Assumptions of Physics Summer School 2024

## Thermodynamics and Statistical Mechanics

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https://assumptionsofphysics.org



## Main goal of the project

#### Identify a handful of physical starting points from which the basic laws can be rigorously derived

For example:





#### https://assumptionsofphysics.org

This also requires rederiving all mathematical structures from physical requirements

For example:

Science is evidence based  $\Rightarrow$  scientific theory must be characterized by experimentally verifiable statements  $\Rightarrow$  topology and  $\sigma$ -algebras





If physics is about creating models of empirical reality, the foundations of physics should be a theory of models of empirical reality

Requirements of experimental verification, assumptions of each theory, realm of validity of assumptions, ...





#### *Reverse physics*: Start with the equations, reverse engineer physical assumptions/principles

Found Phys **52**, 40 (2022)



Goal: find the right overall physical concepts, "elevate" the discussion from mathematical constructs to physical principles

*Physical mathematics*: Start from scratch and rederive all mathematical structures from physical requirements



Goal: get the details right, perfect one-to-one map between mathematical and physical objects





## Reverse Physics: Thermo and Stat Mech



#### Puzzling things about entropy and equilibria

Entropy is disorder

If you mix water and vinegar, you increase entropy

If you mix water and oil, you increase entropy

???









#### Puzzling things about entropy and equilibria: dynamic vs thermodynamic

Dissipative forces shrink phase space volume Smaller volume, smaller entropy

Dissipative forces reduce entropy

???



Equilibria are attractors, volume around them shrink

Smaller volume, smaller entropy

Entropy decreases as we go to equilibrium

???



#### Puzzling things about entropy and equilibria: relativity

Thermodynamic equilibrium: wait until nothing changes

Newton's first law: a body remains in motion at a constant speed

No equilibrium

???

Gas in equilibrium in one reference: all macroscopic quantities stay the same Moving reference: position is changing Equilibrium is not an invariant property

???

Gas increasing temperature very slowly, always in equilibrium Moving reference sees a gradient of temperature Equilibrium is not an invariant property ???  $\frac{x}{x}$ 

#### Puzzling things about entropy and equilibria: information and equilibria

Entropy is information:  $I(\rho) = -\int \rho \log \rho$  where  $\rho$  is the distribution over microstates Gas at unknown temperature:  $T_1$  or  $T_2$  with 50% chance. One bit of entropy

Increase of Shannon entropy is less than 1:  $I\left(\frac{1}{2}(\rho_1 + \rho_2)\right) < \frac{1}{2}I(\rho_1) + \frac{1}{2}I(\rho_2) + 1$ 

???

Entropy is information:  $I(\rho) = -\int \rho \log \rho$  where  $\rho$  is the distribution over microstates I forget the temperature of the heat source: entropy is higher

I can extract less energy from the heat source

???



Clearly: in some sense entropy is about information, in some sense entropy is about disorder, thermodynamic equilibria is about things not changing, equilibrium identifies a privileged coordinate system,

....

# But in exactly what sense?!?!?

Fundamental problem of thermodynamics



# Information entropy



## Shannon entropy as variability

Eur. J. Phys. 42, 045102 (2021)



Shannon entropy quantifies the variability of the elements within a distribution

Meaning depends on the type of distribution

Statistical distribution: variability of what is there





Probability distribution: variability of what could be there

Credence distribution:



variability of what one believes to be there

- $-\sum p_i \log p_i$  only indicator of variability that satisfies simple requirements
  - Continuous function of  $p_i$  only 1)
  - Increases when number of cases increases 2)
  - 3) Linear in  $p_i$

#### This characterization works across disciplines



### Shannon entropy as variability



More variability, more questions

Variability is quantified by the expected minimum number of yes/no questions required to identify an element

W  $\frac{1}{N}\log W \approx -\sum p_i \log p_i$ 

More variability, more permutations

Variability is also quantified by the logarithm of the number of possible permutations per element

More variability for a distribution at equilibrium, more fluctuations, more physical entropy



Eur. J. Phys. 42, 045102 (2021)

# Entropy as logarithm of the count of evolutions



 $\mu(s_t)$ : how many evolutions go through  $s_t$ ?

Process entropy:  $S = \log \mu$ 







 $P(s_{t+\Delta t}|s_t) = \frac{\mu(s_t \cap s_{t+\Delta t})}{\mu(s_t)}$ 

 $\mu\bigl(s(t+\Delta t)\bigr) \ge \mu\bigl(s(t)\bigr)$ 

(equal if reversible) (maximum at equilibrium) Determinism: evolutions cannot split  $\mu(s(t + \Delta t)) \ge \mu(s(t))$ Reversibility: evolutions cannot merge  $\mu(s(t + \Delta t)) \le \mu(s(t))$ 

For a deterministic process

 $S(s(t + \Delta t)) \ge S(s(t))$ 

(equal if reversible) (maximum at equilibrium)



System independence: evolutions of the composite are the product of individual systems:  $\mu_{XY} = \mu_X \mu_Y$ 

Entropy additive for independent systems  $S_{XY} = S_X + S_Y$ 

Entropy as logarithm of evolutions



 $\mu(s_t)$ : how many evolutions go through  $s_t$ ?

#### Process entropy: $S = \log \mu$

## Entropy as logarithm of evolutions

Note: defining an evolution count is necessary in physics



We compose processes by connecting inputs and outputs: all evolutions must connect!

#### Recovers other notions of entropy!

If det/rev, one state per evolution, count of evolutions is count of states ⇒ recover fundamental postulate of statistical mechanics!

If microstate fluctuates according to a distribution  $\rho$ , count of evolutions is count of permutations  $\Rightarrow$  recover Shannon entropy!



State space of a system







#### Evolution: complete description of the system at all times



#### A process defines the set of all possible evolutions



#### Each description at each time corresponds to a set of evolutions

We can count the number of evolutions for a particular state s at a particular time with a measure<sup>\*</sup>  $\mu(s)$  since s identifies a set of evolutions.



The probability  $P(s_1|s_0)$  of having  $s_1$  given  $s_0$  corresponds to the fraction of evolutions that go from state  $s_0$  to state  $s_1$ 





#### A process is deterministic if knowing the state at a time allows us to predict the state at a future time

For these processes, we can properly write a law of evolution  $s(t + \Delta t) = f(s(t))$ 



#### In a deterministic process, the evolutions can never split, only merge

That is,  $\mu(s(t + \Delta t)) \ge \mu(s(t))$ 



A process is reversible if knowing the state at a time allows us to reconstruct the state at a past time



#### In a reversible process, the evolutions can never merge, only split

That is,  $\mu(s(t + \Delta t)) \leq \mu(s(t))$ 



In a det/rev process, evolutions can never merge nor split

That is,  $\mu(s(t + \Delta t)) = \mu(s(t))$ 



For a deterministic process

 $\mu(s(t + \Delta t)) \ge \mu(s(t))$ 

(equal if reversible)



Consider a process where a system reaches a final equilibrium that can be predicted from the initial state

At equilibrium, evolutions cannot merge anymore



For a deterministic process

 $\mu(s(t + \Delta t)) \ge \mu(s(t))$ 

(equal if reversible) (maximum at equilibrium)



#### Suppose we have a composite of two systems



 $\{x(t),y(t)\}$ 

If the systems are independent, the evolution of one does not constrain the evolution of the other: all pairs are possible

For each pair of states there is a state for the composite system:  $#(S) = #(S_1)#(S_2)$ 

For each pair of evolutions there is an evolution of the composite:  $\mu(s_1 \cap s_2) = \mu_1(s_1)\mu_2(s_2)$ 

Note:  $\log \mu = \log \mu_1 \mu_2 = \log \mu_1 + \log \mu_2$  $\log \mu$  is additive for independent systems



Define the process entropy as  $S = \log \mu$ The log of the count of evolutions per state

# It is additive for independent systems $S = S_1 + S_2$

For a deterministic process  $S(s(t + \Delta t)) \ge S(s(t))$ (equal if reversible) (maximum at equilibrium)



Recover fundamental postulate of statistical mechanics (entropy is the logarithm of the count of microstates)

Suppose process deterministic and reversible at microscale

- ⇒ States and evolutions are one-to-one
- ⇒ Count of microstates equals count of evolutions
- $\Rightarrow$  Entropy is the logarithm of the count of microstates





Suppose we have a dissipative system (e.g. damped harmonic oscillator)

⇒ Evolutions concentrate on fewer states ⇒ While count of states decreases, the density of evolutions (evolutions per state) increases



Focusing on the evolutions seems to solve the paradox of entropy for dynamical equilibrium



### Recover information entropy

Suppose macrostate X is a dynamical equilibrium of microstates  $\Rightarrow$  Microstate fluctuations can be characterized by a stable probability distribution  $\rho(x)$  in each small  $\Delta t$ 

 $\Rightarrow$  An evolution  $\lambda(t)$  for the microstate is a dense sequence of infinitely many microstates whose recurrence matches  $\rho$ 

⇒ Macrostate measurements cannot be sensitive to permutations of microstates: possible evolutions equals all possible permutations

 $\Rightarrow$  Shannon entropy counts all possible permutations of an infinite sequence (dense in  $\Delta t$ ) which equals all possible evolutions





# Macrostate/equilibrium is a "tube" of evolutions at the lower level

Equilibrium means that no evolution enters or exits the "tube" (i.e. external agents have equilibrated)

The variables describing the macrostate can still change (i.e. the "tube" moves around in state space)

We can now study the "tube" as if it were single line (i.e. internal dynamics and environment are decoupled)

Equilibrium = evolution decoupled from environment and internal dynamics





Equilibrium = evolution decoupled from environment and internal dynamics

Automatically relativistic: about evolutions (i.e. timelines)

Quasi-static evolution NOT relativistic





## Process entropy

- We have not mentioned uncertainty, disorder, statistical distributions, information, lack of information, ...
  - Therefore those concepts are not fundamental in this context
- We have not discussed what type of state or system we have (classical, quantum, biological, economic, ...)
  - Therefore everything we said is valid independently of the type of system, which would explain the success of thermodynamic ideas outside the realm of physics
- The process entropy increase is explained by the definitions and the settings (processes with equilibria that depend on the initial state)
  - The explanation is straightforward (i.e. does not require a complicated discussion)
  - The explanation is not mechanical (i.e. given by a particular mechanism)



How does process entropy become the entropy state variable?

Why would we need to define a count of evolutions?



Why would we need to define a count of evolutions?

Note: if we want to "switch" processes (e.g. mix and match preparations, evolutions and measurements) the evolution count at the junction must be uniquely defined

⇒ Evolution count is a necessary feature of a theory for states and processes



## Equilibria can be assigned a unique entropy

# Suppose the same state x is an equilibrium for two processes A and B

Two ways of combining the processes: first A then B and vice versa All the evolutions of A that end in x will also end in x under AB and B All the evolutions of B that end in x will also end in x under BA and A

Count of evolutions of x must be process independent

Equilibria allow us to assign unique (maximal) entropy to states



A

В

#### For composite systems, recall that in general the process entropy is not unique

Due to correlations between subsystems

If the systems are independent, however, the process entropy is well defined

It sums and corresponds to the maximum

System independence allows us to assign unique (maximal) entropy to composite states



 ${x(t), y(t)}$ 

## State entropy

- We can assign a unique maximal process entropy to "states of independent equilibria", which we call state entropy
  - Both equilibria and independence maximize process entropy
  - We leave these notions somewhat "vague" for now (we are still doing better than standard thermodynamics anyway)
- Given a set X of states of equilibria, we can define the function  $S: X \to \mathbb{R}$  that returns the state entropy for each equilibrium
  - We call this the equation of state in entropic form
- First goal reached: under very general definitions, we have found a simple notion of entropy (logarithm of the count of evolutions) that has a fundamental (almost trivial) link to irreversibility



## Takeaways

- We need a well defined count of evolutions to "stitch" together preparations, evolutions and measurement processes
- The logarithm of the count of evolutions recovers the properties of the entropy and can recover both definitions of entropy under suitable additional assumptions
- Equilibrium = evolution decoupled from environment and internal dynamics
- All properties descend directly from simple requirements and considerations
- TODOs:
  - Actually write down the full theory



# Recovering thermodynamics



## "Reversing" thermodynamics

Assume states are equilibria of faster scale processes

Assume states identified by extensive properties

Assume one of these quantities is energy  $\boldsymbol{U}$ 

 $S(U, x^i)$ 

Existence of equation of state

Study interplay of changes of energy and entropy



Reservoir: energy only state variable, entropy linear function of energy All energy stored in entropy



 $\beta = \frac{1}{k_{\rm p}T} = 0$ 

 $\beta = \frac{1}{k_B T} = \frac{\partial S}{\partial U}$  and  $-\beta X_i = \frac{\partial S}{\partial x^i}$ 

Define intensive quantities

$$dS = \frac{\partial S}{\partial U} dU + \frac{\partial S}{\partial x^{i}} dx^{i} = \beta dU - \beta X_{i} dx^{i}$$
$$k_{B}TdS = dU - X_{i} dx^{i}$$
$$dU = T(k_{B}dS) + X_{i} dx^{i}$$

Recover usual relationships

 $\Delta U = 0 = \Delta U_A + \Delta U_R + \Delta U_M$  $= \Delta U_A - Q + W$ 

Recover first law

 $0 \le \Delta S = \Delta S_A + \Delta S_R + \Delta S_M$   $= \Delta S_A + \beta_R \Delta U_R + 0 = \Delta S_A + \frac{-Q}{k_B T_R}$ ed in entropy Recover second law

Second law recovered from definition of entropy as count of evolutions

First law recovered from existence and conservation of Hamiltonian



Suppose we take a composite system and at some point we split it such that each part will follow its own process



Not only do we need a well defined evolution count for the composite, but also for each part

This requires us to extend the notion of equilibria to the parts



## Thermodynamic process

- Thermodynamic processes extend the notion of deterministic process with equilibria to composite systems
- We define a thermodynamic process as a deterministic process with equilibria such that:
  - in the final equilibrium all parts are independent and at equilibrium
  - the final equilibrium depends non-trivially on the initial state of any part



## Thermodynamic equilibrium



- A thermodynamic equilibrium is the output of a thermodynamic process
- Two systems are in thermodynamic equilibrium if they are parts of the same thermodynamic equilibrium

Mathematically, systems under composition form a Boolean algebra. An equilibrium is a downward set with a greatest element.



## Thermodynamic equilibrium is transitive



Suppose A is in thermodynamic equilibrium with B and B is in thermodynamic equilibrium with C.

Then A and B are parts of the output of the same thermodynamic process. But B and C are also parts of the output of the same thermodynamic process.

Therefore *A* and *C* are parts of the output of the same thermodynamic process: they are in thermodynamic equilibrium.

This recovers the zeroth law of thermodynamics



## Thermodynamic systems

- We say A is a thermodynamic system if
  - the state space  $\mathcal{S}_A$  is formed by states of equilibrium
  - all state variables (i.e. quantities that identify the state of the system) are extensive properties of the system (i.e. sum under system composition, like entropy)\*
  - One of these quantities, called internal energy, is conserved under all thermodynamic processes\*
- We will indicate with U the internal energy and with  $x^i$  all other state variables

\* It may be possible to derive the existence of extensive quantities... For now we leave this as an extra assumption

\* This may be justified by isolation of system + env, which leads to existence and conservation of Hamiltonian



## Existence of an equation of state

- Because the states are equilibria, we have a function  $S: S_A \to \mathbb{R}$  that returns the state entropy (maximized process entropy) for each state
- Because  $(U, x^i)$  are state variables, we can express  $S(U, x^i)$  as a function of the variables

# A thermodynamic system has an equation of state $S(U, x^i)$



### Thermodynamic quantities

• Define the following variables:

$$\beta = \frac{1}{k_B T} = \frac{\partial S}{\partial U} \text{ and } -\beta X_i = \frac{\partial S}{\partial x^i}$$
$$dS = \frac{\partial S}{\partial U} dU + \frac{\partial S}{\partial x^i} dx^i = \beta dU - \beta X_i dx^i$$
$$k_B T dS = dU - X_i dx^i$$
$$dU = T(k_B dS) + X_i dx^i$$

- Compare to  $dU = TdS_{Thermo} pdV + \mu_i dN^i + \cdots$
- $k_B dS$  corresponds to the thermodynamic entropy
- The other variables correspond to thermodynamic pairs



## Changes of energy and entropy

- Now we want to study how changes in energy and changes in entropy relate to each other
- To do that, it is useful to characterize two "orthogonal" directions:
  - changes of energy at equal entropy
  - changes of energy at maximum entropy change



#### Reservoir

• We define a reservoir R as a thermodynamic system where the energy  $U_R$  is the only state variable and  $\frac{\partial S_R}{\partial U_R} = \beta_R = \frac{1}{k_B T_R} = const$ . We call heat  $Q = -\Delta U_R$  the energy lost by the reservoir during a transition.

- Heat is energy exchanged under a purely entropic change
  - no other extensive quantity changes



### Mechanical system

• We define a mechanical system M as a system such that the entropy is the same for all states. That is:  $S_M(U_M, x_M^i) = const$ . We call work  $W = \Delta U_M$  the energy acquired by a purely mechanical system during a transition.

$$dS_M = 0 = \beta_M dU_M - \beta_M X_{Mi} dx_M^i$$
$$dU_M = X_{Mi} dx_M^i$$

 Work is energy exchanged at constant entropy. Constant entropy (as we saw) corresponds to deterministic and reversible processes. The energy is effectively "stored" in the other variables and can be retrieved later.



## First law

- Consider a composite system made of a generic system *A*, a reservoir *R* and a purely mechanical system *M*. Consider a transition where we go to a new equilibrium.
- Since the energy is extensive (i.e. additive under system composition), let *U* be the total energy. We also assumed the energy is conserved. We have:

• 
$$\Delta U = 0 = \Delta U_A + \Delta U_R + \Delta U_M = \Delta U_A - Q + W$$

• 
$$\Delta U_A = Q - W$$

This recovers the first law of thermodynamics



## Second law

 Since entropy is extensive (i.e. additive under system composition), let S be the total entropy.
Since the process is deterministic, the entropy cannot decrease. We have:

• 
$$0 \le \Delta S = \Delta S_A + \Delta S_R + \Delta S_M = \Delta S_A + \beta_R \Delta U_R + 0 = \Delta S_A + \frac{-Q}{k_B T_R}$$
  
•  $k_B \Delta S_A \ge \frac{Q}{T_R}$ 

This recovers the second law of thermodynamics









The least we can have is a single evolution

The case where the equilibrium can be reached from only one starting condition

$$S \ge \log 1 = 0$$

State entropy is non-negative, bounded from below at zero

Evolution of a pure ground state fits into the single evolution case

This recovers part of the third law of thermodynamics



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Assumptions Physics

#### Existence of equilibria forces S(U) to be concave

#### Since S(U) is non-negative, we have three cases:

a) No maximum energy, entropy monotonically increasingb) No minimum energy, entropy monotonically decreasingc) Minimum and maximum energy, entropy minimum at either edge

The first 2 cases can't both exist:

If we combined two systems, one strictly monotonically increasing with another strictly monotonically decreasing, maximization of entropy would happen at infinity: we have no equilibrium

By convention, we say energy is bounded from below. Minimum entropy is reached at the lowest energy state.

This recovers the remaining part of the third law of thermodynamics





Assumptions Physics Other argument

Entropy is additive for independent systems

$$S_{AB} = S_A + S_B$$

Null state  $\emptyset$  : the system is missing/has zero particles Acts as a "zero" under system composition:  $A \cup \emptyset = A$ .

$$S_{\emptyset} = S_{\emptyset\emptyset} = S_{\emptyset} + S_{\emptyset} = 0$$

Single possible evolution for null system

No state can describe a system more accurately than stating the system is not there in the first place

Principle of maximal description

Equivalent to the third law



## Takeaways

- Thermodynamics recovered as describing equilibria of systems and parts
  - The notion of process entropy maps to thermodynamic entropy in a very natural way
  - The notion of thermodynamic equilibrium as an equilibrium at all scales is already something people discuss (citation needed)
- Again: we have not mentioned uncertainty, disorder, statistical distributions, information, lack of information, ...
- Again: we have not discussed what type of state or system we have (classical, quantum, biological, economic, ...)
- TODO:
  - Actually write down the whole theory



## Prelude to quantum





#### Classical uncertainty principle

Classical mechanics has no lower bound on entropy ⇒ violates third law! What happens if we impose one?

Let  $W_0$  be the volume of phase space over which a uniform distribution has zero entropy.

Minimum uncertainty

Region with

distributions

classical



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Equality for independent Gaussians

Excluded by 3<sup>rd</sup> law

Lower bound on entropy ⇒ lower bound on uncertainty

Don't need the full quantum theory to derive the uncertainty principle: *only the lower bound on entropy* 



## 3<sup>rd</sup> law of thermodynamics and uncertainty principle



## Wrapping it up

- Basic concepts, like entropy and equilibria, are linked to fundamental requirements for defining physical systems
  - Thermodynamics is more fundamental than people think
- Thermodynamics extends these concepts to equilibria among subsystem
- Ideas are general and could explain why techniques from thermodynamics have found place in ecology, economics and other fields
- We think we have good foundational ideas, but we still need to put them together



