus: $dU = \overset{\text{heat}}{TdS} - \overset{\text{generalized work}}{PdV} + \mu dN$

Form for $S = S(U, V, N)$
parameter choice: $dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$

- Can identify coefficients with *partial derivatives*.
- Examples, do $S = (UVN)$ or $S = (UVN)^{1/3}$ obey extensivity requirement?

Specific example: Ideal gas (monatomic, e.g. helium)

$$U = \frac{3}{2} N k_B T. \quad \text{Energy, can show (independent of volume)}$$

$$PV = N k_B T. \quad \text{Equation of state showed last time.}$$

- Heating with no work (& const. N): can show from first law, $\Delta S = \frac{3}{2} N k_B \ln \left(\frac{U_2}{U_1} \right) = \frac{3}{2} N k_B \ln \left(\frac{T_2}{T_1} \right)$

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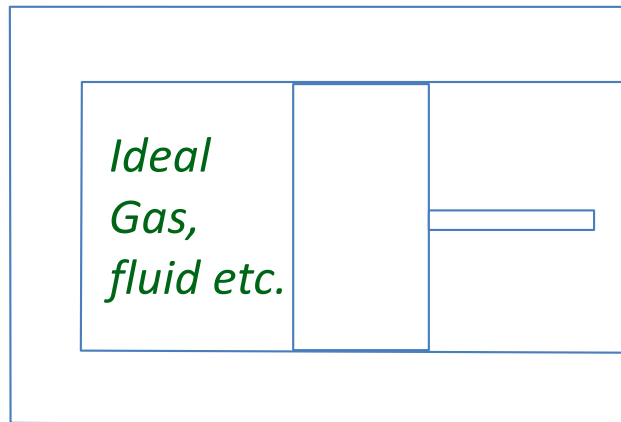
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- Adiabatic case from first law & $U = \frac{3}{2} PV$: $P_2 = P_1 \left(\frac{V_2}{V_1} \right)^{-5/3}$

Recall example from before

($N = \text{const inside}$)



Expand suddenly to 2x volume.

sign of Q , W ? ΔU ? ΔT ?

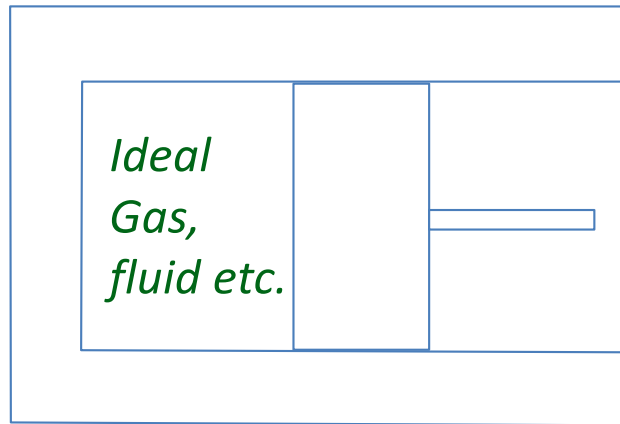
0 0 $?$ 0 if *ideal gas*

Perfectly Insulated cylinder (“**Adiabatic Process**”) $Q = 0$

This **increases entropy**.

& Note pressure decreases 2x in uncontrolled process

($N = \text{const inside}$)



Expand suddenly to 2x volume.
sign of Q , W ? ΔU ? ΔT ?

Further process: slowly return piston to original position.

>>> *Now can calculate this.*

- Find, work done: $W = \frac{3}{2} P_1 V_1 (2^{2/3} - 1)$
- Entropy change? For this process & entire process?