

Lecture: Fundamentals of SM / Intro to SM; Boltz SM 15 Nov 2017 ①

SM: deals w/ large #s of identical syss (10^{23} molecules in gas, liquid, atoms in solid)

- class mech: few particles, specify position, mom/vel of each.
⇒ phase space 6n-dim, specify any or function of pos + vel/mom ⇒ evol of particles

- can't do this for 10^{23} particles

- computationally intractable (both specifying 10^{23} pos + mom/vel and solving 2×10^{23} coupled pdes)

- practically useless - knowing all that wouldn't tell us anything about properties of matter we care about (pressure, temp, etc.)

⇒ "average over" all pos + mom/vel in some statistically meaningful way, specify "initial averages", figure out "dynamics" based on micro-dyns, solve for evol of that

⇓ Purposes of SM

1) given N identical syss (N "large"), how are they distributed over all possible states? how do that dist evolve?

2) how to define "macro-properties" (thermo) from that distribution and its evol? (both abstractly - laws - and for specific kinds of syss, e.g. gas & liquid)

⇒ both fundamental and practical aspects to understanding SM

fundamental: explain/justify "thermo" behavior of macro-syss based on micro-state of dyns; explain predictive/explanatory success of SM itself

- interp of "ensembles" and "averages"

- role of probability

- why ^{and interp} _{probabilities} of thermo are correct

- irreversibility at macro from micro reversibility

practical: derive behavior of specific kinds of macro systems (e.g. gas, liquid water, blocks of lead)

Equal vs Non-Equal SM

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Equil vs Non Equil SM

- Equil:

- 1) how to characterize equil?
- 2) what conditions are sys in equil?
- 3) how to calculate averages from micro states?

- Non-Equil

- 1) what conditions do sys approach equil? why?
- 2) how does that approach take place? why unidirectional?
- 3) what macro-properties are defined out of equil, how calculated? how do they change? how related to equil thermo properties?

Oddity of SM

most theories: widely accepted set of formal mathematical concepts and ways to translate between them

not SM: many formalisms, not clear at all how they relate to each other —> either mathematically or conceptually approaches, schools,

→ stat mech, \exists 2 dominant architectures, Boltzmann & Gibbs, and almost all specific formalisms can be thought of as falling under one of those 2, at least with formalism

→ each gives way to precisely articulate the probs; each also has its own idiosyncratic set of probs

⇒ weird foundational situation

Boltz SM

Formalism

(T, Φ_E, μ)

"microstates"
↑
"physical possibilities", def'n of modality in phys

- T : phase space, br chn
 - Φ_E : "flow mappings", dyns, dependent on micro-stuff
 - μ : "volume fraction", measure
- draw pics; explain reversibility -
for $T, \Phi_E, T(p), \mu, \Phi(p)$
is given by $\Phi_E(T(p))$

⇒ now restrict T to "accessible region" (eg., fixed micro volume); generally, fix total enrgy, so we get hypersurf E in accessible region; normalize $\mu(A) = 1$ (or $\mu(E)$ depending on purpose)

- fix M_i , finite # of macro states (in thermalized space of states, generalized now to include non-equl states, viz. non-constant pressure, temp, etc. (can generalize to so, not nec for our purposes))

Fundamental Axiom: macrostates supervene on micro states

1) mapping from microstates to macrostates, defines equiv class

of microstates: $\sigma_i := \{p \in E \text{ s.t. } "p \in M_i"\}$

2) no change in macro s/o. change in micro

Following Frags, all σ_i macro region

3) $\{\sigma_i\}$ form partition of E (they jointly cover it)

many configs of microstate give same macro state

Entropy: $S(M_i) = k_B \log(\mu(\sigma_i))$

⇒ can also be regarded as property of micro-state, of "system itself"

Equilibrium: macro-state w/ maximal entropy, $M_{eq}(\sigma_{eq})$

How to justify?

modal odds of molecules to state the sys is not actually in - and property that we justified only by the fact that in another 'higher' theory, viz. therm

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Approach to Equil: explain why "generally",
starting from $p \in \mathcal{E}$, \mathcal{Q}_t takes one to σ_{eq}
 \Rightarrow smells a lot like 2nd Law - at least: entropy can decrease princ. no guarantee yet,

though, that approach to maximum entropy is monotonic, only that it eventually always increases entropy; most we can hope for is probabilistic statement

H-theorem, or Boltzmann's Law: assume $\text{sys} \in M_i$;
at t_1 , "far" from equil; then highly probable that at any $t_2 > t_1$, $S(M(t_2)) \gg S(M(t_1))$

no way to forbid Clausius, Kelvin, Planck Postulates in classical SM - can't distinguish work from heat at micro level of molecular kinetics

Not thermo'l 2nd Law (which is universal, not probabilistic; no refs to heat & work problems)

- 1) is this reasonable, useful, fruitful "explanation" & or "reduction" of thermo 2nd Law to BSM (Boltz SM)?
- 2) how to justify or "prove" H-theorem? Under what conditions, for what kinds of sys. is it true?
- 3) why/how the error from rev micro-dyns?
- 4) what is "probability" here?

Probability

- 1) Macro: assign prob to M_i by postulating that $p(M_i) \propto \Omega(\sigma_i)$, & some normalizing constant
 \Rightarrow most likely M_i is M_{eq} (from def'n of S), viz, one of largest volume "takes up most of \mathcal{E} "
H-th^{em}: sys evolves from smaller (less likely) to larger (more likely) macrostates most of the time - depends implicitly on \mathcal{Q}_t (dynamics)

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2) Micro (probabilities) - assign probs to sets of microstates:

if sys is in macrostate M_i , then prob that it lies in subset $\mathcal{E} \subseteq \Omega_i$ is $\mu(\mathcal{E}) / \mu(\Omega_i)$

(or just $\mu(\mathcal{E})$, if we've normalized $\mu(\Omega) = 1$)

now H -the depends explicitly on q_t (dynam)

Combinatorial Any function (T, q_t, ω_a) (now write T_{micro} for previous T)

- redefine T to be 6-d phase space (or just phase space of one of identical sys), parameterize by pos of mom (q, p) , define q_t accordingly, etc

- & define cells ω_a to be finite boxes rectangular in (q, p) that partition $\Omega \Rightarrow$ coarse-grain Ω

coarse-grained microstate is specification of $\omega_a \in \Omega$ that particle/micro-sys lies in; coarse-grained microstate of entire system is specification of which ω_a each particle/microsys lies in

\Rightarrow arrangement

Axiom/Demand/Constraint:

macro properties are approximately constant across cell ω_a
 \Rightarrow many arrangements correspond to same macrostate, or all that matters are how many particles (microsys) are in each cell, not what exact particles are in each cell

\Rightarrow Distribution $D_j = (n_1, n_2, \dots, n_k)$ occupation #s

$$\sum_{j=1}^M n_j = n$$

$$G(n) = \frac{n!}{n_1! \dots n_k!} \quad \therefore \text{how many arrangements (combinations) distribution}$$

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[DRAW PICTURE relating T + T_n w/ partition]

- D_j corresponds to region $\Delta_j \subset T_n$, and they partition it
 \Rightarrow each $g \in T_n$ corresponds to one D_j , but each D_j corresponds to many $g \in T_n$

where $\mathcal{D}_j := \{g \in T_n : D(g) = D_j\}$

$\Rightarrow \mu(\mathcal{D}_j) = G(D_j)(\delta w)^n$

where δw is size of w cell (all the same)

\Rightarrow what D_j has maximum size?

make 2 assumptions

1) energy of particle depends only on cell it's in (no non-local interactions) \rightarrow E_j for w_j
~~energy~~ energy doesn't depend on where in cell it is

2) \exists many particles ($n_j \gg 1$) in each cell

\Rightarrow maximum μ occurs for Maxwell-Boltzmann distribution

$n_j = d e^{-\beta E_j}$

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interpolated notes
notes of 15 Nov 2017

Problem

How do ΣD_i relate to σ_i (macroregion of T_W associated with macro state M_i)?

$\Rightarrow \Sigma D_i$ is $6N$ -dim object (but σ_i is $(6N-1)$ -dim object (lying in accessible region of T_W constrained by external constraints, e.g., constant fixed energy)

- "obvious remark": relation σ_i to be $6N$ -dim object
prob: most of σ_i consists of states never visited by system, accessible region is 'vanishingly small', so what ~~can it mean~~ can it mean to calculate g_s (eg, pressure) by averaging over vanishingly small region of microstates?

Classical Problems

- 1) reth. of μ - micro to macro dyns
- 2) probabilities - introduction of interpret
- 3) Reversibility (Loschmidt)
- 4) Recurrence (Zermelo)
- 5) Justify coarse-graining
- 6) Limitations of formula
- 7) reduction of thermo

1) dyns

- how to ensure that ^{microstate} sys 'generally' moves by dyns towards largest macrostate? if motion is too "regular", it doesn't matter how big macrostate is (typically 10^N larger than regular states), the system may just stay in non-equil macrostate

→ one approach: stipulate system "moves randomly" over whole energy surface

→ but how to define 'random' and how to justify? → independent of where it starts from

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(8)

(file notes of
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2) probabilities

i) many diff't kinds, all prob. func. unrelated, in BSM

a) macro probabilities $p(M_i)$

b) micro probabilities $p(A_i)$, $A_i \in \Omega_i$

c) "prob of finding randomly chosen particle in cell w_i "
 \Rightarrow relative freqs

ii) two broad types of interp., existence of ontic

iii) how to justify Boltzmann's Law?

- $p(M_i)$ we absolutely don't say anything about
succession of states, so can't show evol towards

"most likely" state

\Rightarrow what does it mean that 'sys most likely to be in eq. ill.'
when we find sys out of eq. ill. at the time?

- $p(\Omega)$ ($\Omega \in \Omega_i$) give right conditional probs that
can be used for evolution, but this leads directly
to recurrence and reversibility objections

Makeup lectures

M₀ 12-14

D₁ 12-14

M₁ 14-16

make sure latest Giovanni paper
for next week