Lecture: Fdns Therm & SM — Therm I   25 Oct 2017

(1)

Outline

→ remark on 'anthropocentricity' of thermo

- thermo: heat, work, and their inter-transformability {work: force × distance moved (why energy expended when push on wall?); heat: subtle — related to temp change, temp}
- studying phys syss: 1st task, identify type of system matching theory (always a dialectical process, matching theory to world)
  - → in our case, out of the ∞ complexity of this glass of water, we want to study its gross properties involved in exchanges of heat and work w/ environment: p, V, T
- concept of state of system (related to id of system (type of sys) and matching it w/ theory): p, V, T diagrams, eq'n of state, only 2 are independent ⇓ ∃ eq'n of state for (p,V), (V,T), (T,p)
- {define p, V, T: why is T peculiar in its lack of prima facie unique def'n?
- secondary properties: energy, e.g.: peculiarity of energy → and values are constant for whole sys
- equilibrium: state doesn't change — very subtle
  - compare to isolated (state may change, e.g., Solar System)
  - sys may be interacting w/ its environ: if it's doing work and having work done on it at same time so as to cancel out; two heat baths of diff temp on opposite sides, constant temp gradient
  - equil is defined by a relevant set of parameters — as measured by
    - e.g. ang mom, Solar System is in equil and planetary orbital radii
  - space of states in thermo: equilibrium states: exactly one for every (p,V), (V,T), (p,V)

(time-scale dependent (wrt Solar system))

- reversible: (adiabatic: reversible and thermally insulated)
  - in dyns: sequence of states in temporal evol is allowed backwards as well as forwards
  - in thermo: sequence of states each of which differs 'infinitesimally' from an equil state: yet still has flavor of 1st — why does 'differ infinitesimally' bear on temporal symmetry? or does it?
- cycle: system returns to its starting place — not nec'y its environ
- Minus-first Law: already assumes temporal asymmetry? not necessarily
- Zeroth Law: transitivity of equil — grounds construction of state space (if two states not connected by path, they're not states of the same system)
- First Law → grounded on principle of fungibility of all types of energy

def'n of heat {
- experiments showing transferability of heat into work and vice versa, and constancy of relation between them, irrespective of how heat and work are produced, what substances used

(margin: (*) [illegible] work of process-ibility [illegible]; [illegible] heat flow or work)

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- Second Law
  - 1st Law places no constraints on transformations of energy – impossibility of perpetual motion of 1st kind
  - 2nd Law places constraints on transforming heat into work
  - Planck's formulation: "It is impossible to construct a periodically functioning motor that does no more than lift a load (work) and cool a heat reservoir."
    → impossibility of perpetual motion of 2nd kind (we could 'indirectly mine heat' from Earth)
  - Kelvin & Clausius Postulates
    - discuss proof that Kelvin ⇒ Clausius (violation of Kelvin: transform heat of constant body into work; then transform work into friction to heat body of higher temp ⇒ violate Clausius)
    - allows definition of absolute temp scale (kind of like ideal gas law from simple form)
      ⇒ since efficiency is $\frac{L}{Q_2} = 1 - \frac{Q_1}{Q_2}$ and $\frac{Q_1}{Q_2} = \frac{\Theta_1}{\Theta_2}$ (temp),
      this shows perfect efficiency only if heat sink is at absolute zero – that would violate Kelvin's Postulate
    - wipes out retrodiction, fixes prediction
  - def of entropy $\Delta S = \frac{\Delta Q}{T}$ → from Kelvin Postulate
    ⇒ $\Delta S \geq 0$ for isolated sys
  - proof of Zeroth Law: Kelvin + constancy of temp
  - Oddity of Laws (see notes 08 Nov 2017 p.2 for theme II of these lectures).

Thermo Not Just 4 Laws

- state space of equil states
- temp as predictor / measure of physical couplings
- classification of processes as reversible, adiabatic, quasistatic
- impotent energy relations between intensive & extensive Σ's
- additivity of entropy
- equil states maximize entropy & minimize free energy
- Clausius & Kelvin Postulates
- absolute temp scale
- eqn of state for particular kind of stuff

Where the asymmetry? Work can fully into heat, but not heat all into work (Kelvin explicitly and Planck) → but not temporal asymmetry, at least not as obvious from conceptual necessity

measure of amount of heat transformable into work – when $\Delta S = 0$, none is possible ⇒ defined only up to fixed constant

2 examples
1) heat flows from hotter to cooler body: $\Delta S = \frac{Q}{T_1} - \frac{Q}{T_2} > 0$
2) heat by friction: $\Delta Q > 0$ for heated body, but only work done by rubbing body, so $\Delta S = 0$

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Zeroth Law: something is constancy of temp - not enough - doesn't imply transitivity of equil - but transitivity of equil does imply constancy of temp (Kelvin + constancy ⇒ transitivity)

First Law: define "engy of system", "engy sys receives from env during ℝ transformation"

- we assume we know work, assume that engy is constant for changes in isolated sys (how to define isolated? subtle)

⇒ $U_B - U_A = -W$ (U_A = engy state A, W = work done by sys)

⇒ if this doesn't hold, ∃ other forms of engy besides work (sys not isolated!) ⇒ 1st Law just a def? doesn't seem so - can derive non-trivial physical predictions from it: motion of particles in potentials; discovery of new forms of interactions when $U_B - U_A \neq -W$)

in thermo, any unaccounted engy we call heat — so heat defined by 1st Law ⇒ no way to define "heat content" of body simplicity

⇒ $\Delta U + W = Q$ (FIRST LAW)

Q = engy received by sys in all other forms

⇒ work performed by sys during cycle = Q absorbed by sys

Joule's experiment to show that U of ideal gas is function of temp only

Third Law: ① Entropy of every sys at abs zero can be taken to be zero

② no physical process can reduce temp of sys to abs zero (follows from def of efficiency and Kelvin's postulate)

(① is violated by QM)

+ stuff needed for mutual equil: ≠ spontaneous heat flow or work

Deriving the Zeroth Law (Crude Sketch)

three ordinary thermodynamical systems A, B and C

1. assume A and C in mutual equilibrium, and B and C, but not A and B
2. bring A and C into contact: no heat spontaneously transferred, so they are same temperature (similarly for B and C) $\Rightarrow$ A and B same temperature
3. bring A and B in contact
4. *ex hypothesi*, one must spontaneously perform work on the other
5. $\Rightarrow$ violation of the Kelvin Postulate
6. $\Rightarrow$ they are in mutual equilibrium

Lecture: Fnds of Therm & SM – II

oddity of "laws"

- most "laws of nature" are quantitative exact, allow exact predictions, involve dynamics
  (NGT, Maxwell, Newton's 1st Law, etc.)

  ⇒ not these
  (except 1st Law)

- also: they pick out types of systems
  (grav fields, em fields, electric charges, etc.)
  but therm is truly universal (well, kind of like gravity)